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Electrical conductivity and transparency of polymer hybrid nanocomposites based on poly(trimethylene terephthalate) containing single walled carbon nanotubes and expanded graphene

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Abstract

Single-walled carbon nanotubes (SWCNT)/expanded graphite (EG)/poly(trimethylene terephthalate) (PTT) hybrid nanocomposites were prepared via *in situ* polymerization. Raman spectroscopy and scanning electron microscopy (SEM) were employed to determine both, purity and morphology of the nanofillers and the dispersion of nanotubes and nanosheets. The electrical and optical properties of thin polymer films based on both “single” nanocomposites and hybrid nanocomposites were studied. For PTT/SWCNT nanocomposites, results confirmed that films optical transmittance decreases as the concentration of SWCNT

increases, attaining almost no optical transmittance for 0.3 wt % of nanofiller. On the other hand, the electrical conductivity of nanocomposites was found to increase by increasing the nanofiller amount and the σ_{dc} values indicate that percolation occurs at a very low SWCNT content (around 0.05 wt %). In the case of PTT/SWCNT+EG nanocomposites, when the content of SWCNT is 0.05%, the hybrid system presents lower conductivity than that corresponding to the "single" nanocomposite. The incorporation of additional EG to the PTT/SWCNT nanocomposite has a small effect on the electrical conductivity but inhibits the transparency of the system.

1. Introduction

Transparent conducting oxides (TCOs) are materials of utmost importance due to the combination of optical transparency, in the visible region, and electrical conductivity [1]. The most commonly used TCOs in optoelectronics are thin laminated indium tin oxides (ITO) [2]. These materials provide the best available performance with respect to the conductivity and transmission, combined with reproducibility, good surface morphology and, most of all excellent environmental stability [3]. However, there are still several drawbacks such as relatively high processing temperature, possibility of delamination of ITO film, fabrication costs and weak mechanical properties [4]. ITO layers are found to be brittle and have a poor adhesion to flexible substrates such as plastics [5]. Conducting composites based on carbon nanofillers, such as carbon nanotubes and graphene derivatives may constitute an alternative. Since their discovery in 1991 [6], single-walled carbon nanotubes (SWCNT) have attracted much attention due to their exceptional mechanical [7, 8], electrical and thermal properties [9] along with large aspect ratio (typically ca. 300-1000), small diameter and low mass density [10]. A percolating behaviour of SWCNT, and therefore a significant improvement in the electrical conductivity in various polymer matrices i.e. poly(ethylene terephthalate) (PET)

[11], polyimide (PI) [12], poly(methyl methacrylate) (PMMA) [5], polystyrene (PS) [13] among others, has been already reported.

The experimental discovery of graphene as a new nanomaterial [14, 15] with its intrinsic strength of ~ 130 GPa and elastic modulus of 125 GPa [16], electron mobility at room temperature ($250\,000\text{ cm}^2/\text{Vs}$) [14, 16], extremely high surface area (theoretical limit: $2630\text{ m}^2/\text{g}$) and gas impermeability [17] has opened an interesting and novel area in material science in recent years. Graphene based composite materials exhibit a nonlinear increase of the electrical conductivity as a function of the filler content at certain amount of filler loading, known as percolation threshold. Kim et al. [18] showed that in thermoplastic polyurethane (PU)/graphene nanocomposites a percolation threshold $< 0.5\text{ vol. \%}$ was obtained for thermally reduced graphene oxide while for graphite it was $> 2.7\text{ vol. \%}$. On the other hand, Shen et al. [19] has revealed that the electrical conductivity of chemically reduced graphene oxide using glucose (rGO-g) ($2.5 \times 10^3\text{ S/m}$) is higher by four orders of magnitude compared to the conductivity of TRGO (thermally reduced graphene oxide) ($2.8 \times 10^{-1}\text{ S/m}$), and much higher than that of GO (graphene oxide) ($2.7 \times 10^{-7}\text{ S/m}$). Moreover, Pham et al. [20] reported an interesting study on simple, environmentally friendly approach for preparing highly conductive PMMA-RGO composites with low percolation threshold of $0.16\text{ vol. \%}$ and electrical conductivity of $\sim 64.1\text{ S/m}$ at $2.7\text{ vol. \%}$ by self-assembly of positively charged PMMA latex particles and negatively charged graphene oxide sheets through electrostatic interactions, followed by hydrazine reduction. Furthermore, Paszkiewicz et al. [21] studied the influence of platelets' size of exfoliated graphite nanoplatelets (EG) on the processing, physicochemical properties, morphology and, most importantly, electrical conductivity and barrier properties of thin polymer films based on poly(trimethylene terephthalate) (PTT). It was clearly found that platelets with the size of $50\text{ }\mu\text{m}$, enabled to obtain conductive thin

polymer films with nanoplatelets' content of 0.3-0.5 wt %. However, nanocomposite based on PTT with 0.5 wt % of EG with the flake size of 500 μm proved to be non-conductive.

Notwithstanding, the relative high cost of carbon nanotubes CNTs, especially SWCNT, in comparison to other fillers, like graphite, carbon black (CB) and carbon fibers (CF), limits the widespread applications of CNT-based conducting composites. Therefore, nanocomposites containing hybrid system of nanofillers of CNT and other inexpensive particles were developed in recent years [22-25]. Hybrid fillers with unique geometric shapes and different dispersion characteristics may offer a new way to lower the final cost of CNT-based nanocomposites with multifunctional properties, which might find use in a wide range of applications such as EMI shielding, microelectronics, large area displays etc. [26, 27]. Moreover, carbon nanofillers, such as SWCNT and graphene derivatives, due to van der Waals attractions among one another and high surface areas, tend to form agglomerates, which prevent from the efficient transfer of their superior properties to the nanocomposite [11]. The influence of aggregation level on the conductivity in CNT composites [28, 29] and graphene derivatives composites [30-32] has been already reported. Therefore, it seems reasonable to use *in situ* polymerization in order to obtain polymer nanocomposites with optimized nanoadditive dispersion. The *in situ* polymerization technique is particularly attractive as it enables control over both, the polymer architecture and the final structure of the composite. This method has been already widely used to prepare polymer composites containing carbon nanofillers [11, 33-38]. The key point of this approach relies on good dispersion of carbon nanofillers in the monomer or solvent, followed by *in situ* polymerization initiated either by heat or by the addition of suitable compounds.

The aim of this paper is to study electrical and optical properties of nanocomposites based on PTT containing hybrid nanofillers, i.e. SWCNT and expanded graphite (EG), obtained by *in situ* polymerization.

2. Experimental section

2.1 Nanofillers

The single walled carbon nanotubes (SWCNT, KNT 95) were purchased from Grafen Chemical Industries (Grafen Co., Ankara, TURKEY). From providers data: diameter: <2 nm, Electrical Conductivity: > 100 S/cm, length: 5 – 30 μm , purity: >95%, surface area: 380 m^2/g . Expanded graphite (EG) was provided by Polymer Institute of Slovak Academy of Science with platelets size of around 50 μm . XPS analysis provide following information: C1s: 99.21% and O1s: 0.79%.

2.2. Preparation of PTT/SWCNT+EG nanocomposites

Nanocomposites with SWCNT and EG were prepared by *in situ* polymerization following the procedure described in details in [39]. Carbon nanotubes' concentration in polymer nanocomposites varied from 0.025 to 0.5 wt %. Two resulting hybrid nanocomposites contain 0.1wt % of EG + 0.05 wt % of SWCNT and 0.1 wt % of EG + 0.1 wt % of SWCNT. Additionally, for comparison purpose, PTT based nanocomposite with 0.1 wt % of EG has been prepared. The following substances were put into 1dm³ polycondensation reactor (Autoclave Engineering Inc, USA): dimethyl terephthalate (DMT) (Sigma - Aldrich); bio-1,3-propanediol (bio-PDO) (Susterra[®] Propanediol, DuPont Tate&Lyle, USA), catalysts: the tetrabutylorthotitanate (Ti(OBu)₄, Fluka) and an antioxidant the tetrakis(methylene(3,5-di-butyl-4-hydroxyphenylhydro-cinnamate))methane (Irganox 1010, Ciba-Geigy, Basel, Switzerland). Additionally, before the synthesis, both nanofillers were dispersed in bio-PDO using high-speed stirrer (Ultra-Turrax[®] T25) and ultrasonic homogenizer (Sonoplus HD

2200, Bandelin) for 30 min. Additionally, in order to improve the exfoliation of EG in bio-PDO, an extra step of dispersion process was added, where an ultra-power lower sonic bath was applied for 8 hours. The polymerization process was conducted in two stages: 1) a transesterification reaction between DMT and bio-PDO under nitrogen flow at atmospheric pressure and in a temperature range of 160-180 °C and 2) the polycondensation at temperature of 260 °C, pressure of about 20 Pa and under continuous stirring. The progress of the synthesis was monitored by the changes of viscosity of the polymerization mixture. The reaction was considered complete when the viscosity of melt reached 14 Pa·s. The obtained systems were extruded from the reactor in the form of polymer wires under nitrogen flow into the water bath, granulated and injection moulded using injection moulding machine Boy 15 (Dr. BOY, Germany) at the pressure of 70 MPa and at temperature of 245°C, into a mould at temperature of 30°C and a mold clamping force of 150 kN.

2.3 Thin films preparation

Amorphous films with a thickness of $\approx 300\text{-}500\text{ }\mu\text{m}$ were prepared for conductivity and transparency studies by press moulding (Collin P 200E) at 250 °C, and pressure of 5 bar for 2 min and 10 bar for another 1 min and subsequently quenched in ice water (250 °C/min). The thickness of thin films was measured with a Micrometer mod. 293-521 from Mitutoyo. Five measurements were taken for each sample, with an experimental error of $\pm 0.001\text{ mm}$. The thickness is an average value.

2.4 Characterization methods of *in situ* prepared nanocomposites

The morphology of both nanoparticles and nanocomposites was observed by scanning electron microscopy (SEM, JEOL JSM 6100). The samples were cryofractured in liquid nitrogen and subsequently coated (2-5 nm) in vacuum with a thin gold film before the test.

Raman spectra of both nanoparticles and nanocomposites were obtained with a Renishaw Raman Spectroscope in the 180° backscattering geometry with the 632.8 nm line of a 2 mW HeNe laser, the data acquisition time of 1 s and the accumulation time of 1 s. The polarized laser was focused on the surface of the dumbbell shaped specimen through x50 objective lens, and the diameter of the laser spot is about 2 micrometers.

In order to study electrical properties circular gold electrodes (20 mm in diameter) were deposited by sputtering gold onto both free surfaces of the sample film. The complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' represents the permittivity and ε'' the dielectric loss, was measured as a function of frequency (10^{-2} Hz < F < 10^7 Hz, being F the frequency of the applied electric field) by using a Novocontrol broadband dielectric spectrometer. The measurements were carried out at room temperature and the electrical conductivity was derived by $\sigma(F) = \varepsilon_0 2\pi F \varepsilon''$ where ε_0 is the vacuum permittivity.

Transparency of the films was evaluated by measuring the optical transmittance in a range of wave lengths from 190 nm to 110 nm by means of an Analytik Jena Specord 205 Spectrophotometer.

3. Results and discussion

3.1 Morphology and chemical structure of nanofillers used in this study

Both nanofillers used in this study were characterized by scanning electron microscopy (SEM) and Raman spectroscopy. First of all, samples were characterized using SEM, which provides visual information about the ratio of SWCNT to carbonaceous impurities and, in the case of EG, the level of exfoliation of graphene nanoplatelets (Fig.1a

and Fig. 1b). SWCNT were found to possess high purity, seeing that only fiber-like areas with almost no other particles or lumps (correspond to carbonaceous impurities) were visible. EG platelets are strongly connected to one another. This morphology differs from the one previously observed for EG obtained via thermal expansion (SGL Carbon SE, Germany) [30]. These observations will be reflected in the measurement of electrical conductivity of EG and SWCNT/EG based nanocomposites.

Raman spectra of both nanofillers (SWCNT and EG) are presented in Fig. 2. On one hand, the Raman spectrum of SWCNT (Fig. 2a) exhibits the graphitic G band around 1580 cm^{-1} that consists of two components, a pronounced G^+ ($\sim 1580\text{ cm}^{-1}$) associated to tangential vibrations along the tube axis, and a smaller G^- ($\sim 1570\text{ cm}^{-1}$) that becomes from the tangential vibrations along the circumferential direction of SWCNT and is influenced by the electronic type (semiconductor or metallic nature) and the diameter of the SWCNT. Also the D band is located at 1350 cm^{-1} , which is related to the disorder-induced double resonant process. The low intensity ratio between D and G band indicates that the sample was of extremely high purity suggesting that the used SWCNT had low concentration of structural defects and amorphous material, confirming the aforementioned good quality of nanotubes. Moreover, radial breathing mode (RBM), that corresponds to the coherent vibration of the carbon atoms in radial direction [40] and depends on the SWCNT diameter, was also observed between $100\text{--}350\text{ cm}^{-1}$. Finally, the G' band is also observed around 2600 cm^{-1} which gives important information about the electronic structure [41].

On the other hand, in the bottom figure (Fig. 2b), the Raman spectrum obtained from EG exhibits at 1581 cm^{-1} the characteristic G band attributed to the bond stretching. Moreover, the D band at 1350 cm^{-1} , which corresponds to the breathing mode of sp^2 atoms in rings and indicates the existence of local defects and disorder [42, 43], can be observed. The

intensity of the G band is known to be higher than that of the D band for GO, whereas it is opposite for the RGO [44, 45]. This change in the intensity ratio of the D to G bands is attributed to the increased defect concentration present in RGO relative to that in GO [44, 45]. Therefore, one can conclude that the Raman spectra of EG, used herein, resembles the Raman spectra of reduced graphene oxide [45, 46], which confirms the preparation process of EG by the Polymer Institute of Slovak Academy of Sciences [47].

3.2 Morphology and structural characterization of polymer nanocomposites

It is known, that due to van der Waals interactions between carbon nanotubes with high aspect ratio and large surface area, tend to form agglomerations. And the agglomerations prevent efficient load transfer from matrix to nanotube. Furthermore, the majority of nanotubes exhibit pulling out and sliding forces at the polymer/nanotube interface limiting dispersion. SEM analysis of the fracture surfaces of PTT/SWCNT nanocomposites (Fig. 3) indicates rather homogenous distribution of carbon nanotubes in the PTT matrix. For the concentration of 0.05 wt % of SWCNT, single nanofibers uniformly distributed in the polymer can be distinguished (Fig. 3a). On the other hand, individual nanotubes with some entanglements or bundles of CNT, apparently pulled out from the matrix are observed on the fracture surface of PTT/0.3SWCNT (Fig. 3b). Considering the high propensity of carbon nanotubes to form bundles, as mentioned before, the observed effects confirm the efficiency of mechanical mixing along with high-frequency vibration in order to eliminate existing agglomerates.

In addition, Raman spectroscopy was applied in order to characterize nanotube dispersion in nanocomposites. Additionally, the Raman spectrum of neat PTT is presented in Fig. 4. The characteristic bands in Raman spectrum of PTT appear as follows: the 909 cm^{-1} band, assigned to the stretching of the three methylene groups of the glycol residue; small

peak at 937 cm^{-1} reasonably assigned to the band of the vibration of the crystalline glycol residue; 1116 cm^{-1} band assigned to the crystalline phase gauche conformers; the 1612 cm^{-1} and 1714 cm^{-1} bands associated with C=O stretching; 3077 cm^{-1} assigned to C-H stretching [48]. The Raman spectra of nanocomposites containing SWCNT, in turn, resemble the spectrum obtained for the nanofiller itself. Moreover, the intensities of particular bands in the whole series of nanocomposites increase with increasing concentration of SWCNT. These observations resemble those previously reported [25].

Furthermore, SEM was used to visually evaluate the degree of exfoliation/aggregation of nanofillers in polymer hybrid nanocomposites. The efficiency of the hybrid system of SWCNT/EG in modifying the properties of the matrix polymer is primarily determined by the quality of the dispersion. The EG nanosheets seem to exhibit the aggregated morphology in both PTT/0.05SWCNT+0.1EG and PTT/0.1SWCNT+0.1EG hybrid nanocomposites (Fig. 5). Due to the differences in scattering densities between the nanofiller and PTT matrix, the EG aggregates can be easily imaged using SEM. On the other hand, well-dispersed SWCNT are clearly visible in both hybrids. Even when the concentration of SWCNT in hybrid nanocomposites has been doubled (from 0.05 to 0.1 wt %), they present an exquisite degree of dispersion in the whole volume of polymer matrix (Fig. 5). Such differences in morphologies between EG and SWCNT will be reflected in the electrical conductivity and transparency measurements (Fig. 7-9).

On the other hand, in Fig. 6 Raman spectra for both hybrid nanocomposites (SWCNT/EG) compared to the spectra of neat PTT and non-hybrid nanocomposites containing the same amount of nanofillers (0.1 and 0.05 wt % of SWCNT and 0.1 wt % of EG), as in the presented hybrids, have been plotted. In the case of PTT/0.1EG nanocomposite, the Raman spectrum clearly coincides with the spectrum obtained for the PTT matrix, with

only small differences. This difference is only observed in 1714 cm^{-1} band, associated with C=O stretching. That, in turn, may imply some interactions between the PTT matrix and EG. Similarly, as previously observed for PTT based nanocomposites containing SWCNT, in the case of hybrid nanocomposites, stronger Raman response is observed for SWCNT than for EG. The only disparity between the spectra is observed in the case of the intensities of particular peaks (the intensity of 0.1 SWCNT+0.1EG is lower than for 0.05SWCNT+0.1EG), which can be related with the interactions between EG and SWCNT [49]. For both hybrid nanocomposites a marked decrease in G band intensity (attributed to the bond stretching) was visible. Similar conclusions have been already found for PTT-PTMO/SWCNT+GNP hybrid nanocomposites [25].

3.3. Electrical conductivity and transparency

In addition to their exceptional mechanical properties, SWCNT also possess very high intrinsic electrical conductivity. As result, they can impart conductivity in highly insulating materials, like polymers, by preparing polymer nanocomposites. The enhancement in electrical conductivity of insulating polymers by several orders of magnitude has been achieved with a very small content of nanotubes, without compromising other performance aspects of the polymers such as optical clarity, mechanical properties, low melt flow viscosities, etc. [50] [51]. Thus, conducting polymer composites are in growing demand in different application area such as transparent conductive coatings, electrostatic dissipation, electrostatic painting and electromagnetic interference shielding applications.

3.3.1 Electrical conductivity

The electrical conductivity, $\sigma(F)$, as a function of frequency for the PTT/SWCNT and PTT/SWCNT/EG nanocomposites is presented in Fig. 7a and 7b, respectively. As shown, both systems follow a similar behavior: i) the overall electrical conductivity of

nanocomposites increases with increasing the SWCNT loading; ii) at low nanoadditive concentrations $\sigma(F)$ exhibits a linear dependence with frequency with a slope close to 1 which is characteristic for insulating materials [52, 53]. This is similar to that followed by the PTT matrix; iii) for high nanoadditive concentrations $\sigma(F)$ adopts a characteristic behavior which can be formally described by the sum of two contributions: a frequency-independent direct-conductivity, σ_{dc} , and a frequency dependent conductivity, σ_{ac} .

Values of σ_{dc} for the investigated nanocomposites are represented in Fig.8. For insulating samples the value of the conductivity represented corresponds to one measured at the lowest measured frequency (10^{-2} Hz). For the hybrid systems studied here, it is worth to note (see Fig. 8) that for 0.05 wt % of SWCNT the electrical conductivity is lower than that corresponding to the analogous system without EG. However, when the content of SWCNT is 0.1 wt % both systems reach similar electrical conductivity value. Most likely, at low SWCNT content, there will be a small number of conducting paths that might be disrupted by the presence of EG. For higher concentrations of SWCNT, the number of these conducting paths will be large enough so that the conductivity is not significantly affected by the presence of EG. Thus, both types of PTT/SWCNT and PTT/SWCNT+EG systems show similar conductivity values. Even the hybrid system has a slightly higher conductivity which might be due to a synergistic effect between both types of additives [25]. According to the percolation theory, for heterogeneous materials at a critical concentration (percolation threshold) the additive forms a three-dimensional conductive network throughout the matrix, hence electron can tunnel from one filler to another, and in doing so it overcomes the high resistance offered by insulating polymer matrix. It has been extensively reported the capability of SWCNT to form physically connected networks even at low additive content when added into polymer matrices [11, 47, 54]. Our previous research on polymer hybrid

nanocomposites, based on copolymers with PTT as a rigid segment and containing carbon nanotubes and graphene nanoplatelets, presented the occurrence of synergic effect in both electrical and thermal conductivity [25, 36]. However, herein, the lack of such effect can be attributed to the quality of expanded graphite, which has been characterized in details via Raman spectroscopy (Fig. 2b).

3.3.2. Optical transparency

The study of electrical properties and optical transparency has been conducting on the same samples, being the corresponding thicknesses the collecting in Table 1.

The transmittance is given by the following equation [5]:

$$\frac{I}{I_0} = e^{-\epsilon tp} \quad \text{eq.1}$$

Where t is the sample thickness, p is the additive concentration and ϵ is the attenuation coefficient. Fig. 9 shows transmittance versus the wave length for the homopolymer PTT and for the PTT/SWCNT nanocomposites. For the sake of clarity, the data corresponding to the hybrid system, which have transmittance values close to zero, are presented in the inset.

Due to the fact that the samples with different thicknesses have been measured, we can normalize for thickness and concentration for the sake of comparison [55]. Fig. 10 represents $\text{Log}_{10}[I/I_0]$ versus $t * p$ data. The dashed lines are eye guides. As it can be seen, the data measured for PTT/SWCNT systems studied by us are comparable to those previously reported measurement [11] for PET/SWCNT prepared by a similar method, i.e. in situ polymerization and for PMMA/SWCNT [5]. Higher transmittance (i.e. transparency) has been measured for melt-mixed PET/SWCNT [11] and for solution/surfactant mixed PE/MWCNT [5].

4. Conclusions

An efficient dispersion of SWCNT along with some agglomerates of EG in PTT matrix was achieved and confirmed by SEM. This method included *in situ* polymerization with SWCNT and/or EG and an additional step of dispersing process (mechanical stirring and sonication) before the reaction. Moreover, SEM and Raman spectroscopy were employed in order to determine both, the purity and morphology of the nanofillers as well as the distribution of nanotubes and nanosheets in the whole volume of polymer matrix. The resultant PTT/SWCNT nanocomposites exhibited significant conductivity enhancement (around 8 orders of magnitude) at a very low loading (0.05 wt %) without significantly sacrificing optical transmission. The incorporation of additional EG to the PTT/SWCNT nanocomposite has a small effect on the electrical conductivity but inhibits the transparency of the system. At 0.05 wt % content of SWCNT there are very few conducting paths, which might be interrupted by the presence of EG in the hybrid systems. Therefore, the conductivity corresponding to PTT/0.05SWCNT/0.1EG is lower than that corresponding to PTT/0.05 SWCNT. For higher SWCNT content (0.1 wt %) there are so many conducting paths that the presence of EG hardly affects to the conductivity presenting both types of systems similar conductivity values. However, the much higher cost of producing the highly conductive SWCNT in comparison to EG is a major drawback, severely limiting their applications as conductive nanofiller. Therefore, the research on hybrid systems consisted of carbon nanotubes and graphene derivatives forms in PTT will be continued, since these SWCNT/EG polymer nanocomposites can potentially be useful in a variety of aerospace and terrestrial applications, due to their combination of electrical conductivity and high optical transmission.

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References

1. Ba, J., Rohlfing, D.F., Feldhoff, A., Brezesinski, T., Djerdj, I., Wark, M. and Niederberger, M. *Chem. Mater.* **2006**, 18, 2848-2854.
2. Ginley, D.S. and Bright, C. *MRS Bull.* **2000**, 25, 15-18.
3. Lewis, B.G. and Paine, P.C. *MRS Bull.* **2000**, 25, 22-27.
4. Ramasubramaniam, R., Chen, J. and Liu, H. *Appl. Phys. Lett.* **2003**, 83, 2928.
5. Dettlaff-Weglikowska, U., Kaempgen, M., Hornbostel, B., Skakalova, V., Wang, J., Liang, J. and Roth, S. *Phys. Stat. Sol. B* **2006**, 243(13), 3440–3444.
6. Iijima, S. *Nature* **1991**, 354, 56-58.
7. Wong, E.W., Sheehan, P.E. and Lieber, C.M. *Science* **1997**, 277, 1971–1975.
8. Lu, J.P. *Phys. Rev. Lett.* **1997**, 79, 1297–1300.
9. Monthieux, M. *Carbon* **2002**, 40, 1809-1823.
10. Gao, G., Cagin, T. and Goddard III, W.A. *Nanotechnol.* **1998**, 9, 184-191.
11. Hernández, J.J., García-Gutiérrez, M.C., Nogales, A., Rueda, DR, Kwiatkowska, M., Szymczyk, A., Roslaniec, Z., Concheso, A., Guinea, I. and Ezquerro, T.A. *Compo. Sci. Technol.* **2009**, 69, 1867–1872.
12. Park, C., Ounaies, Z., Watson, K.A., Crooks, R.E., Smith Jr, J., Lowther, S.E., Connell, J.W., Siochi, E.J., Harrison, J.S. and St Clair, T.L. *Chem. Phys. Lett.* **2002**, 364, 303-308.
13. Barraza, H.J., Pompeo, F., O'Rear, E.A. and Resasco, D.E. *Nano Lett.* **2002**, 2, 797-802.

14. Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., Grigorieva, I.V. and Firsov, A.A. *Science* **2004**, 306, 666-669.
15. Geim, A.K. and Novoselov, K.S. *Nature Mater.* **2007**, 6, 183–191.
16. Lee, C., Wei, X., Kysar, J.W. and Hone, J. *Science* **2008**, 321, 385–388.
17. Bunch, J.S., Verbridge, S.S., Alden, J.S., van der Zande, A.M., Parpia, J.M., Craighead, H.G. and McEuen, P.L. *Nano Lett.* **2008**, 8, 2458–2462.
18. Kim, H., Miura, Y. and Macosko, C.W. *Chem. Mater.* **2010**, 22(11), 3441-3450.
19. Shen, Y., Jing, T., Ren, W., Zhang, J., Jiang, Z.G., Yu, Z.Z. and Dasari, A. *Compo. Sci. Technol.* **2012**, 72(12), 1430-1435.
20. Pham, V.H., Dang, T.T., Hur, S.H., Kim, E.J. and Chung, J.S. *ACS Appl. Mater. Inter.* **2012**, 4(5), 2630-2636.
21. Paszkiewicz, S., Pawelec, I., Szymczyk, A., Špitalský, Z., Mosnáček, J., Kochmańska, A. and Roslaniec, Z. *Polym. Engin. Sci.* **2015**, 55(10):2222-2230.
22. Li, J., Wong, P.S. and Kim, J.K. *Mater. Sci. Eng. A* **2008**, 483–484, 660–663.
23. Bokobza, L., Rahmani, M., Belin, C., Bruneel, J. and Bounia, N.E.E. *J. Polym. Sci. B* **2008**, 46, 1939–1951.
24. Fan, Z.J., Wang, Y., Luo, G.H., Li, Z.F. and Wei, F. *New Carbon. Mater.* **2008**, 23, 149–153.
25. Paszkiewicz, S., Szymczyk, A., Sui, X.M., Wagner, H.D., Linares, A., Ezquerra, T.A. and Roslaniec, Z. *Compo. Sci. Technol.* **2015**, 118, 72-77.
26. Gordon, R.G. *MRS Bull.* **2000**, 25, 52–57.
27. Crawford, G.P. Flexible flat panel displays; Crawford, G., Ed.; Wiley: New York, 2005, Chapter 1.

28. Sandler, J.K.W., Kirk, J.E., Kinloch, I.A., Shaffer, M.S.P. and Windle, A.H. *Polymer* **2003**, 44, 5893–5899.
29. Gojny, F.H., Wichmann, M.H.G., Fiedler, B., Kinloch, I.A., Bauhofer, W., Windle, A.H. and Schulte, K. *Polymer* **2006**, 47, 2036–2045.
30. Paszkiewicz, S., Szymczyk, A., Špitalský, Z., Soccio, M., Mosnáček, J., Ezquerro, T.A. and Roslaniec, Z. *J. Polym. Sci. B* **2012**, 50(23), 1645–1652.
31. Wang, Y., Shan, J.W. and Weng, G.J. *J. Appl. Phys.* **2015**, 118, 065101.
32. Stankovich, S., Dikin, D.A., Dommett, G.H.B., Kohlhaas, K.M., Zimney, E.J., Stach, E.A., Piner, R.D., Nguyen, S.T. and Ruoff, R.S. *Nature* **2006**, 442, 282–286.
33. Park, C., Ounaies, Z., Watson, K.A., Crooks, R.E., Smith Jr, J., Lowther, S.E., Connell, J.W., Siochi, E.J., Harrison, J.S. and St. Clair, T.L. *Chem. Phys. Lett.* **2002**, 364(3–4), 303–308.
34. Velasco-Santos, C., Martínez-Hernández, A.L., Fisher, F.T., Ruoff, R. and Castaño, V.M. *Chem. Mater.* **2003**, 15(23), 4470–4475.
35. Potts, J.R., Lee, S.H., Alam, T.M., An, J., Stoller, M.D., Piner, R.D. and Ruoff, R.S. *Carbon* **2011**, 49(8), 2615–2623.
36. Paszkiewicz, S., Szymczyk, A., Livanov, K., Wagner, H.D. and Roslaniec Z. *EXP. Polym. Lett.* **2015**, 9(6), 509–524.
37. Fabbri, P., Bassoli, E., Bon, S.B. and Valentini, L. *Polymer* **2012**, 53(4), 897–902.
38. Chatterjee, S., Wang, J.W., Kuo, W.S., Tai, N.H., Salzmann, C., Li, W.L., Hollertz, R., Nuesch, F.A. and Chu, B.T.T. *Chem. Phys. Lett.* **2012**, 531, 6–10.
39. Paszkiewicz, S., Pawelec, I., Szymczyk, A. and Roslaniec, Z. *Polimery* **2016**, 61(3), 172–180.

40. Ahmed Jamal, G.R. and Mominuzzaman, S.M. *J. Nanosci. Nanoeng.* **2015**, 1(2), 74-83.
41. Souza Filho, A.G., Jorio, A., Swan, A.K., Ünlü, M.S., Goldberg, B.B., Saito, R., Hafner, J.H., Lieber, C.M., Pimenta, M.A., Dresselhaus, G. and Dresselhaus M.S. *Phys. Rev. B* **2002**, 65, 085417.
42. Ferrari, A.C. *Solid. State. Commun.* **2007**, 143, 47–57.
43. Ferrari, A.C., Meyer, J.C., Scardaci, V., Casiraghi, C., Lazzeri, M., Mauri, F., Piscanec, S., Jiang, D., Novoselov, K.S., Roth, S. and Geim, A.K. *Phys. Rev. Lett.* **2006**, 97, 187401.
44. Stankovich, S., Dikin, D.A., Piner, R.D., Kohlhaas, K.A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S.T. and Ruoff, R.S. *Carbon* **2007**, 45, 1558–1565.
45. Ramesha, G.K. and Sampath, S. *J. Phys. Chem. C* **2009**, 113(19), 7985–7989.
46. Sahoo, M., Anthony, R.P., Mathews, T., Dash, S. and Tyagi, A.K. *AIP Conf. Proc.* **2013**, 1512, 1262-1263.
47. Špitalský, Z., Tasis, D., Papagelis, K. and Galiotis, C. *Progr. Polym. Sci.* **2010**, 35, 357-401.
48. He, X., Chuah, H.H. and Ellison, M.S. *Polym. Bull.* **2004**, 51, 285-291.
49. Patole, A.S., Patole, S.P., Jung, S.-Y., Yoo, J.-B., An, J.-H. and Kim T.-H. *Europ. Polym. J.* **2012**, 48(2), 252–259.
50. Du, F., Scogna, R.C., Zhou, W., Brand, S., Fischer, J.E. and Winey, K.I. *Macromol.* **2004**, 37, 9048-9055.
51. Mittal, G., Dhand, V., Rhee, K.Y., Park, S.-J. and Lee, W.R. *J. Industr. Engin. Chem.* **2015**, 21, 11–25.

52. Kilbride, B.E., Coleman, J.N., Fraysse, J., Fournet, P., Cadek, M., Drury, A., Hutzler, S., Roth, S. and Blau, W.J.J. *Appl. Phys.* **2002**, 92, 4024-4030.
53. Kirkpatrick, S. *Rev. Mod. Phys.* **1973**, 45, 574-588.
54. Bauhofer, W. and Kovacs J.Z. *Compo. Sci. Technol.* **2009**, 69, 1486-1498.
55. Schmidt, R.H., Kinloch, I.A., Burgess, A.N. and Windle, A.H. *Langmuir* **2007**, 23, 5707-5712.
56. Zhang, Y., Li, Z., Li, H., Gao, J., Zhang, J. and Zeng, Y., *Mater Sci: Mater Electron* 2014, 25(6), 2692–2696.

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Table 1 Sample thickness (mm) for both series the investigated nanocomposites

% wt SWCNT	Thickness (mm)
0.000	0.349
0.025	0.568
0.050	0.363
0.100	0.311
0.300	0.515

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Fig. 1 SEM micrographs of as received SWCNT (a) and EG (b).
302x105mm (300 x 300 DPI)

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Fig. 2. Raman spectra of SWCNT (a) and EG (b).
289x217mm (300 x 300 DPI)

Fig. 3 SEM micrographs of (a) PTT/0.05SWCNT and (b) PTT/0.3 SWCNT.
125x44mm (300 x 300 DPI)

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93x65mm (300 x 300 DPI)

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Fig. 6 Raman spectra for the PTT based nanocomposites containing SWCNT and/or EG.
282x214mm (96 x 96 DPI)

Fig. 7 . Broadband electrical conductivity, as a function of frequency, for composites with different concentration of nanoadditive (labeled as weight percentage on the right) (a) PTT/SWCNT and (b) PTT/SWCNT/EG.
114x139mm (300 x 300 DPI)

Fig. 8 Electrical conductivity for PTT/SWCNT (●) and PTT/SWCNT/EG (■) nanocomposites. Optical transparency (▲) for PTT/SWCNT systems. The lines are a guide for the eye.
289x202mm (300 x 300 DPI)

Fig. 9 Transmittance as a function of wavelength for PTT/SWCNT nanocomposites. The inset shows data for the PTT/SWCNT/EG hybrid nanocomposites.
289x202mm (300 x 300 DPI)

Fig. 10 Transmittance versus weight*thickness for the measured by us PTT/SWCNT composites (circle) and for other values in the literature: PET/SWCNT melt mixed (square) [11], PET/SWCNT in situ polymerization (up triangle) [11]; PMMA/SWCNT solution mixed (down triangle) [5] and PE/MWCNT solution/surfactant mixed (star) [56].

289x202mm (300 x 300 DPI)