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MICROWAVE DIELECTRIC PROPERTIES OF POLYIMIDE COMPOSITES BASED ON TiO_2 NANOTUBES AND CARBON NANOTUBES

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A study of the microwave dielectric properties of a series of polyimide composites based on titanium dioxide nanotubes and carbon nanotubes is presented. The composites were prepared through casting technique onto glass plates of a poly (amic acid) solution incorporating different amounts of titanium dioxide nanotubes and/or carbon nanotubes, followed by thermal imidization under controlled temperature conditions. The dielectric properties were analysed through broadband dielectric spectroscopy within a frequency domain spanning from 1 MHz up to 3 GHz. The effects of filler content, temperature and frequency on samples' microwave dielectric behaviour are discussed. The interfacial/Maxwell-Wagner and dipolar/orientational polarization were highlighted by the results. The samples demonstrated very stable dielectric properties while varying the temperature but are strongly depending on the filler content.

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1. Introduction

Aromatic polyimides are polymers having exceptional thermal, mechanical and electrical characteristics, and are thus suitable for use as polymeric matrices for the preparation of high performance organic/inorganic composites [1-3]. The introduction of inorganic fillers, like ceramics having high dielectric constant, can improve the dielectric properties of polyimides. Thus, polyimide composites containing different inorganic fillers were prepared in order to improve their dielectric properties. For example $BaTiO_3$, TiO_2, etc, are reported in the literature as having good stability at elevated temperature and larger dielectric constant, being used in different fields [4-6]. However, the concentration of inorganic fillers in the polymer composite (matrix) is limited because at a very high content the materials lose their flexibility.

Carbon nanotubes (CNTs) have been used extensively as inorganic fillers for polymeric composites due to their excellent thermal, electrical and mechanical properties [7, 8]. The presence of CNTs in a polymeric matrix greatly improves electrical and thermal conductivity, even at a very low concentration of the filler [9]. CNTs-based polyimide composites have been studied due to their interesting properties, such as high thermal stability, increased electrical conductivity and good mechanical properties [10-18]. At a low concentration of CNTs, the conductivity increases remarkably especially near the percolation threshold and presents a typical insulator-conductor transition. Also, in this concentration region of CNTs, the dielectric constant increases considerably.

Previously, we prepared polyimide composite films containing TiO_2 nanotubes (TNs) and their properties~~,~~ such as morphology, thermal, electromechanical and electrical characteristics

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were studied in correlation with filler content [19, 20]. Within the papers mentioned above, dielectric properties were determined by broadband dielectric spectroscopy (BDS) in the frequency range 1-10^6 Hz. Recently, we investigated the electromechanical behavior of the same polyimide composite films incorporating both TNs and CNTsbut not the dielectric properties [21]. On the other hand, many studies have been previously realized and published regarding the evolution of dielectric properties of various composites within classical frequency domain spanning up to 10 MHz [22-24]. However, the literature is limited in respect to analysis of dielectric parameters behavior at higher frequencies due to complicated measurement protocol and more difficult interpretation of the dielectric results [25-28]. Herein we present a study of the microwave dielectric properties of polyimide films containing CNTs and TNs by using BDS technique at high frequency region (10^6 - 3×10^9 Hz). The introduction of CNTs increased substantially the electrical conductivity of the films and therefore, it was not possible to be studied their dielectric characteristics at low frequency range by BDS. The advantage of working at microwave frequencies is that even the highly conductive materials can be analyzed from electrical viewpoint as the effect of electrode polarization [29], which may lead to giant values of the dielectric constant and losses, is not strongly influencing the determinations. Thus, the herein study is discussing the effect of filler content, frequency and temperature variation upon dielectric behavior of the samples under test.

2. Experimental

2.1. Materials

4,4′-(1,3-phenylenedioxy)dianiline (PFDA), 4,4′-oxydiphthalic anhydride (ODPA), multi-walled carbon nanotubes (O.D.×L: 6-9 nm×5 µm, > 95% carbon) (CNTs), 3-aminopropyltriethoxysilane (APTS) were provided from Sigma-Aldrich and used as received. N-methyl-2-pyrrolidone (NMP) was dried over phosphorus pentoxide and distilled under vacuum. Titanium dioxide nanotubes (TNs) with inner diameter of 4-5 nm, outer diameter of around 10-12 nm and length of several hundreds of nanometers were prepared by the hydrothermal method starting from commercial titanium dioxide (Riedel de Haen) (12 m^2 g^{-1} specific surface area). The surface of TNs was modified by silylation with the aim to improve organic-inorganic interfacial cohesiveness and to minimize the tendency for agglomeration of the inorganic filler [20].

2.2. Preparation of polyimide composite films

Polyimide composite film P1 containing 3% CNTs was prepared by physical mixing technique of different amounts of filler in a poly(amic acid) (PAA) solution obtained by polycondensation reaction of equimolecular amount of diamine PFDA with dianhydride ODPA, in NMP as solvent. The resulting dispersions were cast onto glass plates followed by drying and thermal imidization under controlled temperature conditions at 70°C for 3 h, at 100, 150, 200°C, each for 1 h, and at 250°C for 2 h. Flexible free standing films were stripped off the glass plates by immersion in hot water.

Polyimide composite films containing CNTs and TNs, P2, P3, P4, having 10% TNs and 1, 3 and 6% CNTs, respectively, as well as P5 having 20% TNs and 3% CNTs, were similarly produced by casting a dispersion of TNs and CNTs in PAA solution, as was previously reported [21].

2.3. Measurements

The FTIR spectra were recorded on a Bruker Vertex 70 Spectrometer. Microscopic investigations were performed on an Environmental Scanning Electron Microscope type Quanta 200 operating at 30 kV with secondary and backscattering electrons in low vacuum mode. Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Budapest, Hungary) in air, at a heating rate of 10°C min^{-1}. The initial decomposition temperature is characterized as the temperature at which the sample achieved a 5% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded. The dielectric measurements were performed with the help of a

Novocontrol Dielectric Spectrometer and measured within a frequency range spanning from 1 MHz up to 3 GHz. Temperature was controlled between 298.15 K and 473.15 K with the help of a purge gas system. Previously, samples were held within the temperature control system for 24 hours at 383.15 K in order to dry them completely and remove any solvent.

3. Results and discussion

3.1. General characterization

The structure of the composite films was confirmed be FTIR spectroscopy. In the FTIR spectra characteristic bands for polyimide rings appeared at around 1775, 1708, 1371 and 742 cm^{-1}. The absorption band of poly(amic acid) precursor at 1650 cm^{-1} was not observed indicating that the imidization reaction was complete.

The morphology of the composites was investigated by SEM analysis. Figure 1 presents the cross-sectional images of P1, P4 and P5. A good compatibility between polyimide matrix and filler was observed. By increasing the filler content, some areas of agglomerations and microvoids formation appeared, especially for the sample P5 with 20% TNs and 3% CNTs.

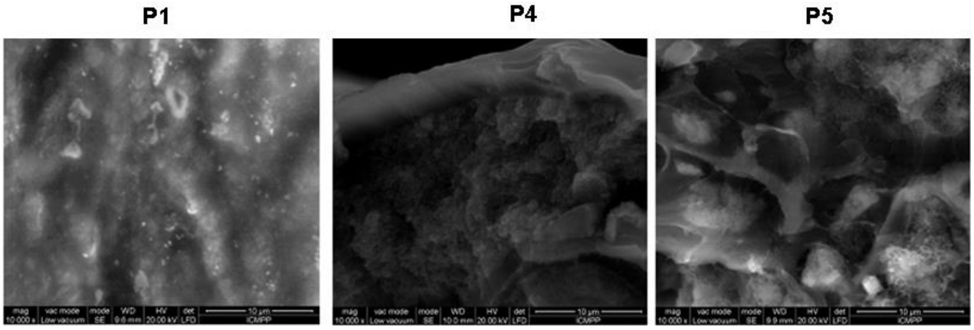


Fig. 1. SEM micrographs of the samples P1, P4 and P5

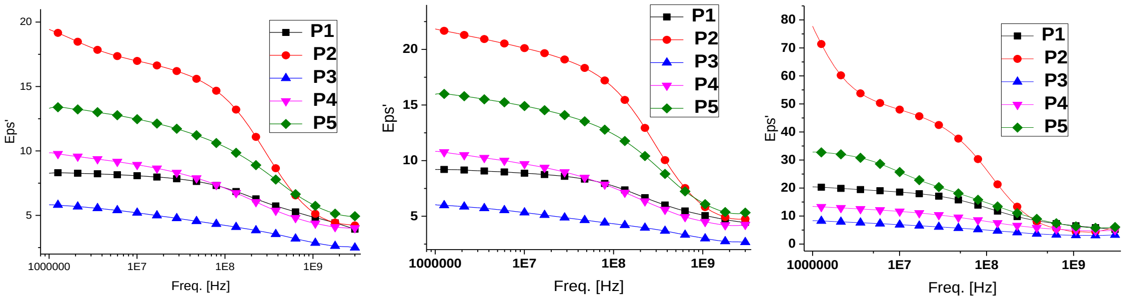
The thermal stability was evaluated by TGA in air atmosphere. The film samples showed very good thermal stability, with initial decomposition temperature over 475°C and the temperature of 10% weight loss in the range of 535-540°C. The maximum of decomposition was in the range of 585-600°C and the weight loss at 700°C was between 54 and 60%.

3.2. Complex permittivity versus TNs and CNTs content

The electrical properties of the composite films were studied using dielectric relaxation spectroscopy (BDS). The dielectric analysis revealed a strong dependency between the filler content, in our case TNs and CNTs, and the variation of dielectric parameters. Figure 2 presents the dependence of dielectric permittivity (ε') with frequency at three selected temperatures: 298.13, 373.15 and 473.1 K. The ε' is mainly quantitatively affected by the variation of TNs and CNTs percentage, fact which is more obvious when analysing the values of relaxation strength for each sample. The relaxation strength, which is the difference between ε_s, low-frequency limit of the dielectric function, and ε_∞, high-dielectric limit of the composite dielectric limit, is increasing while raising the percentage of TNs and CNTs. For all the samples the ε' decreased dramatically with the increase of the frequency, especially in the frequency domain of 10^8-$3*10^9$ Hz, as expected. This behavior can be explained by the fact that at lower frequency dipoles are able to reorient and contribute to orientation polarization while at higher frequency the dipole orientation decreases thus decreasing the orientation polarization. The introduction of TNs in the composite sample, in the case of P3 (containing 3 % CNTs and 10 % TNs) in comparison with sample P1 (containing only 3 % CNTs), slightly increased the ε' at 1 MHz and temperature till 373.15 K. This behavior was also observed in the case of P5 containing 20 % TNs and 3 % CNTs. Regarding the samples P2, P3 and P4 having the same content of 10 % TNTs and different CNTs amounts of 1, 3 and 6 % respectively, the real permittivity increased with CNTs percentage meaning that a higher quantity of CNTs is leading to higher values of dielectric constant as expected. This can be explained if we consider the model of nanocapacitor principle, nanocapacitor formation in the composite [30] in which each nanocapacitor is formed of two CNTs particles as electrodes and the dielectric material is formed from the polymer containing TNs. The introduction of TNs as inorganic filler increases the overall dielectric characteristic between CNTs nanoparticles thus increasing ε'. The sample P5 containing 20 % TNs and 3 % CNTs exhibited higher ε' when compared with samples P3 containing 3 % CNTs and lower concentration of TNs (10 %). In this case the material based on polymer incorporating TNs exhibited higher dipole concentration which leads to an increase of ε' value. By enlarging the concentration of CNTs, the number of nanocapacitors increased leading to a higher value of ε'. Thus, ε' values of samples containing 10 % TNs and different amount of CNTs, P2 (1 % CNTs), P3 (3 % CNTs) and P4 (6 % CNTs) were 5.81, 9.84 and 13.45, respectively, at 298.15 K and 1 MHz. CNTs in polymers form some interconenected structures even at low concentrations, which give rise to electron flow between them and therefore lead to high values of ε', especially at lower frequencies. P2 having the lowest concentration of CNTs exhibited the lowest ε'. In this case taking into account the model of nanocapacitor formation, the number of the nanocapacitors and the dipole concentration were low and the material behavior was of a dielectric. This means also that CNTs were well distributed without forming conductive percolation networks.

Table 1. The ε' values of all the samples at 1MHz, 100 MHz and 1 GHz at three selected temperatures: 298.15, 373.15 and 473.15 K.

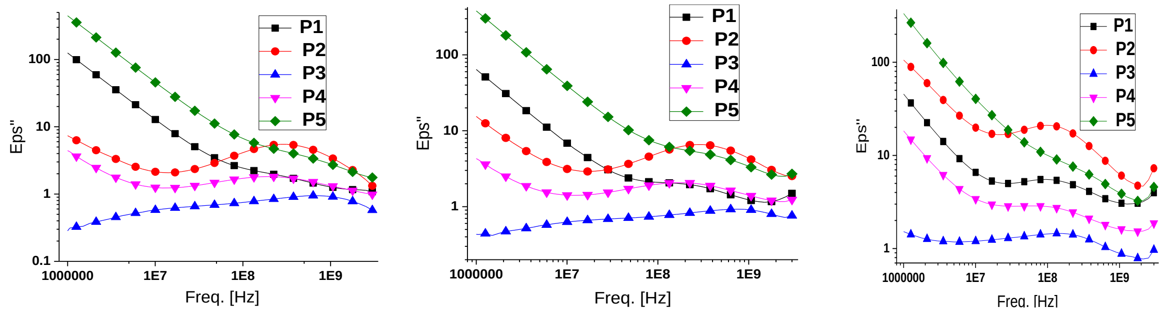
Sample	1MHz	100MHz	1GHz	1MHz	100MHz	1GHz	1MHz	100MHz	1GHz
	T= 298.15K			T=373.15K			T=473.15K		
P1	8.27	7.02	4.82	9.20	7.58	5.05	20.41	12.47	6.52
P2	5.81	4.17	2.85	6.03	4.27	2.99	8.34	4.88	3.12
P3	9.84	6.96	4.37	10.82	7.38	4.50	13.41	7.842	4.92
P4	13.30	10.13	5.73	15.96	12.14	6.08	32.82	14.21	6.32
P5	13.45	8.21	5.43	14.86	8.73	5.61	18.04	9.62	6.32



a) b) c)

Fig. 2. The frequency dependence of ε' at 292.15 (a), 373.15 (b) and 473.15 K (c) for the samples P1-P5.

Fig. 3 presents the dependence of imaginary permittivity (ε'') with frequency at three selected temperatures: 298.13, 373.15 and 473.1 K. The ε'' decreased significantly in the frequency range 100 MHz - 3 GHz. Thus, at 298.15 K ε'' values were in the intervals 0.29-428 at 1 MHz and 0.91-2.81 at 1 GHz. From 100 MHz downwards, a significant increase of the imaginary permittivity may be observed for all the samples. The increase of ε'' at lower frequencies may be ascribed to interfacial or Maxwell-Wagner polarization which occurs due to charges blocking at interfaces inside inhomogeneous materials. At higher frequencies the maximum reached by the losses can be attributed to dipolar or orientational polarization which may be induced by polar group rotations [31]. The sample containing 1 % CNTs and 10 % TNs exhibited the lowest ε'', in the range of 0.29-0.91, over the entire interval of frequency, fact which is emphasising the role played by the filler content on ε'' of others samples. Thus, the interfacial polarization is not so visible at the level of samples containing a smaller number of interfaces, practically, in the case of samples with lower percentage of filler. At high frequencies, however, the ε'' is low and remains more or less constant because the orientation polarization due to chain motion of polymer cannot keep phase with the rapidly oscillating electric field. Thus, the ε'' values of P1 and P4 were 120.8 and 424, respectively, at 1 MHz. This is due to the existence of a higher concentration of CNTs than percolation concentration due to the presence of DC-conductivity. The percolation theory predicts that at a critical volume concentration, there is a percolation transition in which the composite is converted from a capacitor to a conductor. However, the introduction of TNs decreased the ε'' values of the samples. For example ε'' of P5 was 5.39 while for the sample P1, in the absence of TNs, ε'' value was 120.8 at 1 MHz. This is due to the fact that the mobility of polymer chains decreases with addition of TNs since the rotational potential barrier energy increases gradually by increasing the TNs concentration thus limiting the chain motion of polymer due to the electric field.



a) b) c)

Fig. 3. The frequency dependence of ε'' at 292.15 (a), 373.15 (b) and 373.15 K (c) for the samples P1-P5.

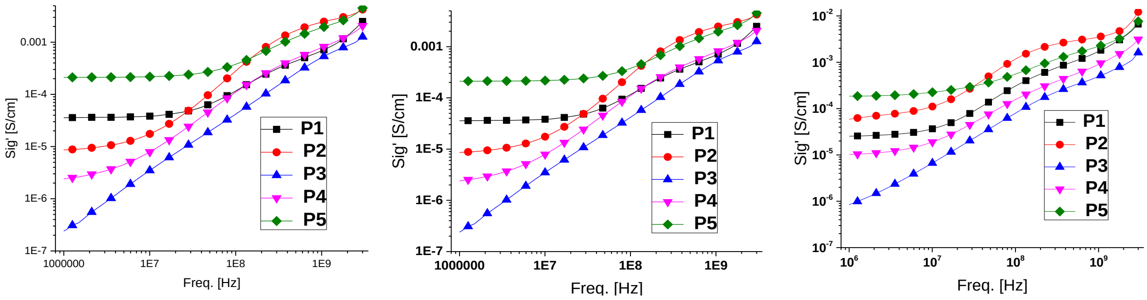
Table 2. Imaginary permittivity (ε'') values of the samples at 1MHz, 100 MHz and 1 GHz at three selected temperatures: 298.15, 373.15 and 473.15 K.

Sample	1MHz	100MHz	1GHz	1MHz	100MHz	1GHz	1MHz	100MHz	1GHz
	T = 298.15			T=373.15 K			T=473.15 K		
P1	120.80	2.48	1.20	59.19	2.10	1.21	44.06	5.71	3.01
P2	0.29	0.76	0.91	0.43	0.77	0.91	1.48	1.43	1.01
P3	4.22	1.69	1.20	4.28	2.01	1.41	18.10	2.91	1.62
P4	424.00	6.69	2.81	382.01	6.75	3.23	310.20	10.08	3.87
P5	5.39	2.36	1.42	8.22	2.73	1.62	47.08	3.79	2.19

In respect to ε'', no important shift of the losses peak towards higher or lower losses can be observed, fact which is once again suggesting that the solvent from the material was completely removed during the thermal pre-treatment process (Fig. 3, Table 2). At high frequencies, ε'' remains more or less constant with increasing temperature because the orientation polarization due to chain motion of polymer cannot keep phase with the rapidly oscillating electric field.

3.3. AC and DC conductivity versus TNs and CNTs content

Fig. 4 presents the dependence of the real conductivity vs frequency, at three selected temperatures: 298.15, 373.15 and 473.15 K. For low concentration of CNTs (1 %, sample P2) the conductivity is frequency dependent, it increases linearly with increasing frequency, which corresponds to the behavior of a dielectric material. For the samples containing 3 % and 6 % CNTs (Samples P1, P3, P4 and P5) it can be observed that the real conductivity is frequency independent, but only below a critical frequency (f_c). The frequency independent regime of the curve is characteristic for conductive materials where σ* relates to DC conductivity (σ_{DC}). σ_{DC} is activated by the mobile charge carriers that are moving through polymer network. At 25°C and 1 MHz, the sample containing 6 % CNTs, P4, exhibited the highest value of σ_{DC} of 2.66×10^{-4} S cm^{-1}. P1 (3% CNTs) exhibited a σDC of 7.36×10^{-5} S cm^{-1}. A decrease of σ_{DC} was observed in the case of P3 and P5 containing 10 and 20 % TNs, respectively. Thus, the σ_{DC} of P3 and P5 was 2.46×10^{-6} and 3.17×10^{-6}, respectively (Table 3). For further increasing in temperature the plateau region of σ_{DC} slightly increased to higher frequencies f_c. This critical value of frequency is one decade larger in the case of P1 and P4. In the case of the samples containing 10 % of TNs and 3 and 6 % of CNTs, respectively, one can notice that the percolation is shifting to higher frequencies when the CNTs percentage is augmented; practically, the frequency domain where the DC-conductivity is observable is increasing for the sample P5 and the conductivity is rising as well.



a) b) c)

Fig. 4. The frequency dependence of real conductivity at 298.15 (a), 373.15 (b) and 473.15 K (c).

Table 3. Real conductivity values of the samples at 1MHz, 100 MHz and 1 GHz and two selected temperatures 298.15and 473.15 K; σDC at 1 MHz and two selected temperatures 298.15 and 473.15 K; fc values at 298.15 and 473.15 K.

Sample	f_c (Hz)		T= 298.15K				T=473.15K			
	298.15 K	473.15 K	Real conductivity (Scm^{-1})			σ_{DC}	Real conductivity (Scm^{-1})			σ_{DC}
			1MHz	100MHz	1GHz		1MHz	100MHz	1GHz	
P1	3.6E7	3.5E6	7.36 E-5	1.4 E-4	1.8 E-3	8.10 E-5	2.48 E-4	3.29 E-4	6.2E-3	2.73 E-4
P2	-	-	1.80 E-7	4.16 E-5	9.64 E-4	-	8.93 E-7	8.24 E-5	1.6 E-3	-
P3	1.96E6	2.27E6	2.46 E-6	1.05 E-4	1.9 E-3	2.71 E-6	1.03 E-5	1.71 E-4	3.2 E-3	1.13 E-5
P4	5.2E7	8.23E7	2.66 E-4	5.4 E-4	2.9 E-3	2.93 E-4	1.78 E-5	5.8 E-4	7 E-3	1.96 E-5
P5	3.49 E6	5.10 E6	3.17 E-6	1.2 E-4	2.1 E-3	3.49 E-6	2.8 E-5	1.86 E-4	4.2 E-3	3.08 E-5

The DC and AC conductivities till 373.15 K, for all the samples, are strongly dependent on temperature and are augmenting when temperature is raised. In addition, till 373.15 K as well as the low frequency dispersion region is not visible for none of the sample even if the temperature is increased, one can assume that the electrode polarization is not influencing the results presented within the herein paper. Thus, at lower frequencies the conductivity observed is influenced only by interfacial polarization and not by the charges accumulated at the interface between the electrode and the sample. However, at 473.15 K, the general behaviour of the samples is similar, but in the case of P1, at low frequencies, an additional steeped increase of both ε' and ε'' is noticeable, fact which is highlighting the fact that, besides the interfacial polarization, the electrode polarization is occurring and is strongly affecting samples' conductivity.

4. Conclusions

Polyimide composite films based on TNs and CNTs were developed and characterized within microwave frequencies (10^6 - 3×10^9 Hz) with the help of BDS. The TNs and CNTs percentage within the films significantly affected the dielectric parameters and two polarizations, interfacial or Maxwell/Wagner and orientational/dipolar, could be distinguished from the dielectric graphical characteristics. Especially at lower frequency (in the interval 1 MHz-100 MHz), the real and imaginary dielectric permittivity considerably increased with the increase of CNTs contents while the content of TNs exhibits a lower influence. At high frequency (100 MHz - 3 GHz) their values substantially decreased.

The real conductivity values of the samples considerably increased by introducing CNTs in concentration of 3 and 6 % while the introduction of TNs lead to a decrease of the values. All the composites exhibited high conductivity and very good thermal stability while from measuring set-up viewpoint the electrode polarization, which is a parasitic phenomenon leading to giant ε' and ε'', could be avoided at relative high frequencies. The strong thermal stability of the composite films is revealing the outstanding potential of these materials for electromagnetic shielding applications as well as for screen printing flexible operating at microwave frequencies.

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References

[1] M. Sato, Polyimides, in: O. Olabisi (Ed.), Handbook of Thermoplastics, Marcel Dekker, New York, 1997, pp. 665-699.
[2] D. Wilson, "Polyimides as resin matrices for advanced composites", in: D. Wilson, H. D. Stenzenberger, P. M. Hergenrother (Eds) Polyimides, Springer, Netherlands, 187-226, 1990.
[3] C. E. Sroog, Polyimides, Prog.Polym. Sci. **16**, 561 (1991).
[4] E. Hamciuc, C. Hamciuc, I. Bacosca, M. Cristea, L. Okrasa, Polym. Compos. **32**, 846 (2015).
[5] Y. Tong, Y. Li, F. Xie, M. Ding, Polym. Int. **49**, 1543 (2000).
[6] J. W.Zha, Z. M. Dang, H. T. Song, Y. Yin, G. Chen, J. Appl. Phys. **108**, 094113 (2010).
[7] W. Khan, R. Sharma, P. Saini, "Carbon nanotubes-Current progress of their polymer composites", M. R. Berber, I. H. Hafez, ed., InTech, 2016.
[8] R. Andrews, M. C. Weisenberger, Carbon nanotube polymer composites, Curr. Opin. Solid State Mater. Sci. **8**, 31 (2004).
[9] C. Min, X. Shen, Z. Shi, L. Chen, Z. Xu, Polymer Plast. Technol. Eng. **49**, 1172 (2010).
[10] T. C. Mo, H. W. Wang, S. Y. Chen, Y. C. Yeh, Polym. Compos. **29**, 451 (2008).
[11] Y. C. Huang, J. H. Lin, I. H. Tseng, A. Y. Lo, T. Y. Lo, H. P. Yu, M. H. Tsai, W. T Whang, K. Y. Hsu, Compos. Sci. Technol. **87**, 174 (2013).
[12] Q. Jiang, X. Wang, Y. Zhu, D. Hui, Y. Qiu, Mechanical, electrical and thermal properties of aligned carbon nanotube/polyimide composites, Composites: Part B **56**, 408 (2014).
[13] H. H. So, J. W. Cho, N. G. Sahoo, Eur. Polym. J. **43**, 3750 (2007).

[14] Q. Y Tang, Y. C. Chan, N. B. Wong, R. Cheung, Polym. Int. **59**, 1240 (2010).
[15] Z. Yang, X. Chen, Y. Pu, L. Zhou, C. Chen, W. Li, L. Xu, B. Yi, Y. Wang, Polym. Adv. Technol. **18**, 458 (2007).
[16] E. Logakis, Ch. Pandis, P. Pissis, J. Pionteck, P. Potschke, Compos. Sci. Technol. **71**, 854 (2011).
[17] D. Thuau, V. Koutsos, R. Cheung, J. Vac. Sci. Technol. B **27**, 3139 (2009).
[18] S. M. Yuen, C. C. M. Ma, C. L. Chinag, Y. Y. Lin, C. C. Teng, J. Polym. Sci. Part A **45**, 3349 (2007).
[19] E. Hamciuc, M. Ignat, C. Hamciuc, I. Stoica, L. Dimitrov, Y. Kalvachev, M. Olariu, High Perform. Polym. **27**, 590 (2015).
[20] M. Olariu, C. Hamciuc, L. Okrasa, E. Hamciuc, L. Dimitrov, Y. Kalvachev, Polym. Compos. **38**, 2584 (2017).
[21] M. Ignat, D. Ovezea, E. Hamciuc, C. Hamciuc, L. Dimitrov, J. Polym. Res. **21**, 536 (2014).
[22] X. Jiang, Y. Bin, M. Matsuo, Polymer **46**, 7418 (2005).
[23] M. Iacob, A. Bele, X. Patras, S. Pasca, M. Butnaru, M. Alexandru, D. Ovezea, M. Cazacu, Mater. Sci. Eng. C **43**, 392 (2014).
[24] S. Cetiner, M. Olariu, R. Ciobanu, H. Karakas, F. Kalaoglu, A. S. Sarac, Fibers and Polym. **11**, 843 (2010).
[25] S. Kashi, R. K. Gupta, Th. Baum, N. Kao, S. N. Bhattacharya, Mater. Design **109**, 68 (2016).
[26] A. J. Bur, Polymer **26**, 963 (1985).
[27] B. Luo, X. Wang, Q. Zhao, L. Li, Compos. Sci. Technol. **112**, 1 (2015).
[28] A. S. Roy, S. Gupta, S. Sindhu, A. Parveen, P. C. Ramamurthy, Composites: Part B **47**, 314 (2013).
[29] F. Kremer, A. Schönhals, (Eds.), “Broadband Dielectric Spectroscopy”, Springer-Verlag Berlin Heidelberg (2003).
[30] Y. Jin, N. Xia, R. A. Gerhardt, Nano Energy **30**, 407 (2016).
[31] P. B. Ishai, M. S. Talary, A. Caduff, E. Levy, Y. Feldman, Measur. Sci. Technol. **24**, 10 (2001).