Poly(butylene cyclohexanedicarboxylate/diglycolate) random copolymers reinforced with SWCNTs for multifunctional conductive biopolymer composites

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Abstract. The objective of this work was to develop a versatile strategy for preparing multifunctional composite films with tunable properties. Novel conductive composites based on the combination of single walled carbon nanotubes (SWCNTs) and biodegradable poly(butylene cyclohexanedicarboxylate/diglycolate) random copolymers (P(BCEmBDGn)) are here presented. In particular, synthesized PBCE homopolymer and two copolymers containing different amounts of ether–oxygen containing co-units, P(BCE90BDG10) and P(BCE70BDG30), have been considered as matrices of SWCNTs based composites. The effect of incorporation of different amounts of SWCNTs (0.1–0.5–0.75–1 wt%) on morphological, thermal, mechanical and electrical properties was deeply investigated. The morphology of the fracture surfaces is affected by the SWCNT presence, while the increase in the SWCNT content does not provide significant microstructure modifications. The thermal properties underlined that nanotubes can act as nucleating agents, favouring the polymer crystallization process. The mechanical behavior demonstrated that the introduction of carbon nanotubes both in the case of PBCE homopolymer and in random copolymers based formulations exerted a reinforcing effect. All composites exhibit high electrical conductivity in comparison to the neat polymers. This work demonstrates that this combinatorial approach can be used to develop materials with tunable and advanced functional properties.

Keywords: biopolymers, biocomposites, carbon nanotubes, electrical properties

1. Introduction

Over the past years, much attention has been paid towards biodegradable polymeric materials, as an answer to the urgent environmental issues related to terrestrial and aquatic pollution [1]. Thus, a novel category of materials has been developed, often reported as ‘environmentally-friendly’. These materials are capable to undergo hydrolytic and/or enzymatic degradation, resulting in harmless low molecular weight substances [2, 3]. Aliphatic polyesters are one of the most studied classes of biodegradable polymers, as they possess

promising physical/mechanical properties and they can be synthesized at moderate costs [4]. Poly(butylene cyclohexanedicarboxylate) (PBCE), obtained by polycondensation of 1,4-butanediol and 1,4-*trans*-cyclohexanedicarboxylic acid, is undoubtedly a very interesting aliphatic polyester. As a matter of fact, the presence of the aliphatic ring along the polymer backbone enables the material to have high melting temperature above 160°C, good thermal stability, to show interesting mechanical properties and to maintain biodegradability [5, 6]. Moreover, the monomers employed in the PBCE synthesis can be obtained

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from either fossil or renewable resources. In particular, 1,4-butanediol and 1,4-cyclohexanedicarboxylic acid can be produced starting from bio-based succinic acid [7] and bio-based terephthalic acid (derived from limonene) [8], respectively.

Unfortunately, given its high crystallinity degree and hydrophobicity, PBCE displays slow biodegradation rate and poor flexibility [8].

In this view, copolymerization is an effective tool to tailor the polymer properties and to make it suitable for the desired application. In particular, the authors recently focused on the PBCE modification through the introduction of ether linkages along its macromolecular chain. This strategy permitted to improve the surface wettability and to depress the crystallinity degree as well as to decrease the glass transition temperature of the starting homopolymer. These factors play indeed a significant role in the modification of both mechanical properties and hydrolytic and enzymatic degradation rate [9–11]. Increasing demand for special materials has led to the conception of composites, since valuable properties can be combined. The chance to incorporate functional nanostructures with unique properties in a polymer matrix, is a versatile strategy to transfer and to integrate specific properties into a single material, enabling to realize multifunctional composites to be used in advanced applications like catalysis, energy storage, nanobiotechnology, etc. [12, 13]. The new designed materials might possess the unique properties offered by the synergistic interaction of the nanostructures with the polymer matrix [14, 15].

Carbon nanotubes (CNTs) have been considered as ideal reinforcing candidates for the production of multifunctional polymer composites, since they simultaneously display high aspect ratio and nanometer dimensions, and more importantly, extraordinary mechanical strength and high electrical and thermal conductivity [16–19]. However, in order to obtain the desired performance in the final composites, a tailored CNT dispersion in the polymers has to be reached and the strong Van der Waals interaction between the tubes [20, 21] has to be overcome. We have recently focused on the development of conductive composites by using carbon nanotubes, and mixing them with commercial biodegradable polymers [12, 22, 23].

On the contrary, the present research work aims to evidence the evolution and potentiality of a versatile strategy to prepare polymeric nanostructured mate-

rials combining newly synthesized biodegradable random copolymers based on 1,4-*trans*-cyclohexanedicarboxylic acid and diglycolic acid [11] with a composite approach, by using single walled carbon nanotubes (SWCNTs) as reinforcement and functional phase. The thermal, structural, electrical and dielectric properties of the novel developed film formulations were investigated and correlated to SWCNT content and polymer chain microstructure.

2. Experimental part

2.1. Materials

1,4-dimethylcyclohexanedicarboxylate (DMCE) containing 99% of *trans* isomer, dimethyldiglycolate (DMDG), 1,4-butanediol (BD), and titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$) (Aldrich) were reagent grade products; DMCE, DMDG, and BD were used as supplied, whereas $\text{Ti}(\text{OBu})_4$ was distilled before use. All the reagents used were purchased from Sigma Aldrich (Milan, Italy). Single walled carbon nanotubes (SWCNTs) were supplied by Thomas Swan & Co. Ltd (ElicarbTM, Durham, UK), with typical nanotube dimensions of 2 nm diameter and ca. 1 μm in length. Nanotubes were morphologically characterized by field emission electron microscopy (FESEM, Supra 25-Zeiss, Germany).

2.2. Composite film development

Poly(butylene cyclohexanedicarboxylate/diglycolate) random copolymers (P(BCEmBDGn)) were synthesized in bulk by the usual two step melt polycondensation, as reported elsewhere [24]. Briefly, 1,4-butanediol (BD) and different molar ratios of DMCE and DMDG, were employed in the syntheses, using 20% mol in excess of glycol with respect to dimethylesters and a concentration of catalyst ($\text{Ti}(\text{OBu})_4$) of about 150 ppm of Ti/g of polymer. Three different polyesters have been prepared: the homopolymer PBCE and two copolymers, namely P(BCE90BDG10) and P(BCE70BDG30) containing 10 and 30 mol% of BDG units, respectively.

The reactions were carried out in a 250 mL stirred glass reactor, with a thermostated silicon oil bath; temperature and torque were continuously recorded during the polymerization. The first stage was run under pure nitrogen flow at a temperature equal to 190 °C until more than 90% of the theoretical amount of methanol was distilled (about 90 min). In the second stage, the pressure was reduced to about 0.1 mbar and the temperature was increased to 250 °C; the

polymerizations were carried out until a constant torque value was measured.

Composite films were prepared by solvent casting method in chloroform (CHCl_3). SWCNTs were dispersed in CHCl_3 by using a tip sonicator (VIBRA CELL Sonics mod. VC 750, USA) for 30 min in ice bath and for further 30 min in an ultrasonic bath (Ultrasonic bath-mod.AC-5, EMMEGI). The different polymer matrices were mixed with nanotube dispersions (polymer/solvent ratio was chosen as 5% wt/v) by magnetic stirring for 5 h. After complete polymer dissolution, the mixture was cast onto a glass Petri substrate and air dried at room temperature (RT) for 24 h and for additional 48 h in vacuum. Composite samples containing 0.1, 0.5, 0.75 and 1 wt% with respect to polymer initial weight were prepared with different matrices. Sample formulations are summarized in Table 1. Composite films of 90 μm thickness were obtained. Neat PBCE, P(BCE90BDG10) and P(BCE70BDG30) polymeric films were also prepared by solvent casting for comparison. In the following P(BCE90BDG10) and P(BCE70BDG30) will be named BDG10 and BDG30, respectively.

2.3. Composite film characterization

2.3.1. Microstructure

Field emission scanning electron microscopy (FESEM, Zeiss Supra25) was used to analyze the fractured surfaces of the produced composite films. Cross-section samples were fractured after immersion in liquid nitrogen, gold sputtered and then analyzed.

2.3.2. Thermal analysis

Thermogravimetric analysis (TGA) was performed using a quartz rod microbalance (Seiko Exstar 6300, Japan) in the following conditions: sample weight 10 mg, nitrogen flow ($250 \text{ mL} \cdot \text{min}^{-1}$), temperature range 30–800 $^{\circ}\text{C}$, heating rate $10^{\circ}\text{C} \cdot \text{min}^{-1}$.

Calorimetric measurements (Perkin Elmer DSC7) were conducted in order to determine the glass tran-

sition and the melting temperature of the samples under study. In the typical setup, the external block temperature control was set at -120°C and weighed samples of c.a. 10 mg were heated up to 40°C above fusion temperature at a rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$ (1st scan), held for 3 min, quenched (about $100^{\circ}\text{C} \cdot \text{min}^{-1}$) to -80°C and finally reheated up to 40°C above the melting point (heating rate of $20^{\circ}\text{C} \cdot \text{min}^{-1}$, 2nd scan).

2.3.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of polymeric films were carried out by using a PANalytical X'PertPro diffractometer equipped with a fast solid state X'Celerator detector and a copper target ($\lambda = 0.15418 \text{ nm}$). Data were acquired at each 0.10° step for 100 s in the $5\text{--}60^{\circ} 2\theta$ interval. Crystallinity degree (X_c) was evaluated from the XRD profiles as the ratio between the crystalline diffraction area (A_c) and the total area of the diffraction profile (A_t), $X_c = A_c/A_t$. The crystalline diffraction area has been obtained by subtracting the amorphous halo (modelled as bell shaped peak baseline) from the total area of the diffraction profile. The non-coherent scattering was taken into consideration.

2.3.4. Dynamic-mechanical analysis (DMA)

Dynamic-mechanical analysis (DMA) was performed with an ARES N_2 instrument (Rheometric Scientific, USA) in a dynamic time sweep test, at a frequency of 1 Hz, at room temperature (RT). The strain 0.05% was chosen by means of an iso-frequency test in the elastic linear region. The reported storage elastic modulus (G') is the average of tests performed on five rectangular samples (10 mm $\times$ 40 mm, about 90 μm thick).

2.3.5. Electrical properties

Electrical resistivity measurements were conducted (ASTM D-257) by using a Keithley 6517A electrometer and a Keithley 8009 test fixture, by applying a square wave ranging from 400 V (for pure poly-

Table 1. Material formulations

PBCE based formulations	Formulations		Polymer [wt%]	SWCNTs [wt%]
	P(BCE90BDG10) based formulations	P(BCE70BDG30) based formulations		
PBCE	BDG10	BDG30	100	0
PBCE_0.1SWCNTs	BDG10_0.1SWCNTs	BDG30_0.1SWCNTs	99.9	0.1
PBCE_0.5SWCNTs	BDG10_0.5SWCNTs	BDG30_0.5SWCNTs	99.5	0.5
PBCE_0.75SWCNTs	BDG10_0.75SWCNTs	BDG30_0.75SWCNTs	99.25	0.75
PBCE_1SWCNTs	BDG10_1SWCNTs	BDG30_1SWCNTs	99	1

mer) to 1 V (for percolated composites) with a period of 60 s in the laboratory conditions, of at least four measurements for each sample.

2.3.6. Dielectric properties

The real and imaginary parts of the complex impedance (Z) of the different polymers and composite films were measured by Hewlett Packard 4284A Precision LCR Meter at RT, in the 20 Hz÷1 MHz frequency range. The AC conductivity of the samples as a function of frequency $\sigma(\omega)$ is calculated as: $\sigma_{AC} = d/(|Z| \cdot A)$ where A is the cross-sectional area and d is sample thickness. The real part of conductivity $\sigma'(\omega)$, was used to evaluate the dielectric behavior of the new systems, and it was calculated by using the Equation (1):

$$\sigma'(\omega) = \varepsilon''(\omega)\omega\varepsilon_0 \quad (1)$$

where $\omega = 2\pi f$ is the angular frequency of the signal applied to the samples, $\varepsilon''(\omega)$ is the imaginary part of the complex permittivity, and $\varepsilon_0 = 8.852 \cdot 10^{-14}$ F·cm⁻¹ is the vacuum permittivity.

3. Results and discussion

3.1. Morphological investigations

Chemical structure of the P(BCEmBDGn) copolymer, FESEM and scheme of SWCNTs and image of the polymer and composite films from PBCE, BDG10 and BDG30 are shown in Figure 1. SWCNTs were deposited on to indium thin oxide substrates, SWNT bundles of about 10 nm diameter were found in the samples.

Neat polymer and composite films with different contents of SWCNTs were successfully developed by solvent casting process. The visual observation image of all samples is shown in Figure 1. PBCE homopolymer and BDG10 neat polymers displayed a white/transparent color, while a more yellowish color was observed for BDG30 film, due to the catalyst employed in the synthesis (i.e. Ti(OBu)₄) [25]. The color of the composite films was dependent on the nanotube loading. Samples containing lower amount of SWCNTs were grey, while those based on higher content of SWCNTs had a completely black appearance, due to the carbon nanotubes and the interconnected microstructure. The different color in the composites with 0.1 wt% could be ascribed to the different interaction with poly(butylene cyclohexanedicarboxylate/diglycolate) copolymers. The SWCNT dispersion in the polymer plays a key role

on the physical properties of composite. Figure 2 shows the FESEM micrographs of the fracture surfaces of the neat polymers (Figure 2a) and of all composites (Figure 2b), containing 0.1, 0.5, 0.75 and 1 wt% of SWCNTs, at different resolutions. Neat polymers present a porous microstructure, due to the solvent cast processing (Figure 2a). It is important to point out that the original structure of the different polymer matrix films has been completely modified by the carbon nanotubes introduction. A dense fractured structure was already observed for low SWCNT content (0.1 wt%). When higher amounts of carbon nanotubes were introduced, (i.e. 0.5, 0.75 and 1 wt%), the composites fractured surface displayed similar features to those containing 0.1 wt% of SWCNTs, indicating that a small amount of SWCNTs can disperse homogeneously in PBCE, BDG10 and BDG30 (Figure 2b). An increase of the fractured surface roughness could be observed by increasing the SWCNT content. Finally, no evidence of individual SWCNTs was found, thus a good dispersion of the nanotubes in the selected polymer matrices was achieved.

3.2. Thermogravimetric analysis

The results of thermogravimetric behavior of PBCE, BDG10 and BDG30 neat polymers and composites are shown in Table 2, that reports the maximum degradation temperature (T_{max}). On the other hand, Figure 3 shows the derivative (DTG) curves of the developed systems. All the analyzed polymeric films highlighted a single degradation peak. A similar behavior was also observed in the composite formulations. Neat PBCE, BDG10 and BDG30 displayed a thermal degradation within a relatively narrow interval centered at 413, 412 and 413 °C, respectively (Table 2), underlining that the BDG co-unit presence did not influence the thermal stability of the produced films, as well as the addition of SWCNTs as already observed [23].

3.3. Thermal and structural characterization

It is well established that the melting behavior of a polymer is affected by its previous thermal history. Therefore, in order to provide the same heat treatments to all samples investigated, each film was kept at room temperature for at least four weeks prior to thermal analysis. DSC traces of different samples after processing are reported in Figure 4 and the data obtained in Table 2.

Figure 1. Chemical structure of the P(BCEmBDGn) copolymers, FESEM and scheme of SWCNTs and image of the polymer and composite films. The SWCNT concentration (wt% on the polymer) is indicated.

All samples appeared as semicrystalline after the solvent casting procedure, the calorimetric traces were characterized by a conspicuous melting endotherm. The DSC data obtained from the first heating scan underlined that the melting temperature and

enthalpy did not change with the increasing of the SWCNT content, in all the composites. To better understand the nature of the crystalline phase present in the polymers under investigation, the structural characterization was carried out by X-ray dif-

Figure 2. FESEM fractured surface of PBCE, BDG10 and BDG30 polymers (a) and composite formulations (b). The film sections are shown in the inserts.

Table 2. Thermal and mechanical properties of PBCE, BDG10 and BDG30 polymer and composite films

Formulations	DSC results							XRD results	TGA results	DMA results
	I scan		II scan							
	T_m [°C]	ΔH_m [J/g]	T_g [°C]	ΔC_p [J/(g·°C)]	T_m [°C]	ΔH_m [J/g]	T_m [°C]			
PBCE										
PBCE	167	45	15	0.082	167	31	167	52±3	413	1.7±0.2
PBCE_0.1SWCNTs	167	43	16	0.074	166	34	167	50±2	414	2.2±0.3
PBCE_0.5SWCNTs	166	45	16	0.073	166	36	166	48±4	414	2.0±0.3
PBCE_0.75SWCNTs	167	43	16	0.092	166	38	167	53±2	414	3.1±0.6
PBCE_1SWCNTs	166	44	16	0.087	166	39	166	51±2	415	3.8±0.5
P(BCE90BDG10)										
BDG10	155	37	−2	0.091	155	29	155	45±1	412	1.6±0.2
BDG10_0.1SWCNTs	154	39	−2	0.102	155	32	154	45±3	413	1.9±0.2
BDG10_0.5SWCNTs	154	36	−3	0.101	155	32	154	45±3	414	1.9±0.3
BDG10_0.75SWCNTs	155	38	−2	0.091	155	34	155	46±2	414	2.1±0.5
BDG10_1SWCNTs	155	41	−3	0.102	155	36	155	45±2	415	2.6±0.4
P(BCE70BDG30)										
BDG30	120	27	−17	0.263	120	21	120	42±1	413	1.3±0.4
BDG30_0.1SWCNTs	119	26	−19	0.246	120	21	119	43±2	413	1.3±0.2
BDG30_0.5SWCNTs	119	24	−18	0.250	120	23	119	43±2	414	1.4±0.2
BDG30_0.75SWCNTs	119	28	−19	0.246	121	26	119	42±4	415	2.1±0.4
BDG30_1SWCNTs	120	28	−18	0.258	120	27	120	43±3	416	2.3±0.3

fraction. The patterns are reported in Figure 5. All the samples, i.e. neat PBCE, BDG10, BDG30 and the composites, showed a well-defined diffraction pattern, whose peaks are situated at the same angular positions and displayed similar intensities (Figure 5a), suggesting the presence of the same crystal phase. The two broad peaks of the SWCNTs (at about 25 and 43°) are not detectable in the composites pattern, as the amount of nanotubes in the polymer matrix is very low. In addition, crystallinity degree evaluation by XRD confirmed the results obtained by DSC during the first heating scan. Indeed, no variation in the X_c was reported with the increasing of SWCNT content for each polymer (Table 2). On the other hand, a decrease in the X_c was observed with the increasing of BDG mol% (Table 2). This trend can be ascribed to the presence of increasing amount of ether-linkages in BDG10 and BDG30 with respect to PBCE. BDG co-units caused a reduction of the chain symmetry, therefore hampering the crystallization process and lowering the crystal perfection.

In order to better evidence and study the glass transition phenomenon, the samples under study were subjected to rapid cooling from the melt. The DSC curves after melt quenching are shown in Figure 4. As it can be seen from the data reported in Table 2, the glass transition temperature and ΔC_p values were not influenced by the presence of nanofillers

and the results here presented are in good agreement with those previously obtained for neat polymers [24].

During the second heating scan, DSC traces of neat polymers showed multiple melting peaks, due to melt-recrystallization processes [26]. With the addition of increasing amounts of SWCNTs, this phenomenon progressively disappeared, and single melting endotherms could be observed. Moreover, an increase of the ΔH_m with the increasing of SWCNT content was highlighted. Both these effects can be explained by taking into consideration that the nanotubes can act as nucleating agents, thus favouring the sample crystallization process [23]. Higher amount of crystal phase and better crystal perfection can be therefore achieved. It is also worth noticing that the film preparation process played a role to determine the degree of crystallinity of the neat polymers, as evidenced by both DSC and WAXS measurements (Figure 5b). The compression moulding process limited the crystallization rate and crystal phase perfection, since a rapid cooling from the melt was adopted; on the other hand the solvent casting method allowed the polymer to develop a higher amount of a more perfect crystal phase. This was evidenced by the absence of the double melting peak in the 1st scan DSC traces, and by the absence of the small reflections at 16.2 and 19.5° in the diffraction patterns of the films obtained by solvent casting, as

well as by the ΔH_m and X_c values reported in Table 2, as compared to those previously obtained [24].

3.4. Dynamic-mechanical characterization

The dynamic-mechanical behavior of neat PBCE, BDG10 and BDG30 polymeric films and their composites was studied in order to evaluate the effect of SWCNT introduction and content on the mechanical response of the systems. Figure 6 shows the stor-

Figure 3. DTG graphs of neat polymer and composite films, for PBCE based fomrulations (a), BDG10 based formulations (b) and BDG30 based formulations (c)

age G' modulus as function of time for polymeric films (Figure 6a) and composites (Figure 6b–6d). All the studied formulations exhibited a linear trend [22, 27]. The G' values are reported in Table 2. As it can be observed in Figure 6a, PBCE homopolymer displayed the highest G' value with respect to the BDG10 and BDG30, highlighting the higher stiffness of this material due to the aliphatic ring that confers rigidity to the polymer chain [11]. Moreover, Figure 6a underlines the effect of BDG co-unit. By varying the amount of ether-linkages, it has been possible to tailor the homopolymer mechanical behavior by progressively reducing the G' value and therefore the rigidity of the film. This is due to the higher flexibility of material induced by the ether–oxygen atoms. BDG30 film displayed in fact the lowest values of storage modulus.

In the composite films an increase of the G' as compared to the corresponding neat polymer matrices was observed (Figure 6b–6d show the G' vs. time dependence of different formulations, while Table 2 summarizes the G' at 500 s and highlights the composition dependence of each studied polymer). This result underlines the reinforcement effect produced by SWCNTs. Figure 6b evidences also the effect of SWCNT content on the mechanical response of PBCE matrix. Comparable results were detected for 0.1–0.5 and 0.75–1 wt% formulations (G' values around $2.1 \text{ Pa} \cdot 10^{10}$ for PBCE_0.1SWCNTs and PBCE_0.5SWCNTs and about $3.5 \text{ Pa} \cdot 10^{10}$ for PBCE_0.75SWCNTs and PBCE_1SWCNTs, respectively). Moreover, PBCE_0.75SWCNTs and PBCE_1SWCNTs displayed the highest values of G' (increase of 106% if compared to PBCE matrix) also with respect to the other composites produced from BDG10 and BDG30, due to the brittle nature of PBCE homopolymer. On the contrary, a clearer trend was detected in the case of BDG10 based composite formulations with respect to the carbon nanotube content. Indeed, a linear increase in the G' values was measured for these materials with the increase of SWCNT content (Figure 6c). BDG10_1SWCNTs displayed the highest G' value, with an increase of about 63% with respect to the pristine BDG10 film. Finally, no particular effects were detected for BDG30_0.1SWCNTs and BDG30_0.5SWCNTs: in this case the G' value was close to that of BDG30 matrix. Finally, a significant reinforcement effect (about 63%) was evident in the BDG30_0.75SWCNTs and BDG30_1SWCNTs due

to the higher content of SWCNTs. In conclusion, the mechanical characterization confirmed for all

the studied formulations, the reinforcement effect guaranteed by the SWCNTs that act as nucleating

Figure 4. Calorimetric curves of neat polymers and composites; I scan and II scan after melt quenching

agents, in agreement with the discussion of the DSC results above reported. The obtained results evidenced that no particular effects over the time (Table 2, G' at 500 s) are present also in the case of SWCNT based systems. Therefore the original mechanical properties over the time, for the different studied formulations, were maintained. This aspect is of high importance for practical applications.

Figure 5. X-ray diffraction patterns of neat polymers, samples containing 1 wt% of SWCNTs and SWCNT powder (a). Comparison between the X-ray diffraction patterns of a PBCE films produced by solvent casting and by compression moulding (b).

3.5. Electrical and dielectric properties

DC electrical conductivity (σ_{DC}) behavior of the different samples is reported in Figure 7 as a function of the SWCNT content. The volume conductivity of neat PBCE and BDG10 was found to be about 10^{-14} S/m. By increasing of BDG mol% co-unit, an increased value of conductivity was measured, up to 10^{-12} S/m, for the BDG30 neat polymer film, probably due to the increasing chain mobility, as underlined by the glass transition values and dynamic-mechanical analysis.

A small addition of nanotubes to the polymers yielded a drastic raise in σ_{DC} . The presence of 0.1 wt% of SWCNTs resulted in an increase of 6 orders of magnitude with respect to neat polymers. Near to the electrical percolation threshold, conductivity showed a sudden rise of several orders of magnitude. In general it is possible to conclude that a conductive behavior was found for SWCNT contents higher than 0.1 wt%, and values higher than 10^{-4} S/m were obtained for 1 wt% of SWCNTs. Moreover, from the plotted curves it can be seen that the percolation threshold is between 0.1 and 0.50 wt% of carbon nanotubes. When these amounts are reached, nanotubes form a network which results in the formation of conductive path, causing the material to behave like a conductor. For SWCNT content lower than 0.1 wt%, the composites contained few conductive networks and/or electron tunneling and therefore acted as insulators. A step-like transition due to the percolation phenomenon could be observed when the SWCNT content increased from 0.1 to 0.50 wt%. The electrical conductivity of the composites with 0.50 wt% SWCNTs was three orders of magnitude greater than that of the composite with 0.1 wt% SWCNTs. These data are in agreement with our recent results obtained by dispersing CNT in poly (L-Lactide) polymer matrix, by using the same dispersing procedure [28].

As expected, the composites produced from the different polymers, presented the same percolation behavior with the introduction of SWCNTs, since the conductive behavior is mainly due to the SWCNT presence, content and process technology. It is clear that the main factors affecting the electrical percolation threshold are the processing conditions, equal for all the investigated polymers.

Dielectric characterization permits to investigate the frequency-dependent electrical properties of the

Figure 6. Storage G' modulus behavior as function of time for PBCE, BDG10 and BDG30 polymers (a) and composite formulations (b–d)

Figure 7. Bulk electrical conductivities of composites based on different content of SWCNTs

CNT-filled systems, identifying the dielectric behavior of SWCNT based composites, that may be masked under the DC time-domain approach previously used [29, 30]. Figure 8 shows the evolution of the real part of the electrical conductivity (σ_{AC}') measurements (log–log scale) with the frequency: of PBCE (a), BDG10 (b) and BDG30 (c) based composites in the 20 Hz–1 MHz frequency range. The

σ_{AC}' of the neat polymer films displayed a linear behavior with respect to the frequency, while composite materials highlighted a plateau until a specific frequency value, named critical frequency (f_c), followed by a linear behavior. The f_c shifted to high frequency with the increasing of the SWCNT content in the composites [31]. At low frequencies, for the samples over the percolation threshold a plateau in conductivity was found, corresponding to the current flowing almost exclusively through the nanotube network, which behaved as a resistive path. As the frequency rose, the capacitive parts, which can be associated to both the capacitive polymer matrix and the tube/polymer/tube structures, contributed to an increasing conductance.

4. Conclusions

Novel composite films based on poly(butylene cyclohexanedicarboxylate/diglycolate) random copolymer and single walled carbon nanotubes were successfully produced by solvent casting. To better understand the effect of filler shape and the ability

to build efficient conductive architecture through the composite, different amounts of carbon nanotubes were dispersed in the polymers. The presence of SWCNTs affected the morphological, thermal, dynamic-mechanical, electrical and dielectric properties of the polymer matrices. The surface structure significantly changed with the introduction of carbon nanotubes. Results underlined that SWCNTs act as nucleating agent and reinforcing phase in all the investigated polymers.

Figure 8. Real part of the AC Conductivity of PBCE (a), BDG10 (b) and BDG30 (c) based composite films

Moreover, SWCNTs improved the polymer electrical and dielectric conductivity already at low concentrations, with a formation of a tridimensional nanotube network in the percolated formulations. The new developed polymeric conductive composites can be considered very promising for several biomedical applications. In particular, such materials can be used to proliferate cells under electrical stimulation, and could offer significant potential benefits for the functional reconnection of damaged nerves in the peripheral and central nervous systems. The findings of this work prove that the preparation of composites represents a winning strategy to improve the final material properties and can be surely considered a valuable starting point to design other high performance conductive composites.

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