

EFFECT OF CARBON NANOTUBE ALIGNMENT AND LENGTH ON THE ELECTRICAL CONDUCTIVITY AND PIEZORESISTIVITY OF CNT/PMMA COMPOSITES

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ABSTRACT

The effect of the length of multiwall carbon nanotubes (MWCNTs) on the electrical properties of MWCNT/polymer composites is investigated. A methodology based on controlled ultrasonic fragmentation was implemented to systematically reduce the length of the MWCNTs, supported by scanning electron microscopy and length measurements. The as-received and fragmented MWCNTs were used to fabricate MWCNT/polymethyl methacrylate composites, evaluating the effect of such a fragmentation in the resulting electrical conductivity of the composites. The effect of length-shortening and carbon nanotube alignment on the piezoresistive properties of such composites is an ongoing work which will be presented at the conference.

1. INTRODUCTION

Recent advances in the nanotechnology field have brought new and more demanding applications which involves smartness and multifunctionality. In the area of materials science, composite materials are nowadays very explored and used for novel applications due to their versatility and combination of properties of the matrices and fillers. In particular, polymer-based composites reinforced with carbon nanoparticles have gained a lot of attention and much research has been developed towards this direction [1]. Carbon black (CB) [2], carbon nanotubes (CNTs) [3-5] and multilayer graphene nanoflakes [6] have been reported as filler materials, improving in a notorious manner the mechanical, electrical, and thermal effective properties of nanocomposites. For the case of CNT/polymer composites, several reports confirm the use of these materials in applications such as mechanical, gas and thermal sensors [1,7,8], for mentioning a few examples. The electrical and piezoresistive properties of the CNTs along with the versatile properties of polymers make them good candidates to be used on several sensing areas. However, the full potential of these materials has not yet been unravelled probably due to the lack of understanding of the underlying mechanisms governing such complex sensorial processes, and also due to the strong structure-property relationship, which is in turn determined by the challenging dispersion and manufacturing process. Among the most relevant parameters influencing the effective electrical and piezoresistive properties of CNT/polymer nanocomposites, the geometry (length, diameter and waviness), concentration and alignment of the CNTs are suggested as the main ones. In a previous work by our group, electrical and piezoresistive properties were enhanced by aligning the CNTs in a specific direction [9]. Whichmann et al. [2] investigated the effect of the concentration and type of particle (CB and CNTs) on the electrical and electromechanical response of epoxy-based nanocomposites. Authors found that the electrical and piezoresistive responses are dominated by the interparticle contacts (determined by the morphology of the conductive network), which can be characterized by a tunnelling mechanism. In a theoretical work by our group, the contribution of CNT dimensional changes to the effective electromechanical response of CNT/polymer composites was investigated; it was found that such a contribution is very low and it was suggested that the main mechanism of the piezoresistive response of composites was

the modification of the CNT network configuration, which is importantly influenced by the geometry and concentration of the filler particles [10]. Thus, it is clear that more efforts should be carried out in order to explore the effect of the morphology of the filler on the electrical and piezoresistive properties of CNT/polymer composites, which would allow to optimize their performance. Therefore, a study on the effect of multiwall carbon nanotube (MWCNT) length on the electrical and piezoresistive properties of MWCNT/polymer composites has been undertaken, reporting in this first part of the work only the electrical properties. A methodology to systematically reduce the MWCNT length by ultrasonic energy was implemented and morphological evidence of such a length reduction is presented. The electrical conductivity of MWCNT/polymethyl methacrylate (PMMA) composites is measured finding the electrical percolation threshold for MWCNT/PMMA composites with fragmented and as-received MWCNTs. Piezoresistive properties and the effect of alignment for as received and fragmented MWCNTs is an ongoing work which will be presented at the conference.

2. EXPERIMENTAL

2.1. Materials and methods

Commercial MWCNTs of a purity >95% were used [11]. As-received MWCNTs have a length of 1-6 μm and external diameters ranging from 30 to 50 nm. For the process of reduction of MWCNTs length, N-N-dimethylformamide (DMF) was used to disperse the MWCNTs using an ultrasonic bath (Branson, 110 W at 40 kHz). An ultrasonic probe of high and concentrated power (Sonics, VC-750, using 225 W at 20 kHz) was used to fragment the MWCNTs, following a procedure explained in the following section. For the observation of the MWCNTs at the microscale, a scanning electron microscope (SEM) (JEOL, FESEM-7600) was used. For the preparation of MWCNT/PMMA composites, chloroform was used as the solvent to disperse the MWCNTs and to dissolve the PMMA pellets. For the electrical characterization, a Keithley 6517B electrometer was used to measure the electrical resistance of the MWCNT/PMMA composites. The more resistive composites required the additional use of a Keithley 8009 resistivity test fixture.

2.2. Fragmentation of MWCNTs

In order to evaluate the influence of the MWCNT length on the electrical properties, MWCNTs were systematically fragmented by a procedure based on using ultrasonic energy. To this aim, 0.9 mg of MWCNTs were dispersed in 15.4 g (16.3 ml) of DMF (concentration of 5.84×10^{-3} wt.%) and mechanically agitated for 30 min at room temperature. After this, the MWCNT/DMF solution was sonicated using an ultrasonic horn (225 W at 20 kHz) for a total of 4 h (2 h effective sonication time), which was programmed with on and off sequences of 30 s to avoid overheating. An ice bath was also used to avoid overheating. As a final step, a drop (~15 mg) of the solution was poured onto Si substrates for SEM imaging of the fragmented MWCNTs. A schematic of the experimental process used for the MWCNT length reduction is shown in Figure 1.

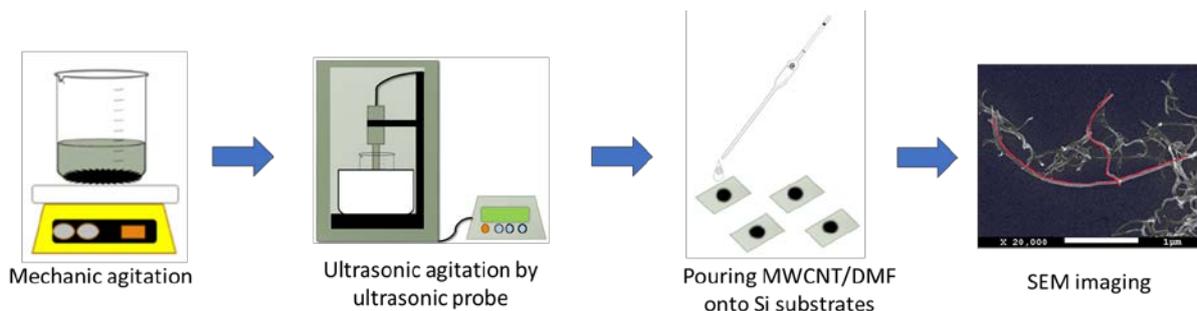


Figure 1. Schematic of the MWCNT fragmentation process.

The reference sample (as-received MWCNTs) was obtained by using a similar procedure, i.e. dispersing the same amount of MWCNTs (0.9 mg) in the same amount of DMF (16.3 ml) but substituting the concentrated power of the ultrasonic horn for 30 min of dispersion in a conventional ultrasonic bath (110 W at 40 kHz), after the initial 30 min of mechanical agitation. Since the bath power (110 W) is spread over the whole volume of the tank (2.8 l) and it is applied for 30 min, this yields an energy density of 70.7 MJ/m³, which was delivered to the as-received MWCNTs. On the other hand, the 225 W of the ultrasonic horn are applied (for 2 h) directly to the 16.3 ml of DMF within the beaker, which yields a total specific energy delivered to the (fragmented) MWCNTs of 99.4 GJ/m³. Although the actual energy density received by the MWCNTs may be slightly less because of damping and losses, the order of magnitude provides a clear picture of what is expected for each group of MWCNTs. As reported in [12] energy densities of the order of 10⁶ Pa are expected to yield dispersion with none or very limited fragmentation, while those of the order of 10⁹ Pa are expected to yield MWCNT fragmentation.

2.3. Fabrication of MWCNT/PMMA nanocomposites

Composite materials with MWCNT weight concentrations of 0.1, 0.3 and 0.5 wt.% were prepared using as-received and fragmented MWCNTs and PMMA as the host matrix by means of the solution casting technique, as illustrated in Figure 2. Initially, MWCNTs were dispersed in chloroform using an ultrasonic bath and the PMMA pellets were dissolved by mechanical agitation using the same solvent, Figure 2a. Afterwards, both solutions were mixed to form a MWCNT/PMMA/chloroform liquid solution. A controlled evaporation of the chloroform was carried out by means of repetitive steps of ultrasonic agitation at room temperature and mechanical agitation at 70 °C, until the majority of the solvent was evaporated and the desired solution viscosity was reached, Figure 2b. The MWCNT/PMMA/chloroform solution was then cast on a glass mould and solid ~300 µm thick MWCNT/PMMA films were obtained, as shown in Figure 2c. As a final step, films were dried in a furnace in sequential steps between 60°C and 80°C, incrementing 10°C each day, Figure 2d.

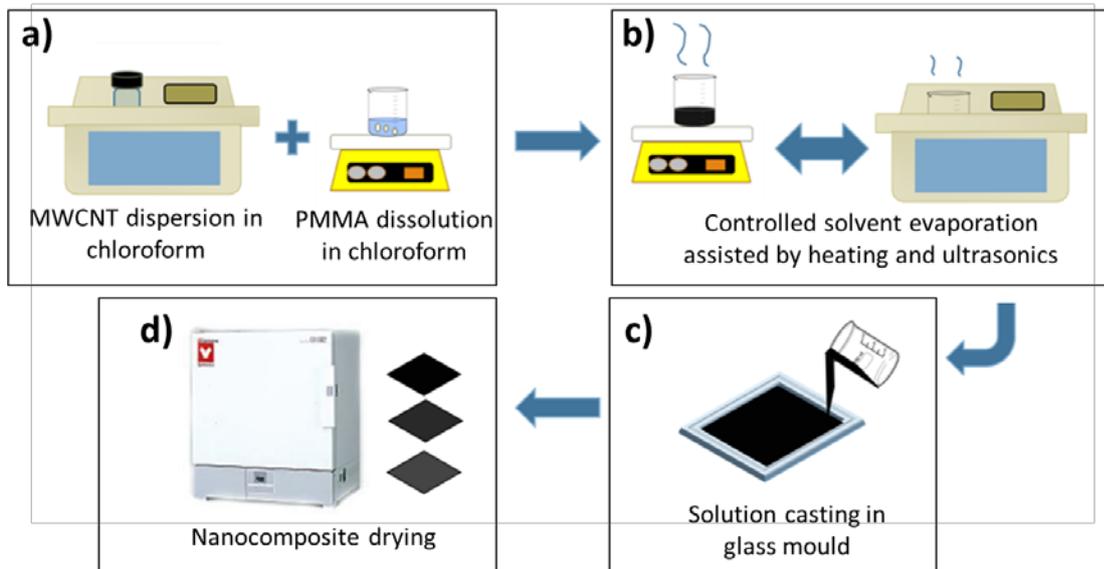


Figure 2. Schematic of the nanocomposite preparation process.

2.4. Electrical characterization of nanocomposites

In order to evaluate the electrical percolation of the MWCNT/PMMA composites with as-received and fragmented MWCNTs, the electrical resistance (R) of specimens using a Keithley 6517B electrometer. For composites with electrical resistances above GΩ, the use of a special resistivity test fixture (Keithley 8009 resistivity test fixture) connected to the electrometer was required and the samples were elaborated in a wafer shape, in accordance to the fixture requirements, see Figure 3a. On the

other hand, for specimens of electrical resistances below $G\Omega$, the test fixture was not required and smaller rectangular specimens were used instead, see Figure 3b. A schematic of the specimens and the experimental setup for the electrical characterization are shown in Figure 3.

The electrical conductivity (σ) of the specimens was then calculated as,

$$\sigma = L_e/AR \quad (1)$$

were L_e and A are the effective distance between the electrodes and the cross-section area of the specimen, respectively, see Figure 3.

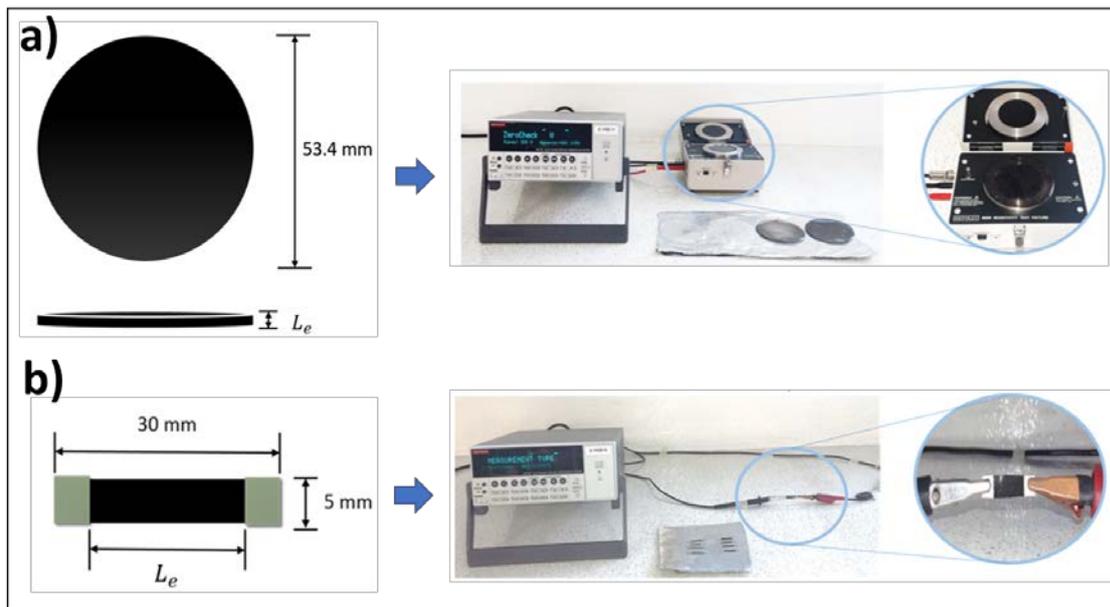


Figure 3. Electrical characterization of MWCNT/PMMA composites. a) Specimens with electrical resistance higher than $G\Omega$ (wafers), b) rectangular specimens with electrical resistance lower than $G\Omega$.

3. RESULTS

3.1. Fragmentation of MWCNTs

Figure 4 presents representative SEM images of the as-received (Figure 4a) and fragmented (Figure 4b) MWCNTs, measured after the dispersion/fragmentation treatments described in section 2.2. In order to obtain a representative MWCNT length for each case and observe if the MWCNTs were consistently fragmented, tenths of images were obtained and a several hundreds of MWCNTs were measured for different specimens. Several statistical distributions were first tried to fit the data, being the log-normal distribution the best fit. The expected value of the MWCNT length for the as-received MWCNTs was estimated as $1.23 \mu\text{m}$ while such a value for fragmented MWCNTs was estimated as $0.58 \mu\text{m}$, thus confirming the systematic length reduction. Several authors have investigated the effect of the ultrasonic energy on the reduction of the MWCNT length, mentioning that the main causes of MWCNT fragmentation are the ultrasonic energy, the time of application and the solvent viscosity, among the main ones [12-16]. These parameters can be collected in a single parameter named an energy density (Pa) as discussed by Huang and Terentjev [12]. Lu et al. [14] reported that the sonication causes high density of defects on the MWCNT such as bending, buckling and breaking on smaller pieces when the cavitation process is very energetic, as for the case of ultrasonic probes acting in low volumes and low viscosity solvents. Chen et al. reported that the ultrasonic energy produces rapidly collapsing cavitation bubbles providing high local solvent velocities which can act as both separating forces and scissoring forces [15]. Such scissoring forces tear down individual CNTs into

multiple shorter CNTs and reduce the average length of CNTs. Huang and Terentjev [12] use energetic terms to quantify such an effect, and argue that specific energy density values can be estimated to avoid significant MWCNT fragmentation, being these values function of the MWCNT aspect ratio (length/diameter). In our case, the energy densities received by the MWCNTs from the ultrasonic bath and ultrasonic horn are in the order of 10^6 Pa and 10^9 Pa, respectively, which are values below and above the fragmentation energy for the MWCNTs here used [12]. As such, it is expected that the 30 min of ultrasonication using the bath (low energy) does not cause significant breakage of MWCNTs, as required for the reference sample (as-received MWCNTs), while the energy delivered by the horn will cause evident fragmentation of the MWCNTs. Therefore, from this analysis, it is clear that the usage of a ultrasonic horn for long elapsed time and over a small volume of low viscosity fluid such as DMF cause of the significant MWCNT shortening shown in Fig. 4.

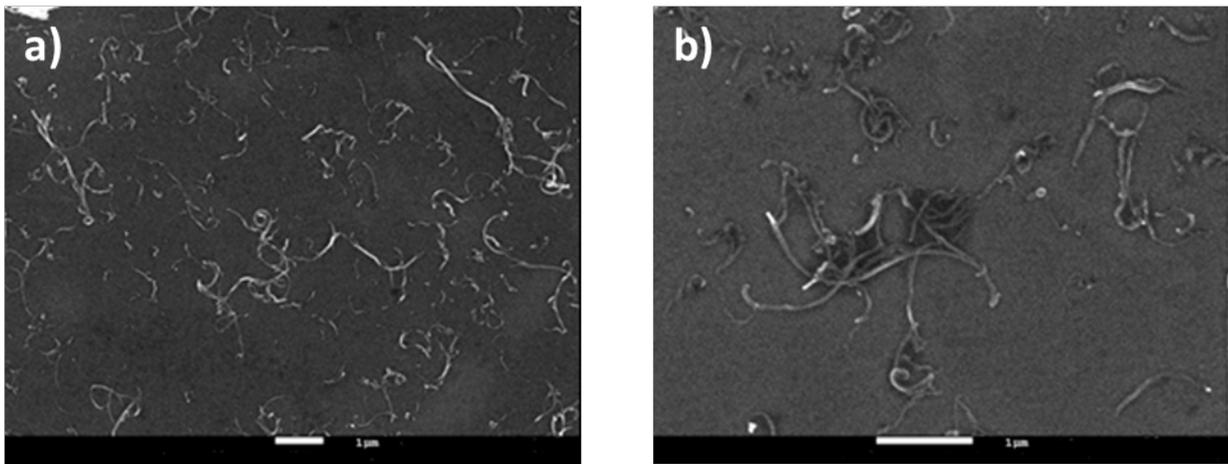


Figure 4. SEM imaging of MWCNTs after sonication processes. a) As-received MWCNTs, b) fragmented MWCNTs.

3.2. Electrical characterization

Electrical resistance was measured from nanocomposites fabricated with as-received and fragmented MWCNTs at low weight concentrations (0.1, 0.3 and 0.5 wt.%) and results are shown in Figure 5. From Figure 5 it can be observed that for the lowest concentration (0.1 wt.%), both composites are under the percolation threshold with conductivities close to 1×10^{-12} S/m. For 0.3 wt%, a dramatical increase in conductivity of ~ 11 orders of magnitude was observed for the composites fabricated with as-received MWCNTs ($\sigma \sim 10^{-1}$ S/m), and such a value was maintained for 0.5 wt% composites. On the other hand, an increase of 6 orders of magnitude in conductivity was observed for composites with fragmented MWCNTs at 0.3 wt% ($\sigma \sim 10^{-6}$ S/m) and then the conductivity increased up to $\sim 10^{-4}$ S/m for 0.5 wt.% composites. Although for both cases the effect of increasing MWCNT concentration on the conductivity of the composite is evident, for concentrations of 0.3 wt% and above composites with as-received (longer) MWCNTs exhibit higher conductivities than those of the composites with fragmented (shorter) MWCNTs. In that respect, Wang et al. reported that longer and thicker CNTs ensure a more effective electron conduction path along individual CNTs [17]. Foygel et al. carried out computational investigations and found that longer CNTs enhance the electrical conductivity of composites as the electrical percolation is reached at lower CNT concentration when CNT aspect ratio (length/diameter) is higher [18]. On the other hand, Martin et al. [19] found lower electrical conductivities of CNT-based composites when the aspect ratio increases, but this was more an (indirect) effective agglomeration issue rather than a direct consequence of the CNT length. These authors based their findings on an accelerated agglomeration of shorter CNTs which rendered higher values of electrical conductivity, which has also been pointed out by other authors [20,21].

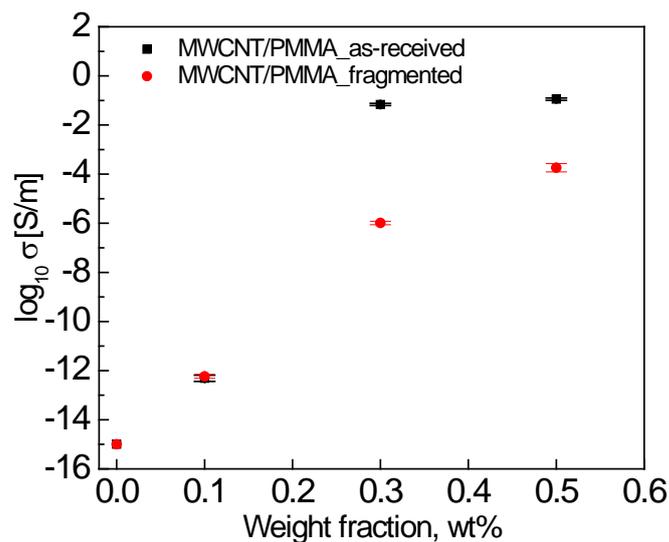


Figure 5. Electrical conductivity of MWCNT/PMMA composites fabricated with as-received and fragmented MWCNTs.

4. CONCLUSIONS

The effect of the MWCNT length on the electrical properties of low concentration MWCNT/PMMA composites was investigated. A procedure to systematically reduce the MWCNT length assisted by ultrasonic energy was implemented and the results were corroborated by SEM imaging. Using this methodology, fragmented and as-received MWCNTs were used to fabricate MWCNT/PMMA composites by solution casting and the electrical conductivity was measured. The conductivity of composites with as-received MWCNTs was higher, being this explained by the higher aspect ratio of the MWCNTs. The higher aspect ratio of MWCNTs yields less contact resistance and less barriers for electron dispersion and promotes better effective electron conduction paths along the composites. The effect of length-shortening and carbon nanotube alignment on the piezoresistive properties of such composites is an ongoing work which will be presented at the conference. A better understanding of the role of the geometric parameters of nanoparticles on the effective electrical and piezoresistive properties of the composites would bring a better optimization of the performance of smart multifunctional nanocomposites.

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REFERENCES

- [1] C. Li, E. T. Thostenson and T.W. Chou. Sensors and actuators based on carbon nanotubes and their composites: A review. *Composites Science and Technology*, **68**, 2008, pp. 1227-1249. (doi: 10.1016/j.compscitech.2008.01.006)
- [2] M.H.G. Wichmann, S.T. Buschhorn, J. Gehrman and K. Schulte. Piezoresistive response of epoxy composites with carbon nanoparticles under tensile load, *Physical Review B*, **80**, 2009, pp. 245437. (doi: 10.1103/PhysRevB.80.245437)

- [3] F. Aviles, A. May-Pat, G. Canche-Escamilla, O. Rodriguez-Uicab, J.J. Ku-Herrera, S. Duarte-Aranda, et al. Influence of carbon nanotube on the piezoresistive behavior of multiwall carbon nanotube/polymer composites, *Journal of Intelligent Material Systems and Structures*, **27**, 2014, pp. 92-103. (doi: 10.1177/1045389X14560367)
- [4] A.I. Oliva-Avilés, F. Avilés, V. Sosa, A.I. Oliva and F. Gamboa. Dynamics of carbon nanotube alignment by electric fields, *Nanotechnology*, **23**, 2012, pp. 465710. (doi:10.1088/0957-4484/23/46/465710)
- [5] Alamusi, N. Hu, H. Fukunaga, S. Atobe, Y. Liu and J. Li. Piezoresistive strain sensors made from carbon nanotubes based polymer nanocomposites, *Sensors*, **11**, 2011, pp. 10691-10723. (doi:10.3390/s111110691)
- [6] T. Kuilla, S. Bhadra, D. Yao, N.H. Kim, S. Bose and J.H. Lee. Recent advances in graphene based polymer composites, *Progress in Polymer Science*, **35**, 2010, pp. 1350-1375. (doi:10.1016/j.progpolymsci.2010.07.00)
- [7] E.T. Thostenson and T.W. Chou Carbon nanotube networks: Sensing of distributed strain and damage for life prediction and self healing, *Advanced Materials*, **18**, 2006, pp. 2837-2841. (doi: 10.1002/adma.200600977)
- [8] I. Kang, Y.Y. Heung, J.H. Kim, J.W. Lee, R. Gollapudi, S. Subramaniam, et al. Introduction to carbon nanotube and nanofiber smart materials, *Composites Part B: Engineering*, **37**, 2006, pp. 382-394. (doi: 10.1016/j.compositesb.2006.02.011)
- [9] A.I. Oliva-Avilés, F. Avilés and V. Sosa. Electrical and piezoresistive properties of multi-walled carbon nanotube/polymer composite films aligned by an electric field, *Carbon*, **49**, 2011, pp. 2989-2997. (doi:10.1016/j.carbon.2011.03.017)
- [10] A.I. Oliva-Avilés, F. Avilés, G.D. Seidel and V. Sosa. On the contribution of carbon nanotube deformation to piezoresistivity of carbon nanotube/polymer composites, *Composites Part B*, **47**, 2013, pp. 200-206. (doi: 10.1016/j.compositesb.2012.09.091)
- [11] Cheaptubes Inc. Multi Walled Nanotubes-MWNTs 30-50nm Specifications. 2015 Cambridgeport, EUA. http://www.cheaptubes.com/MWNTs.htm#multi_walled_nanotubesmwnts_30-50nm_specifications
- [12] Y.Y. Huang and E.M. Terentjev. Dispersion of carbon nanotubes: Mixing, sonication, stabilization, and composite properties, *Polymers*, **4**, 2012, pp. 275-295. (doi: 10.3390/polym4010275)
- [13] L. Dumée, K. Sears, J. Schütz, N. Finn, M. Duke and S. Gray. Influence of the sonication temperature on the debundling kinetics of carbon nanotubes in propan-2-ol, *Nanomaterials*, **3**, 2013, pp. 70-83. (doi:10.3390/nano3010070).
- [14] K.L. Lu, R.M. Lago, Y.K. Chen, M.L.H. Green, P.J.F. Harris and S.C. Tsang. Mechanical damage of carbon nanotubes by ultrasound. *Carbon*, **34**, 1996, pp. 814-816. (doi: 10.1016/0008-6223(96)89470-X).
- [15] S.J. Chen, B. Zou, F. Collins, X.L. Zhao, M. Majumber and W.H. Duan. Predicting the influence of ultrasonication energy on the reinforcing efficiency of carbon nanotubes, *Carbon*, **77**, 2014, pp. 1-10. (doi: 10.1016/j.carbon.2014.04.023)
- [16] R. Socher, B. Krause, M.T. Müller, R. Boldt and P. Pötschke. The influence of matrix viscosity on MWCNT dispersion and electrical properties in different thermoplastic nanocomposites, *Polymer*, **53**, 2012, pp. 495-504. (doi: 10.1016/j.polymer.2011.12.019)
- [17] X. Wang, Q. Jiang, W. Xu, W. Cai, Y. Inoue and Y. Zhu. Effect of carbon nanotube length on thermal, electrical and mechanical properties of CNT/bismaleimide composites, *Carbon*, **53**, 2013, pp. 145-152. (doi: 10.1016/j.carbon.2012.10.041)
- [18] M. Foygel, R.D. Morris, D. Anez, S. French and V.L. Sobolev. Theoretical and computational studies of carbon nanotube composites and suspensions: Electrical and thermal conductivity, *Physical Review B*, **71**, 2005, pp. 104201. (doi: 10.1103/PhysRevB.71.104201)

- [19] C.A. Martin, J.K.W. Sandler, M.S.P. Shaffer, M.-K. Schwarz, W. Bauhofer, K. Schulte and A.H. Windle. Formation of percolating networks in multi-wall carbon-nanotube–epoxy composites, *Composites Science and Technology*, **64**, 2004, pp. 2309-2316. (doi: 10.1016/j.compscitech.2004.01.025)
- [20] J.O. Aguilar, J.R. Bautista-Quijano and F. Avilés. Influence of carbon nanotube clustering on the electrical conductivity of polymer composite films, *Express Polymer Letters*, **4**, 2010, pp. 292-299. (doi: 10.3144/expresspolymlett.2010.37)
- [21] W. Bauhofer and J.Z. Kovacs. A review and analysis of electrical percolation in carbon nanotube polymer composites, *Composites Science and Technology*, **69**, 2009, pp. 1486-1498. (doi: 10.1016/j.compscitech.2008.06.018)