

Dielectric properties of multiwall carbon nanotube-red silicone rubber composites

A. PANTAZI^a, S. PALADE^a, C. BERBECARU^{a,d*}, M. PURICA^b, A. MATEI^b, O. OPREA^c, D. DRAGOMAN^{a,e}

^a*Faculty of Physics, University of Bucharest, P.O. Box MG-11, 077125 Bucharest, Romania*

^b*National Research and Development Institute in Microtechnologies, Str. Erou Iancu Nicolae 126 A, 077190 Bucharest, Romania*

^c*Faculty of Applied Chemistry and Materials Science, University "Politehnica" Bucharest, 1-7 Polizu Str., 011061 Bucharest, Romania*

^d*Romanian Materials Science-Crystal Growth Society, 077125 Bucharest-Magurele, Romania*

^e*Academy of Romanian Scientist, Splaiul Independentei 54, 050094 Bucharest, Romania*

Composites with different mass concentrations of carbon nanotubes in red silicone rubber (MWCN-RSR) were prepared. Both Raman and Fourier Transform Infrared spectroscopy investigations show shifted peaks of composites related to RSR peaks and reveals weak interactions between RSR and MWCNT. Dielectric measurements on large temperature and frequency ranges in cooling-heating cycle show reproducible and almost linear decreases of permittivity with the temperature increases for RSR. Permittivity of composites shows higher values increasing the nanotubes concentrations and decrease with temperature increase with non-reproducible values above room temperature in a heating-cooling cycle. Combined effects of segmental mobility increase of polymers with increasing temperature, thermal expansion and pores in materials could explain this behavior. Losses show non-uniform and non-reproducible temperature behaviour for MWCNT-RSR composite, having an overall increase with nanotube concentration. This can originate in some relaxations mechanisms in the samples, the effect of aggregates and rearrangements within the polymers structure and in the damage of nanotubes. Thermogravimetric investigations show a good mass stability of samples over investigated temperature range. Differential Scanning Calorimetry measurements revealed a weak endothermic effect suggesting some structural rearrangements in the samples. Generally permittivity and losses shows weak frequency dependence for RSR, but for composites dielectric constant show slow decreasing values with the frequency increase.

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1. Introduction

Silicone rubber (SR), or polydimethylsiloxane, is an elastomer with a backbone consisting of an inorganic silicon-oxygen polymer chain, on which freely-rotating organic methyl groups are attached [1]. Therefore, SRs have better chemical stability, heat resistance, and electrical insulating properties in comparison with organic rubber polymers containing carbon backbones. For a recent review on SR, see [1], while properties of several SR compounds can be found, for example, in [2]. For general purpose applications, some methyl groups in SRs can be substituted with vinyl groups, for extremely low-temperature applications while for applications requiring resistance at fuel, oil and solvents, some methyl groups are substituted by fluoro, methyl and vinyl groups. The low permittivity and dielectric losses of SRs make them ideal materials for flexible microwave substrates, especially when filled with micro and nano alumina [3], whereas their good elastic properties over wide temperature ranges make them suitable as sealants. These properties, combined with their low weight, recommend SRs also as materials of choice in automotive applications.

On the other hand, carbon nanotube (CNT)-silicone rubber composites [4], and more generally, CNT-polymer composites [5] are attracting increased attention due to their improved mechanical, electrical and thermal properties. These improvements are caused by the excellent mechanical, thermal and electrical properties of the CNTs [6]. For example, multiwall CNT (MWCNT)-rubber composites [7], in particular MWCNT-SR composites [8], show reversible photomechanical actuation if irradiated with near-infrared radiation.

This paper investigates the dielectric properties of MWCNT-red SR (MWCNT-RSR) composites over a wide frequency and temperature ranges, for different MWCNT mass concentrations. Because these composites can be regarded as biphasic mixtures of materials with different dielectric properties, it is expected that the dielectric properties vary with the MWCNT mass concentration. In fact, the interfacial phases of MWCNT-vulcanization SR were shown to be characterized by a wide range of relaxation phenomena [9]. The present study extends the investigation of dielectric properties to MWCNT-RSR composites.

2. Preparation and structural characterization of MWCNT-RSR composites

MWCNT-RSR composites were prepared from a mixture of a RSR gasket sealant purchased from the Den Braven Company and commercially available unfunctionalized MWCNTs. The L-4060 type MWCNTs with high-purity (> 95 %), from Shenzhen Nanotechnologies Co. Ltd.–China, have diameters of 40–60 nm and lengths between 5 μm and 15 μm . Both RSR and MWCNT components of the mixture, with different mass concentrations, were precisely weighed with a Sartorius CPA225D-OCE analytical balance and then mechanically mixed for homogenization. The as obtained mixtures were filled between two fresh polished rectangular parallel copper plates (carefully rinsed in benzene), which also served as electrical contacts, and deposited in air at room temperature (around 23 °C) for at least 10 days to complete the curing process and mass stabilization.

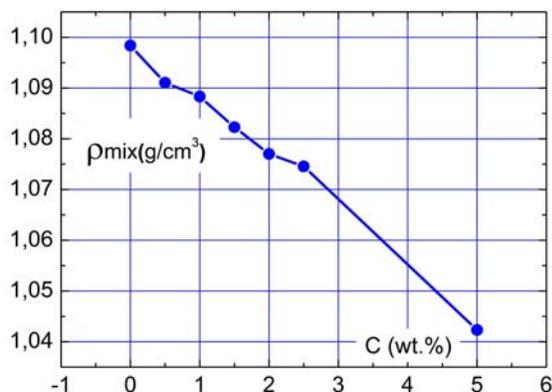
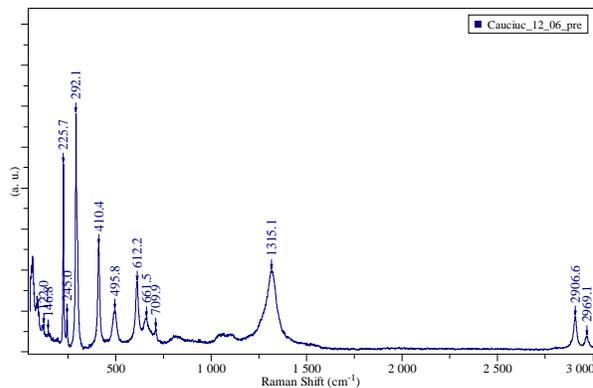
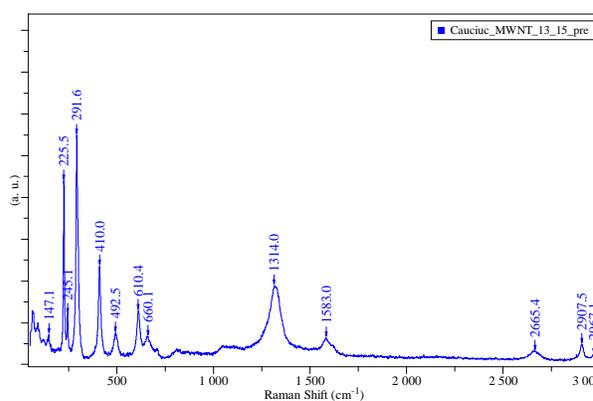


Fig. 1 Density of the MWCNT-RSR composite versus the MWCNT mass concentration

The density of the composites, measured by weighing with the analytical balance (Archimede method), was found to almost linearly decrease with increasing the concentration of MWCNTs, as illustrated in Fig. 1. This figure indicates that the density of the RSR (indicated by the vendor as being 1.08 g/cm³) is higher than that of MWCNTs. As mentioned in [10] (see also the references therein), it is quite difficult to assign a certain value to the density of MWCNTs: their skeletal (true) density is about 2.1 g/cm³, measurements of the MWCNTs density indicate a value of about 1.74 g/cm³, but the bulk density can vary between 0.03 g/cm³ and 0.22 g/cm³. Moreover, it seems that the density of MWCNTs also depends on their diameter and number of walls [11]. Our data in Fig. 1 is consistent with an apparent density of 0.53 g/cm³, due to the existence of pores within composites resulted from the preparation procedures and suggesting that MWCNTs form aggregates inside the polymer matrix.



(a)



(b)

Fig. 2. Raman shift of (a) RSR and (b) 5 wt. % MWCNT-RSR composite

The Raman spectra of the RSR and the 5 wt. % MWCNT-RSR composite are illustrated in Figs. 2(a) and 2(b), respectively. The presence of MWCNTs is evidenced in Fig. 2(b) by the appearance of the G band at about 1583 cm⁻¹ and of the peak at 2665.4 cm⁻¹, consistent with the 2D or G' band. In agreement with [12], the low-frequencies Radial Breathing Mode (RBM), which is associated with the vibrations of C atoms in the radial direction, is commonly not observed in MWCNTs, due to their large diameters. The RBM mode is situated between 120 cm⁻¹ and 250 cm⁻¹ for nanotubes with diameters between 1 nm and 2 nm, and its intensity becomes very weak for nanotubes with diameters larger than 2 nm, in particular for MWCNTs. The G band has an asymmetric lineshape and no multi-peak structure due also to the large diameters of the MWCNTs [12] (this band has a multi-peak structure in single-walled CNTs). The D band of MWCNTs usually seen in the Raman spectra around 1310 cm⁻¹ is not observed in Fig. 2(b), being covered by the more intense peak of the RSR located around 1315 cm⁻¹ [13]. However the presence of the D band is suggested by its related G' second order harmonic band, around 2665.4 cm⁻¹, which appears in defect-free sp² carbons with long range order and serves as an indicator of the crystalline quality and purity of the MWCNT via the ratio of D/G peak intensities

[13, 14]. The other remaining peaks assigned to RSR are slightly shifted by the presence of the MWCNT within the polymer matrix and this can suggest a weak interaction between the two components of mixture.

Complementary investigations were performed by Fourier Transform Infrared (FTIR) spectrometry in order to obtain information on the configuration of chemical bonds. FTIR measurements were performed at room temperature using a Bruker Tensor 27 spectrometer. The spectra were collected in the spectral range of 4000 – 650 cm^{-1} by averaging 64 scans with a resolution of 4 cm^{-1} . The results of FTIR measurements of the RSR and the 5 wt. % MWCNT-RSR composite are shown in Fig. 3 and Table 1. The two FTIR spectra are quite similar, which indicates that no new functional groups appear in the composite. The shifts of the peaks in the FTIR spectrum of RSR when MWCNTs are added are small, consistent with the low chemical reactivity of the high-purity unfunctionalized MWCNTs. These findings are in agreement with results reported in literature, which confirm that pristine MWCNTs are known to display very

weak, if any, specific C = C peaks around 1600 cm^{-1} [15, 16].

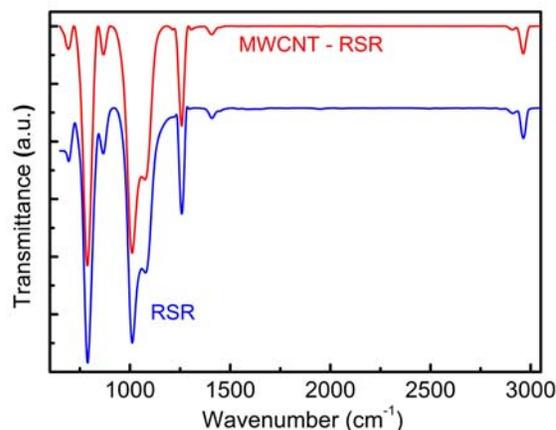


Fig. 3 FTIR spectra of RSR and 5 wt. % MWCNT - RSR composite

Table 1. IR active functional groups for RSR and 5 wt. % MWCNT-RSR

RSR		5 wt. % MWCNT-RSR	
Wavenumber (cm^{-1})	Functional group	Wavenumber (cm^{-1})	Functional group
2963	C-H	2962	C-H
2907	C-H	2908	C-H
1417	C-H	1407	C-H
1258	Si-O	1257	Si-O
1076	Si-O-Si	1077	Si-O-Si
1010	Si-O-Si	1010	Si-O-Si
864	Si-O-C	867	Si-O-C
787	Si-O-C	788	Si-O-C
700	Si-O-C	693	Si-O-C
663	Si-O-C		

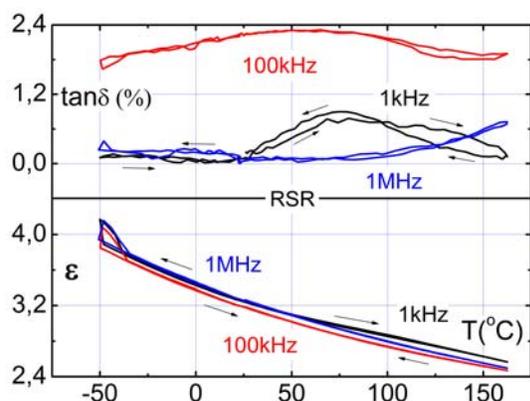
3. Dielectric properties of MWCNT-RSR composites

Dielectric measurements in the 300 Hz \div 5 MHz frequency interval have been performed on a large temperature range, between $-50\text{ }^{\circ}\text{C} \div +150\text{ }^{\circ}\text{C}$, with a cooling/heating rate of about $1.7\text{ }^{\circ}\text{C}/\text{min}$. The Hioki 3532-50 type automatic RLC bridge for capacitance and losses measurements and an Kethley 2010 multimeter, equipped with a chromel–alumel thermocouple for temperature determinations, were controlled by a computer through GPIB interfaces for automatic data registration and further analysis. All samples were subjected to a temperature cycle; they were first cooled from room temperature up to $-50\text{ }^{\circ}\text{C}$, then heated up to $150\text{ }^{\circ}\text{C}$, and cooled again up to room temperature (arrows in Fig.4). The dielectric permittivity was obtained using the classical formula $C = \epsilon_0 \epsilon_r S/d$ for plate parallel capacitance of samples with known S area and d thickness.

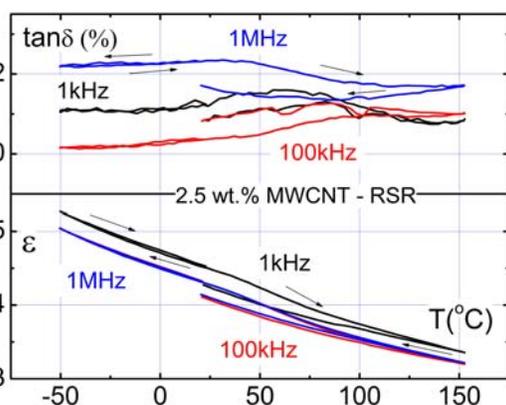
Fig. 4(a) displays the temperature dependence of the dielectric permittivity and losses at selected frequencies for the RSR, while Fig. 4(b) shows the same dependences for a composite MWCNT-RSR containing 2.5 wt. % MWCNT.

For RSR, the permittivity is almost reproducible in a cooling-heating cycle for all frequencies, except for temperatures below $-50\text{ }^{\circ}\text{C}$, in which the rigidity of the material increases. Indeed, the modulus of rigidity increases abruptly below $-30 \div -40\text{ }^{\circ}\text{C}$ in general-purpose silicone rubbers [2], the glass transition temperature being as high as $-40\text{ }^{\circ}\text{C}$ in liquid silicone rubbers [17]. At the same time, for the selected frequencies in Fig. 4(a), a maximum variation of the permittivity values of only 3 % could be registered for the investigated temperature range, this suggesting a low dependence of the dielectric constant versus frequency. Also, the permittivity decreases almost linearly with increasing temperature for all frequencies. This behavior contrasts the usual increase of permittivity with temperature due to an increase in the segmental mobility

of polymers and could be caused by the thermal expansion of the RSR, which leads to an increase of the capacitor thickness and thus affects the measurement conditions [18].



(a)



(b)

Fig. 4 Temperature dependence of the permittivity and losses of MWCNT-RSR composites at different frequencies for MWCNT concentrations of: (a) 0 wt. % and (b) 2.5 wt. %

Typical thermal expansion coefficients of SR are about $2 \div 2.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$, more than one order of magnitude larger than in CNTs, in which the measured value of this parameter is of only $7.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ [19]. An additional contribution to the thermal expansion of RSR could come from the pores in the material, which originate in the mixing process. The discrepancy in thermal expansion coefficients between RSR and MWCNT supports the assumption stated above about the decrease of permittivity with temperature. A corroboration of this fact is provided by the same relative variation of permittivity, of about 23 % of the room temperature (RT) value and over the whole temperature range, found in the RSR and the 2.5 wt. % MWCNT-RSR composite (see Figs. 4(a) and 4(b)).

Generally, dielectric losses of RSR exhibit small values, which is a typical behavior in SRs due to their very good insulating properties. The dielectric losses show a small hysteresis for all frequencies, but recover their initial values after a heating-cooling cycle and for all frequencies. This behavior suggests the existence of some relaxation mechanisms in the samples. At the same time the wide maxima of losses, covering large temperature ranges, suggest the existence of some absorption mechanisms. At 100 kHz the losses show the largest values compared to other frequencies.

For 2.5 wt. % MWCNT-RSR composites the dielectric constant and losses show reproducible values in the cooling-heating process at temperatures below room temperature (RT), for all frequencies. This behavior suggests that the temperature and measuring field have no influence on the sample structure. Above RT, the permittivity displays non-reproducible values with about 4 % decreased values around RT and in the heating-cooling process. The losses also shows non-reproducible values after heating and cooling back to the RT, but their final values can be either larger or smaller than the initial value at room temperature. This behavior above RT suggests a rearrangement of polymeric chains within samples due to both temperature and electric field effects. Generally, the permittivity values of 2.5 wt. % MWCNT-RSR composites are greater than those for RSR, with comparable values for dielectric losses. Also, the permittivity, as for RSR, shows decreasing values as the temperature increases, for all frequencies, Fig. 4(b). The difference between permittivity values for the selected frequencies in Fig. 4(b) does not exceed 6 % for the investigated temperature range.

The different temperature behaviors for RSR and 2.5 wt. % MWCNT-RSR composites can be attributed to formation of aggregates in the composites [20], which change their spatial arrangements in heating-cooling cycles [21]. Also the (partial) damage of the MWCNT in MWCNT aggregates due to the different thermal expansion coefficients of MWCNT and the host is not excluded. The existence of MWCNT aggregates in the composite samples, due to strong van der Waals forces between MWCNTs, is also suggested by the fact that no significant electrical conduction (not shown) was observed in our samples where the MWCNT mass concentration is as large as 5 wt. % (9 vol. %). The MWCNTs used in our samples were not functionalized, which can explain their greater tendency to form aggregates compared to functionalized MWCNTs, for which percolation thresholds in composites with a polymer matrix appear, in general, at MWCNT concentrations of less than 1 vol. %; percolation thresholds at even less than 0.01 vol. % filler concentration are observed for MWCNT with large length-to-diameter aspect ratios [22]. However, as in our case, in composites using a polydimethylsiloxane SR matrix percolation thresholds were observed only at MWCNT concentrations larger than 10 vol. % [23].

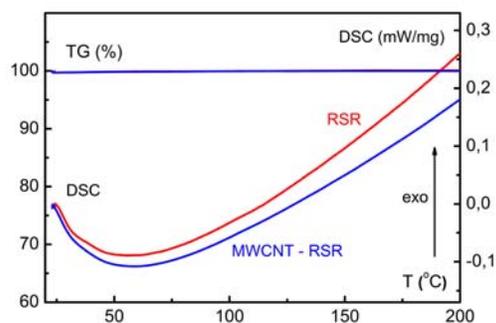


Fig. 5 Thermal analysis of RSR and the composite with 5 wt. % MWCNT

A confirmation of slight rearrangements of molecules, which could be at the origin of the thermal hysteresis observed in dielectric measurements in both RSR and its MWCNT composites is provided by a thermal analysis of these materials. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) studies have been performed with a Netzsch Jupiter STA 449C in an Al_2O_3 crucible with a heating speed of 10 K/min, under the flow of 20 mL/min dry air, the results being displayed in Fig. 5. In the temperature range relevant for the dielectric measurements there was no noticeable change in mass for both samples in TG investigations. The DSC measurements revealed a weak endothermic effect in both samples, at about 55 °C for the composite and 59 °C for the silicone, which suggests some rearrangements in the polymer matrix.

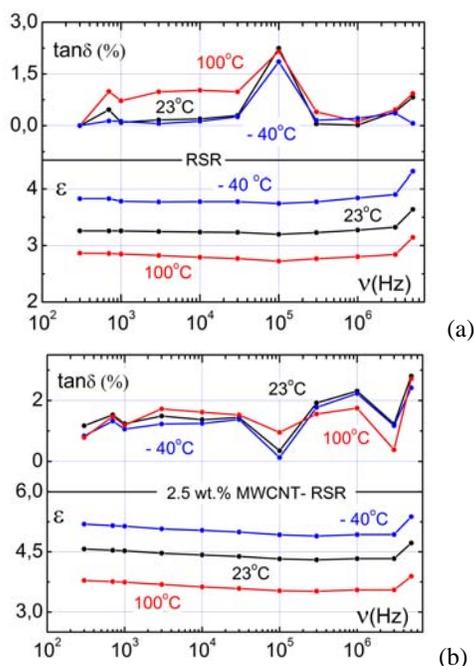


Fig. 6 Frequency dependence of the permittivity and losses of (a) RSR and (b) 2.5 wt. % MWCNT-RSR composites at different temperatures

Thus the addition of MWCNT facilitates this rearrangement of the polymer matrix at a lower temperature.

The dielectric permittivity of RSR shows a slight decrease as the frequencies increase up to 10^5 Hz, followed by a slow increase up to 5 MHz, as can be seen in Fig. 6(a). Around 100 kHz the losses show a pronounced peak, similar to the frequency dependence of permittivity and losses in SR reported in [3], and attributed to relaxation phenomena. The decreased values of losses around -40 °C could be associated with the rigidity increase of the material at low temperatures. Room temperature dielectric measurements up to 1 MHz of polydimethylsiloxane mixed with a cross-linker showed an almost constant dielectric permittivity, of 2.5, and very small and nearly constant losses, in overall agreement with our data [24].

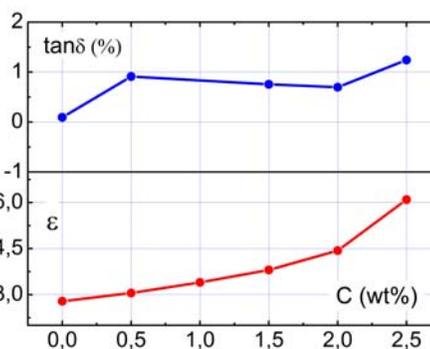


Fig. 7 Dependence of dielectric parameters on the mass concentration of MWCNTs at 1 kHz

The frequency behavior of permittivity and losses versus frequencies for 2.5 wt. % MWCNT-RSR composites is similar to RSR but with greater values, as can be seen from Fig. 6(b). However losses show some pronounced minima around 100 kHz and 2 MHz. A similar frequency dependence of both permittivity and losses was observed in a polydimethylsiloxane SR containing CNT fillers [23].

The mass concentration value of MWCNT in RSR influences the electric parameters, as shown in Fig. 7. Measurements performed at 1 kHz and at RT revealed that the dielectric permittivity of the composites increases with increasing MWCNT mass concentration values. This behavior is consistent with other observations [23]. The losses show an overall increase in values increasing the mass concentration C of MWCNT.

4. Conclusions

Composites containing high-purity unfunctionalized MWCNTs with different mass concentration and RSR were prepared. Structural characterizations of these composites revealed a low chemical reactivity between the polymer matrix and MWCNTs. Dielectric characterization

of the MWCNT-RSR composites over extended frequency and temperature ranges show reproducible permittivity and losses in cooling-heating cycles for temperatures up to 50 °C, above which thermal analysis indicate the occurrence of slight rearrangements of polymers segments. It was found that the permittivity of both RSR and MWCNT-RSR composites decrease almost linearly with temperature and has a weak frequency dependence. The losses of the composites have non-uniform temperature and frequency dependence. The permittivity value increases with the mass concentration of MWCNTs and the losses show an overall increase with this parameter. The results suggest that MWCNT-RSR composites could be used as low-loss materials with permittivity values tunable as a function of temperature or MWCNT mass concentration.

References

- [1] S. C. Shit, P. Shah, *Natl. Acad. Sci. Lett.* **36**, 355 (2013).
- [2] http://www.silicone.jp/e/catalog/pdf/rubber_e.pdf
- [3] L. K. Namitha, J. Chameswary, S. Ananthakumar, M. T. Sebastian, *Ceramics International* **39**, 7077 (2013).
- [4] G. Momen, M. Farzaneh, *Rev. Adv. Mater. Sci.* **27**, 1 (2011).
- [5] J.-H. Du, J. Bai, H.-M. Cheng, *eXPRESS Polymers Lett.* **1**, 253 (2007).
- [6] R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London (1998).
- [7] S. V. Ahir, A. M. Squires, A. R. Tajbakhsh, E. M. Terentjev, *Phys. Rev. B* **73**, 085420 (2006).
- [8] S. V. Ahir, E. M. Terentjev, *Nature Materials* **4**, 491 (2005).
- [9] M.-J. Jiang, Z.-M. Dang, M. Bozlar, F. Miomandre, J. Bai, *J. Appl. Phys.* **106**, 084902 (2009).
- [10] J. H. Lehman, M. Terrones, E. Mansfield, K. E. Hurst, V. Meunier, *Carbon* **49**, 2581 (2011).
- [11] Ch. Laurent, E. Flahaut, A. Peigney, *Carbon* **48**, 2994 (2010).
- [12] A. Jorio, M. A. Pimenta, A. G. Souza Filho, R. Saito, G. Dresselhaus, M. S. Dresselhaus, *New J. Phys.* **5**, 139 (2003).
- [13] D. Cai, A. Neyer, R. Kuckuk, H. M. Heise, *J. Molec. Struct.* **976**, 274 (2010).
- [14] R. A. DiLeo, B. J. Landi, R. P. Raffaele, *J. Appl. Phys.* **101**, 064307 (2007).
- [15] V. T. Le, C. L. Ngo, Q. T. Le, T. T. Ngo, D. N. Nguyen, M. T. Vu, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **4**, 035017 (2013).
- [16] Y. Umasankar, B. Unnikrishnan, S.-M. Chen, T.-W. Ting, *Int. J. Electrochem. Sci.* **7**, 484 (2012).
- [17] C. Tong, Y. J. Chao, X. M. Chen, J. W. Van Zee, *J. Power Sources* **196**, 9536 (2011).
- [18] E. Muhammad Abdul Jamal, P. A. Joy, P. Kurian, M. R. Anantharaman, *Materials Science and Engineering B* **156**, 24 (2009).
- [19] Y. Maniwa, R. Fujiwara, H. Kira, H. Tou, H. Kataura, S. Suzuki, Y. Achiba, E. Nishibori, M. Takata, M. Sakata, A. Fujiwara, H. Suematsu, *Phys. Rev. B* **64**, 241402 (2001).
- [20] C.-H. Kiang, W. A. Goddard III, R. Beyers, D. S. Bethune, in *Carbon Nanotubes*, M. Endo, S. Iijima, M. S. Dresselhaus (eds.), Pergamon, Oxford (1996), p. 47.
- [21] I. Dierking, G. Scalia, P. Morales, D. LeClere, *Adv. Mat.* **16**, 865 (2004).
- [22] S. Pfeifer, S. H. Park, P. R. Bandaru, *J. Appl. Phys.* **108**, 024305 (2010).
- [23] F. Galantini, G. Gallone, G. Levita, F. Carpi, D. De Rossi, *Proc ACTUATOR 2010*, 12th International Conf. New Actuators, Bremen, 2010, p. 862.
- [24] M. Molberg, Y. Leterrier, C. J. G. Plummer, C. Walder, C. Löwe, D. M. Opris, F. A. Nüesch, S. Bauer, J.-A. E. Manson, *J. Appl. Phys.* **106**, 054112 (2009).

*Corresponding author: berbecaru2ciceron@yahoo.com;