RESEARCH ARTICLE

Synergistic effects of carbon black and carbon nanotubes on the electrical resistivity of poly(butylene-terephthalate) nanocomposites

Andrea Dorigato[1] [iD] | Marco Brugnara[2] | Alessandro Pegoretti[1]

[1]Department of Industrial Engineering and INSTM Research Unit, University of Trento, Trento, Italy

[2]UFI Innovation Center Srl, Ala, TN, Italy

Correspondence
Andrea Dorigato, Department of Industrial Engineering and INSTM Research Unit, University of Trento, Trento, Italy.
Email: andrea.dorigato@unitn.it

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Abstract

In this study, novel electrically conductive polymeric nanocomposites based on polybutylene terephthalate (PBT) filled with commercial carbon black (CB) and carbon nanotubes (CNTs) at different relative ratios have been investigated. Field emission scanning electron microscope (FESEM) analysis revealed how a good nanofiller dispersion was obtained both by introducing CB and CNT. Melt flow index measurements highlighted that the processability of the nanocomposites was heavily compromised at elevated filler amounts, and the viscosity percolation threshold was established at 3 wt% for CNTs and between 6 and 10 wt% for CB nanocomposites. Differential scanning calorimetry (DSC) measurements evidenced how the presence of CNT slightly increased the glass transition temperature of the materials, and an increase of 12°C of the crystallization temperature was obtained with a CNT amount of 6 wt%. Also the crystalline fraction was increased upon CNT addition. Electrical resistivity measurements evidenced that the most interesting results were obtained for nanocomposites with a total filler content of 6 wt% and a CNT/CB relative amount equal to 2:1. The synergistic effect obtained with the combination of both nanofillers allowed the achievement of a rapid surface heating through Joule effect even at applied voltages of 2 V.

KEYWORDS

conducting polymers, crystallization, mechanical properties, nanocomposites

1 | INTRODUCTION

In the last years, polymer matrix nanocomposites attracted considerable academic and industrial interest because nanoscale effects can significantly improve physical properties of polymer matrices, such as impact resistance,[1] elastic modulus,[2] thermal stability, and fire resistance.[3–6] In general, polymeric materials display high electrical resistance,[7] but nowadays several methods are available to reduce it.[8–14] One of the most promising methods is to add conductive fillers, such as carbon black (CB), carbon nanotubes (CNTs),[15,16] graphene,[17–22] or metal particles. For instance, several nanocomposite systems were investigated by our group in the last years.[23–27] Above a critical filler amount (i.e., percolation threshold), the formation of a conductive path within the polymer matrix constituted by uninterrupted clusters of connected filler particles can be obtained.[28–30] These materials can be applied where charge dissipation and electrical conductivity are desired, such as films for packaging of sensitive electronics components or materials subjected to Corona treatments. The control of the filler dispersion quality represents one of the most critical and challenging technical issues, because an inhomogeneous dispersion in filled polymers can lead to problems such as heavy process dependency.[31–35]

The thermoplastic polyester poly(butylene terephthalate) (PBT) is obtained by polycondensation of 1,4-butanediol with either terephthalic acid or dimethyl terephthalate.[36] Only in the late 1960s, PBT was brought to market by Celanese. In 1970, Celanese introduced fiber reinforced PBT compounds. Because of its very easy processing and fast crystallization, PBT is nowadays a widely used thermoplastic polymer, and a broad range of injection moldable PBT grades are available. In addition to neat PBT grades, mineral filled, glass fiber reinforced, impact modified, and flame retardant grades, as well as several blends based on PBT, are available. In general speaking, PBT-based components offer high strength and rigidity, low moisture absorption, excellent electrical properties and chemical resistance, rapid molding cycles, and reproducible mold shrinkage. The fast crystallization rate enhances moldability, producing smooth surfaces that can be painted, printed, and ultrasonically welded. Due to its peculiar properties, PBT can be used in many types of products: appliances, automobiles, electrical and electronic parts, industrial components, and consumer items. PBT resistance to heat and chemicals and the wide range of coloring possibilities allow its use in applications where it has been found easier to mold and less expensive than thermosets. The electrical and electronic industry uses PBT for bobbins, connectors, switches, relays, terminal boards, motor brush holders, TV tuners, fuse cases, integrated circuit carriers, and sockets and end bells.

In addition to the production of injection-molded parts, PBT can also be extruded as sheets, films, profiles, or nonwoven fabrics. Due to their low cost and high efficiency, nonwoven polymer fabrics are extensively used in air and liquid filters for the automotive field and industrial equipment.[37] Due to their good properties such as high porosity, large surface area, dust-free, low cost, easy processability, and modifiability, these fabrics can also be suitable for hygiene, family, and medical use. Nonwovens are composed by a web of thin fibers and can be manufactured through different technologies (i.e., wet- or air-laid, spunbond or meltblown).

On the basis of these considerations, the objective of this article is the development and the thermo-electrical characterization of PBT-based nanocomposites filled with commercial CB and CNT masterbatches. This research was performed in collaboration with UFI Innovation Center Srl, a leading producer of solutions for fluid filtration in the automotive field (cars, motorbikes, etc.). The systematic investigation of the thermo-mechanical and electrical properties of PBT-based nanocomposites represents a preliminary experimental activity aimed to the production of novel multifunctional meltblown filters having high electrical conductivity that could be heated through Joule effect.

2 | EXPERIMENTAL PART

2.1 | Materials

Polybutylene terephthalate Lanxess Pocan B 1100, kindly supplied by UFI Innovation Center (UFI Filters Spa, Nogarole Rocca (VR), Italy), was utilized as polymer matrix in the form of pellets (density 1.30 g/cm^3, melt volume-flow rate at 250°C, and 2.16 kg 80 cm^3/10 min). The neat matrix was mixed at various concentrations with (i) Plasticyl PBT 1501 (Nanocyl SA, Sambreville, Belgium), a PBT-based masterbatch containing 15 wt% of multi-walled carbon nanotubes (MWCNTs) (density 1.31 g/cm^3 and melt volume-flow rate at 250°C and 2.16 kg 0.88 cm^3/10 min), and with (ii) PRE-ELEC PBT 1455 (Premix Oy, Rajamäki, Finland), a PBT-based masterbatch containing 15 wt% of high surface area CB (density 1.32 g/cm^3 and melt volume-flow rate at 250°C and 2.16 kg 0.60 cm^3/10 min).

2.2 | Samples preparation

Before melt compounding, all materials were dried in a Moretto X Dry Air drier at a temperature of 130°C for at least 4 hr with an air flow of 7 m^3/hr. Melt compounding was performed in a Thermo-Haake Polylab Rheomix 600p operating at 260°C for 5 min with a rotors speed of 50 rpm. A total material amount of 50 g was processed with this technique for every composition. The compounded materials were then compression molded at 260°C for 5 min under a pressure of 0.33 MPa by using a Carver Laboratory Press. Square sheets (16 × 16 cm) with a thickness in the range from 1.0 to 1.2 mm were thus obtained.

In this way, CB-based and CNT-based nanocomposites with a filler content between 1 and 15 wt% were prepared. In order to evaluate possible synergistic effects between the nanofillers, also nanocomposites samples containing both nanofillers were prepared (total filler contents of 4, 6, and 10 wt%). The samples were denoted indicating the weight percentages of both fillers. For example, PBT-CNT-4-CB-2 refers to a nanocomposite sample with a CNT content of 4 wt% and a CB content of 2 wt%. In Table 1, the list of the prepared samples is reported.

2.3 | Experimental methodologies

Microstructural features of the composites cryofractured surfaces were observed through a Zeiss Supra 40 field emission scanning electron microscope (FESEM), equipped with an exclusive Gemini column. Rectangular samples (30 × 5 × 1 mm^3) were put in nitrogen for 1 hr and were then fractured through an impactive flexural stress. The statistical evaluation of the dimension of the nanofillers has been performed through ImageJ public domain software.

Sample name	CNT content (wt%)	CB content (wt%)	Total filler content (wt%)
PBT	0	0	0
PBT-CNT-1	1	0	1
PBT-CNT-2	2	0	2
PBT-CNT-3	3	0	3
PBT-CNT-4	4	0	4
PBT-CNT-5	5	0	5
PBT-CNT-6	6	0	6
PBT-CNT-10	10	0	10
PBT-CNT-15	15	0	15
PBT-CB-1	0	1	1
PBT-CB-2	0	2	2
PBT-CB-3	0	3	3
PBT-CB-4	0	4	4
PBT-CB-5	0	5	5
PBT-CB-6	0	6	6
PBT-CB-10	0	10	10
PBT-CB-15	0	15	15
PBT-CNT-1.34-CB-2.66	1.34	2.66	4
PBT-CNT-2-CB-2	2	2	4
PBT-CNT-2.66-CB-1.34	2.66	1.34	4
PBT-CNT-2-CB-4	2	4	6
PBT-CNT-3-CB-3	3	3	6
PBT-CNT-4-CB-2	4	2	6
PBT-CNT-3.34-CB-6.66	3.34	6.66	10
PBT-CNT-5-CB-5	5	5	10
PBT-CNT-6.66-CB-3.34	6.66	3.34	10

In order to evaluate the processability of the nanocomposites, the melt flow index (MFI) was measured with a Dynisco melt indexer model LMI 4000 Series according to ASTM D1238 standard. MFI was determined at the temperature of 250°C for all the compositions and with applied weights of 2.16, 5.00, or 10.00 kg, depending on the viscosity of the nanocomposites under investigation.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC30 calorimeter. All the tests consisted of three ramps at 10°C/min: a first heating from 0 to 270°C, a cooling step from 270 to 0°C, and a second heating from 0 to 270°C. All the tests were performed under a nitrogen flow of 100 ml/min, and the glass transition temperature (T_g), the melting temperature (T_m), and the crystallization temperature (T_c) were determined. Moreover, the crystallinity content (X_c) was determined by dividing the specific heat of fusion of the samples by the melting enthalpy of fully crystalline PBT, equal to 140 J/g.[38] The weight fraction of PBT in the composites was also taken into account.

Electrical volume resistivity measurements of the PBT composites under direct current (DC) were performed with a Keithley 6517A electrometer at room temperature. Tests were conducted under applied voltages of 2, 12, 24, and 30 V, following the ASTM D-4496-04 standard. A four contact points configuration was adopted, with a distance of 10 mm between the measuring electrodes. The tested specimens were in the form of strips (16 × 6 mm), with a thickness in the range between 1.0 and 1.2 mm. The resistivity (ρ) of the samples was evaluated with the following equation:

$$\rho = R \cdot \frac{A}{L}$$

where R is the electrical resistance, A is the cross-sectional area of the specimens, and L is the distance between the measuring electrodes.

The evolution of the surface temperature upon voltage applications was measured on nanocomposites with a total filler amount of 6 wt%, by using a Fluke TiRx thermographic

camera, testing samples with a length of 35 mm and a width of 6 mm. The surface temperature was recorded after 1, 5, 10, 30, 60, and 120 s starting from room temperature ($T_0 = 25°C$), under applied voltages of 12 and 24 V, i.e., the typical voltages available on batteries mounted on cars and trucks.

3 | RESULTS AND DISCUSSION

It is well known that the macroscopic properties of polymer nanocomposites are strongly influenced by the dispersion level of the nanofiller within the matrix. Therefore, morphological features of the cryofractured surface of the nanocomposite samples were investigated through FESEM analysis (Figure 1a–d). In general, it is possible to state that both CB and CNT nanofillers are homogeneously dispersed in the matrix, and the presence of nanofiller is proportional to its concentration. This means that the shear stresses generated by the

mixer during the melt compounding procedure were efficient to break the nanofillers aggregates and disperse them in the matrix with a good dispersion. Nevertheless, CB-filled nanocomposites are characterized by the presence of aggregates of primary particles that cannot be broken,[39] while in CNT-filled samples, single filaments of nanometric diameter can be detected. Due to the ImageJ software, it was possible to determine the dimension of the nanofiller aggregates within the matrix, which resulted to follow a Gaussian distribution. It was concluded that CB aggregates are characterized by a mean diameter of 65 ± 15 nm, while CNTs have a diameter of around 20 ± 5 nm. It could be, therefore, expected that the good dispersion degree of both nanofillers within the matrix should improve both thermal and electrical properties.

Considering the intended application of the investigated materials and the hypothesized manufacturing process (melt blowing), it is also important to evaluate their processability. In fact, it is well known how the viscosity of polymer matrices could strongly increase upon nanofiller addition,
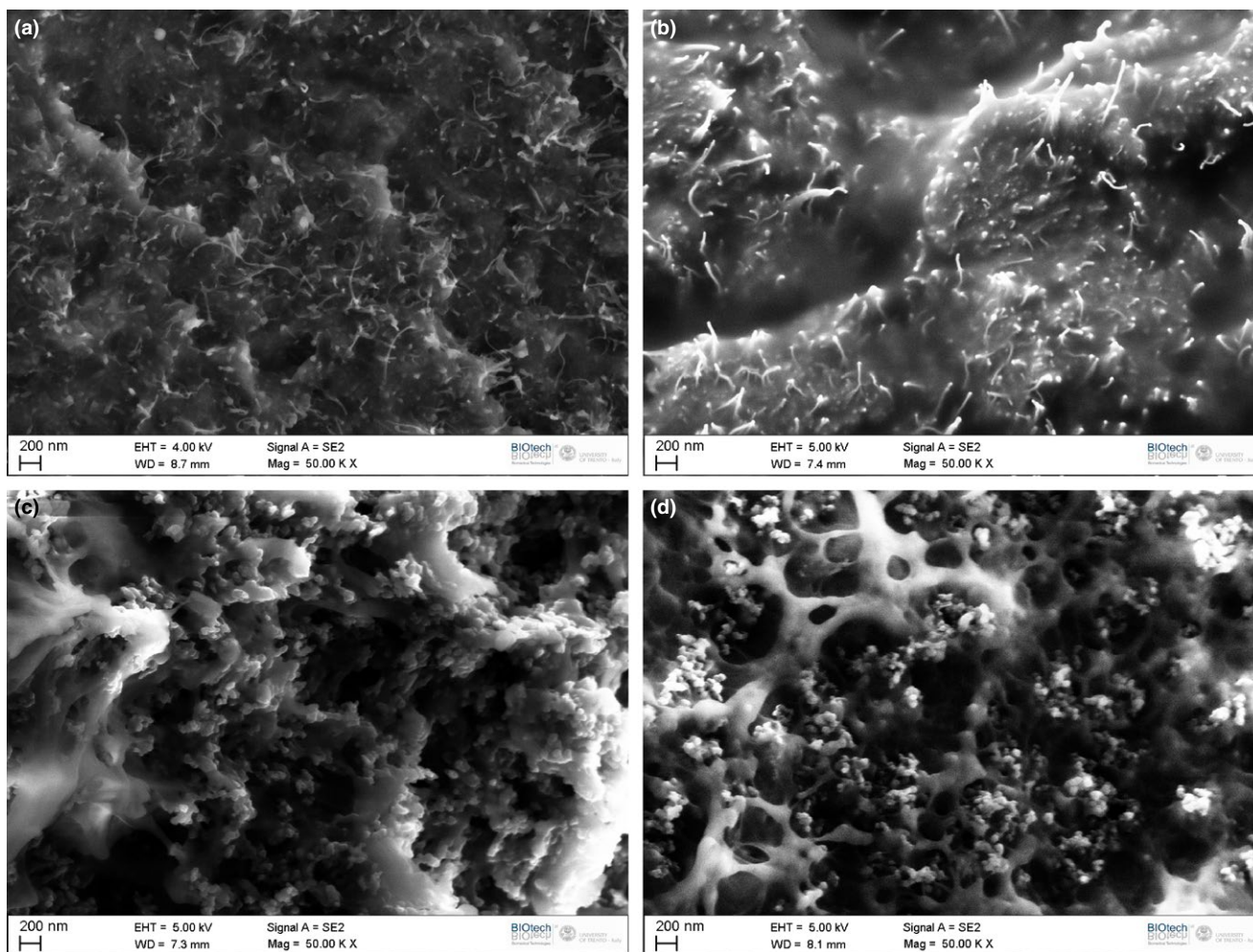
FIGURE 1 FESEM images of the fracture surfaces of (a) PBT-CNT-6, (b) PBT-CNT-15, (c) PBT-CB-6, and (d) PBT-CB-15 nanocomposites. FESEM, field emission scanning electron microscope; PBT, polybutylene terephthalate; CNT, carbon nanotubes; CB, carbon black [Colour figure can be viewed at wileyonlinelibrary.com]

especially at elevated filler loading. Therefore, the evaluation of the MFI can be of crucial importance to evaluate the possibility to prepare electrically conductive filters that could be heated through Joule effect. The results of melt flow index tests on CB and CNTs nanocomposites are reported in Figure 2a. It is important to underline how it was not possible to tests all the samples at the same conditions, and a higher weight was used for nanocomposite samples at elevated filler amounts. As expected, as the nanofiller amount in the material increases, the MFI decreases. CB slightly increases the apparent viscosity of the polymer until a concentration of 6 wt%. Over this threshold, the change is more pronounced until the maximum investigated nanofiller amount of 15 wt%. However, a significant drop of MFI can be observed between 1 and 3 wt% of CNTs. It is, therefore, possible to conclude that the mechanical percolation of the nanocomposites containing CB is reached only for nanofiller amounts between 6 and 10 wt%, while the mechanical percolation of nanocomposites containing CNTs is reached at nanofiller amounts higher than 3 wt%. It is, therefore, clear that by using nanofiller concentration above the percolation threshold, it would

be impossible to process these materials through melt blowing. The introduction of further nanofiller amounts is, therefore, technologically limited by the matrix viscosity. In order to preserve an acceptable processability level, a minimum MFI value of 20 g/10 min at a temperature of 250°C with an applied weight of 5.00 kg can be estimated. Therefore, all the materials with a CNTs amount higher than 5 wt% could not be processed by melt blown because their apparent viscosity is too high for this technology. For the same reason, all the compositions with CB amount higher than 6 wt% could not be used. The MFI of the nanocomposites containing both nanofillers were then measured, and the results are reported in Figure 2b–d. From this set of data it is possible to state that for materials with a total filler amount of 4 and 6 wt%, MFI values substantially follow the rule of mixtures. However, for materials with a total filler amount equal to the 10 wt%, the MFI does not follow the theoretical trend, and negative deviations can be observed. This discrepancy is probably due to the formation of a mechanical percolative network at elevated filler content. However, considering the intended application of these materials and the obtained MFI values, it is clear
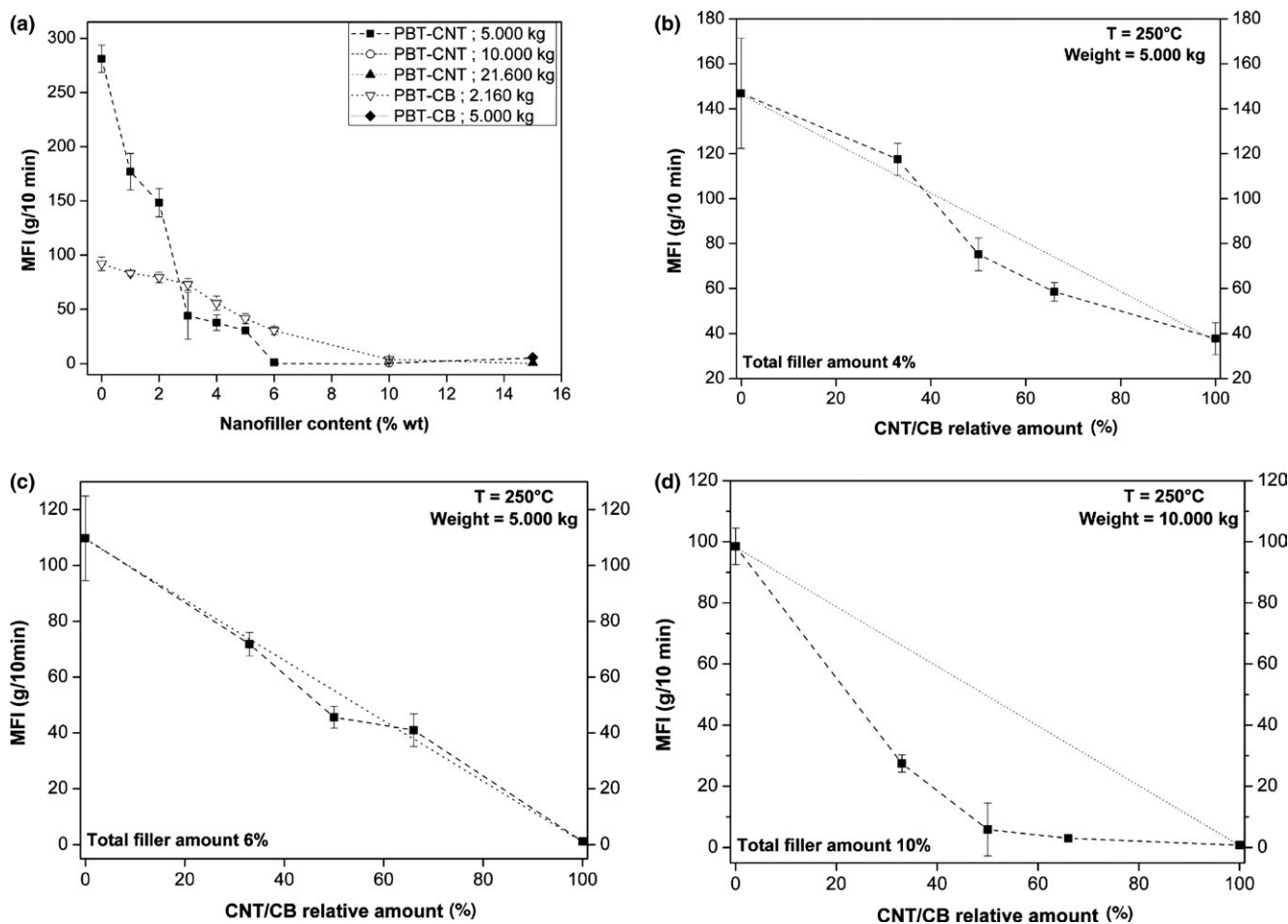
FIGURE 2 Evaluation of the processability of the PBT-based nanocomposites. (a) MFI values as a function of CNT and CB content. MFI of the samples containing both CNTs and CB. Total filler amount of (b) 4, (c) 6, and (d) 10 wt%. PBT, polybutylene terephthalate; CNT, carbon nanotubes; CB, carbon black; MFI, melt flow index

that such high level of filler content is not acceptable from a technological point of view.

Considering the perspective application of these materials as melt-blown fabrics, the investigation of the influence of carbon-based nanofillers on the thermal properties of the resulting materials is of key importance. Therefore, DSC tests were performed on CB and CNT nanocomposites, and also samples with both nanofillers were tested. In Figure 3a and b, representative DSC thermograms of nanocomposites with different CB and CNT amounts are, respectively, reported, while the most important results are summarized in Table 2. It is clear that the melting temperature (T_m) of the material is not affected by the presence of nanofillers nor during the first neither in the second scan (not reported for the sake of brevity). However, the glass transition temperature (T_g) of the samples containing CB is the same of neat PBT, while the CNT-filled specimens present an increase of T_g. While

TABLE 2 Results of differential scanning calorimetry (DSC) test on polybutylene terephthalate (PBT)-based nanocomposites

Sample	T_g (°C)	T_m (°C)	X_c (%)	T_c (°C)
PBT	44.9	224.9	31.8	200.1
PBT-CB-6	45.9	225.1	32.6	200.0
PBT-CB-15	46.3	225.8	29.0	200.3
PBT-CNT-6	49.2	224.6	42.0	212.0
PBT-CNT-15	49.5	224.9	45.8	212.8
PBT-CNT-2-CB-4	43.3	225.8	33.8	210.8
PBT-CNT-3-CB-3	44.2	226.4	40.7	210.1
PBT-CNT-4-CB-2	45.1	224.7	39.6	211.1

T_g, glass transition temperature (first heating run); T_m, melting temperature (first heating run); X_c, crystallinity degree (first heating run); T_c, crystallization temperature (cooling run).
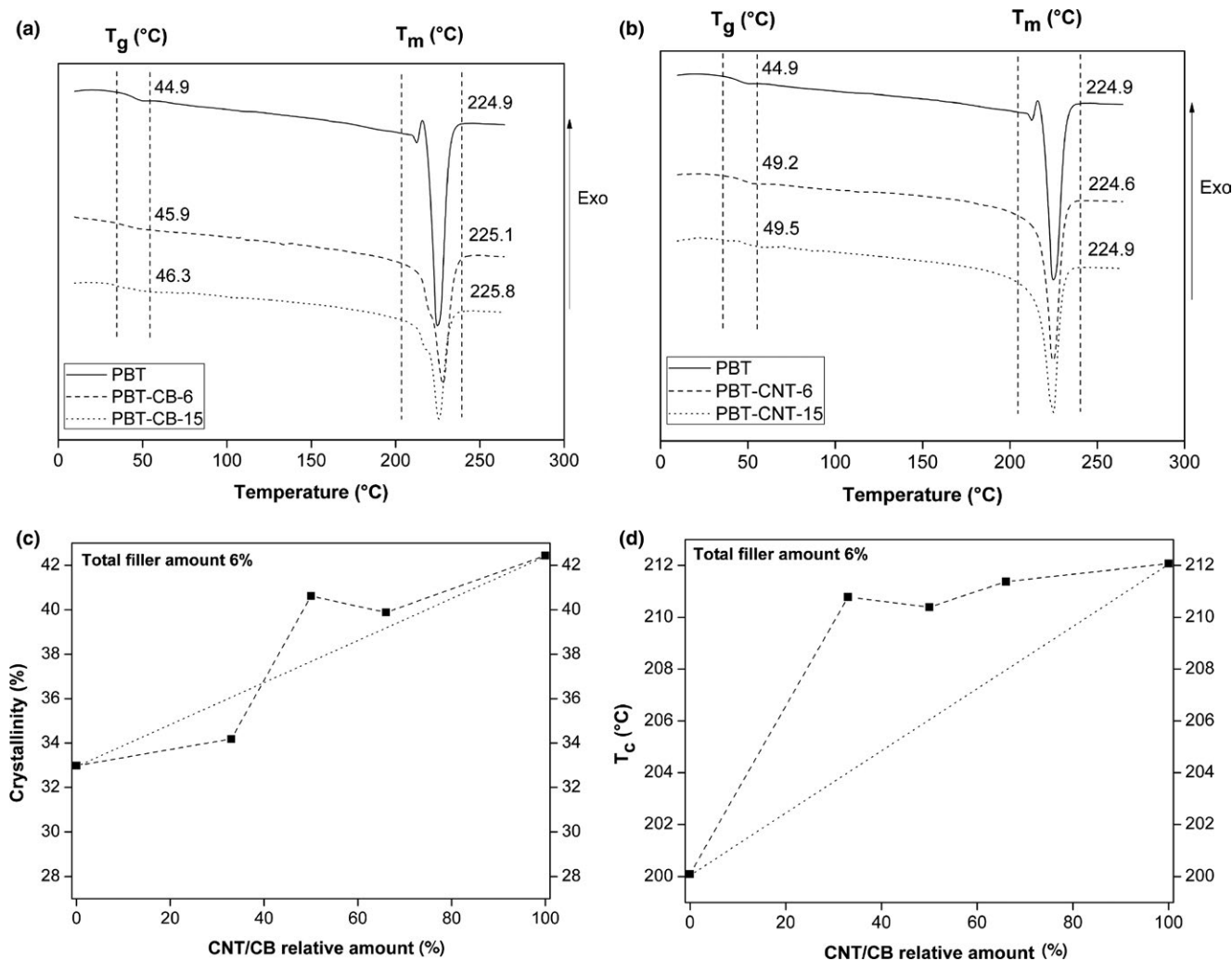

FIGURE 3 DSC thermograms of PBT-based nanocomposites (first heating run). (a) CB-filled nanocomposites, (b) CNT-filled nanocomposites, (c) crystallinity degree, and (d) crystallization temperature of nanocomposites containing both nanofillers (total filler amount of 6 wt%). PBT, polybutylene terephthalate; CNT, carbon nanotubes; CB, carbon black; DSC, differential scanning calorimetry

the introduction of CB to the polymeric matrix does not affect the crystalline fraction with respect to neat PBT, CNT addition increases the crystallinity degree. It could be, therefore, hypothesized that CNT acts as nucleating agent on the polymeric matrix.[40] One of the key parameters for the processing conditions of these materials is the crystallization temperature (T_c) because it determines the die-to-collector distance in the melt-blown technology. The results reported in Table 2 highlight that CNTs act as nucleating agents, with an increase of T_c with the CNT loading, while CB introduction seems to not affect the crystallization temperature. The same tests were then performed on the nanocomposites containing both CNT and CB, with a total filler amount of 6 wt%. As reported in Table 2, it is clear that the melting temperature (T_m) and the glass transition temperature (T_g) are not affected by the relative nanofiller content. However, the crystallization temperature (T_c) and the crystalline fraction (X_c) are strongly affected by the nanofiller composition. These results can be appreciated in Figure 3c and d. CNT introduction, even at very small amount (2 wt%), strongly increases both the crystallization temperature and the crystallinity degree. While X_c trends seems to substantially follow the rule of mixture, a positive deviation of T_c with respect to the theoretical predictions can be observed. It is probable that the formation of a percolative network due to the presence of both nanofillers increases the nucleating capability on the PBT matrix.

Four-point electrical measurements were performed, and the results of bulk resistivity measurements of the samples containing CNT or CB are reported in Figure 4a. This set of data refers to the experiments with an applied voltage of 2 V, while the bulk resistivity of the same samples with an applied voltage of 12 V is shown in Figure 4b. The introduction of the carbon-based nanofiller in the insulating polymeric matrix increases the conductivity of the nanocomposites. As an example, a resistivity value lower than 10^3 Ω cm can be achieved with a CNT content of 6 wt%. It is possible to see that CNTs introduction confers a good conductivity to the samples, and it is possible to appreciate a lower electrical percolation threshold in these samples with respect to CB-filled nanocomposites. This value is equal to the 6 wt% of CNTs. However, only with a CB amount between 10 and 15 wt%, the electrical percolation threshold is reached and a drop of the resistivity occurs. Comparing these results, it is possible to see that the resistivity measured with an applied voltage of 2 V is higher than that measured at 12 V. A non-ohmic behavior of the conductive samples can be, therefore, hypothesized, and this trend can be ascribed to the fact that at higher voltage levels, new current transport mechanisms may occur in nanofilled samples. However, a deeper investigation should be performed to better understand this aspect. A target resistivity value lower than 10^3 Ω cm at an applied voltage equal to 12 V is required to prepare nanocomposite samples

that could be effectively heated through Joule effect. For this reason, all the CB-filled nanocomposites could not be used for the required application. On the contrary, the samples containing a CNT amount equal or higher than 6 wt% reach the requested resistivity value. The problem with these samples is their processability, as shown in Figure 2. In order to combine both these parameters, taking advantage of the synergistic effect of the two nanofillers, samples with a total filler amount of 4, 6, and 10 wt% at different CNT/CB relative amounts were prepared and electrically characterized (Figure 4c–e). From this set of data, it is possible to understand that increasing the CNTs relative amount the resistivity decreases with a nonlinear trend, because of the synergistic effect due to the presence of both nanofillers. In this way, it is possible to reach values of resistivity that could not be achieved with a single nanofiller, even at elevated nanofiller amounts. As an example, with a total nanofiller amount of 6 wt% and a CNT/CB ratio of 2:1, it is possible to obtain an electrical resistivity of 10^2 Ω cm. As reported in our previous article on PLA-based nanocomposites,[41] it is interesting to observe that the combination of two fillers having different morphology at a certain relative ratio promotes a further decrease of electrical resistivity. In these conditions, the formation of a three dimensional conductive network within the matrix is favored. The optimal filler concentration and the relative filler amount depend on the geometrical and the electrical properties of the fillers. An extended modelization activity should be performed to have a more detailed comprehension of the electrical properties of the prepared hybrid composites. In order to underline the technical value of the obtained results, a comparison with the resistivity values reported in the work of Krause et al.[42] on PA6/PA66—CNTs nanocomposites can be made. The electrical percolation threshold was approximately the same, and similar resistivity values were obtained, but in Krause's work, the tests were performed at an applied voltage of 40 V. In the article by Yin et al.[43] on PBT-based nanocomposites, it was demonstrated how with CNTs addition it is possible to reach the percolation threshold at low concentration (0.5 wt%), but the resistivity value obtained above this critical volume fraction is similar to that reported in the present investigation.

The heating capability of PBT nanocomposites was evaluated through a thermocamera. In Figure 5, representative images of the evolution of the surface temperature upon voltage application of PBT-CNT-4-CB-2 sample at an applied voltage of 12 V are reported. It can be easily detected how an effective heating can be detected even after 10 s, and a temperature of 64°C can be reached after 120 s. In Figure 6a,b, the measurements of Joule heating of the samples containing a total filler amount of 6 wt% at 12 and 24 V are, respectively, reported. It is possible to appreciate the evolution of the surface temperature with respect to the applied voltage, the time, and the composition of the
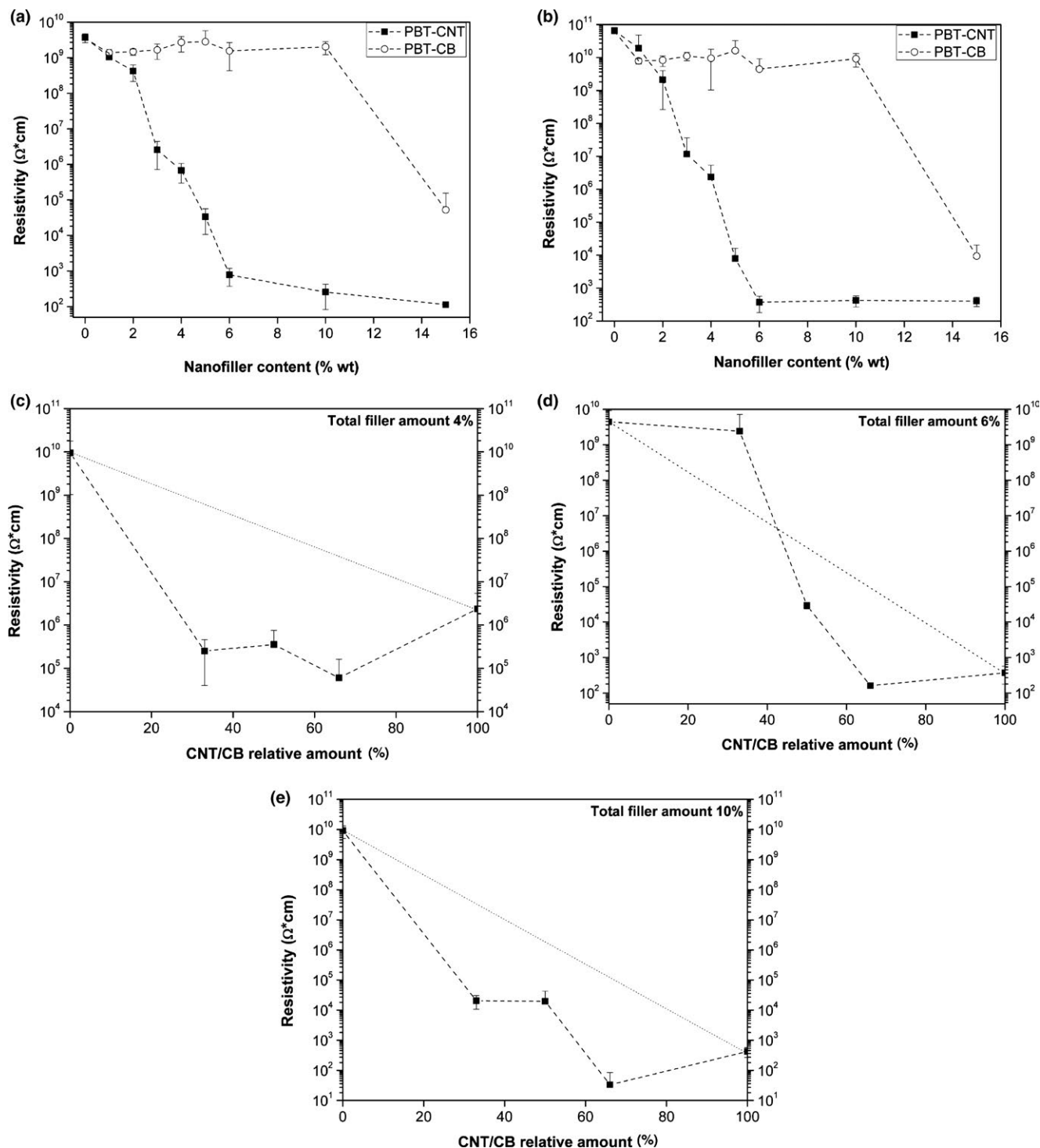
FIGURE 4 Electrical bulk resistivity of the samples containing different amounts of CNTs and CB: (a) applied voltage = 2 V, (b) applied voltage = 12 V. Electrical bulk resistivity of the samples containing both nanofillers at an applied voltage of 12 V: total filler amount of (c) 4, (d) 6, and (e) 10 wt%. CNT, carbon nanotubes; CB, carbon black

nanocomposites. The first aspect to underline is that not all the samples can be heated through the Joule effect under the selected conditions. Only the compositions containing 4 and 6 wt% of CNTs significantly increase their surface temperature once a voltage is applied. Obviously, the higher the voltage, the higher is the temperature reached.

This situation is in agreement with the results obtained with the resistivity measurements (Figure 4). The samples that present the higher conductivity dissipate more thermal power, and in these conditions, the surface heating is more intense. The most interesting aspect is that during the first seconds, there is a rapid temperature increase, and
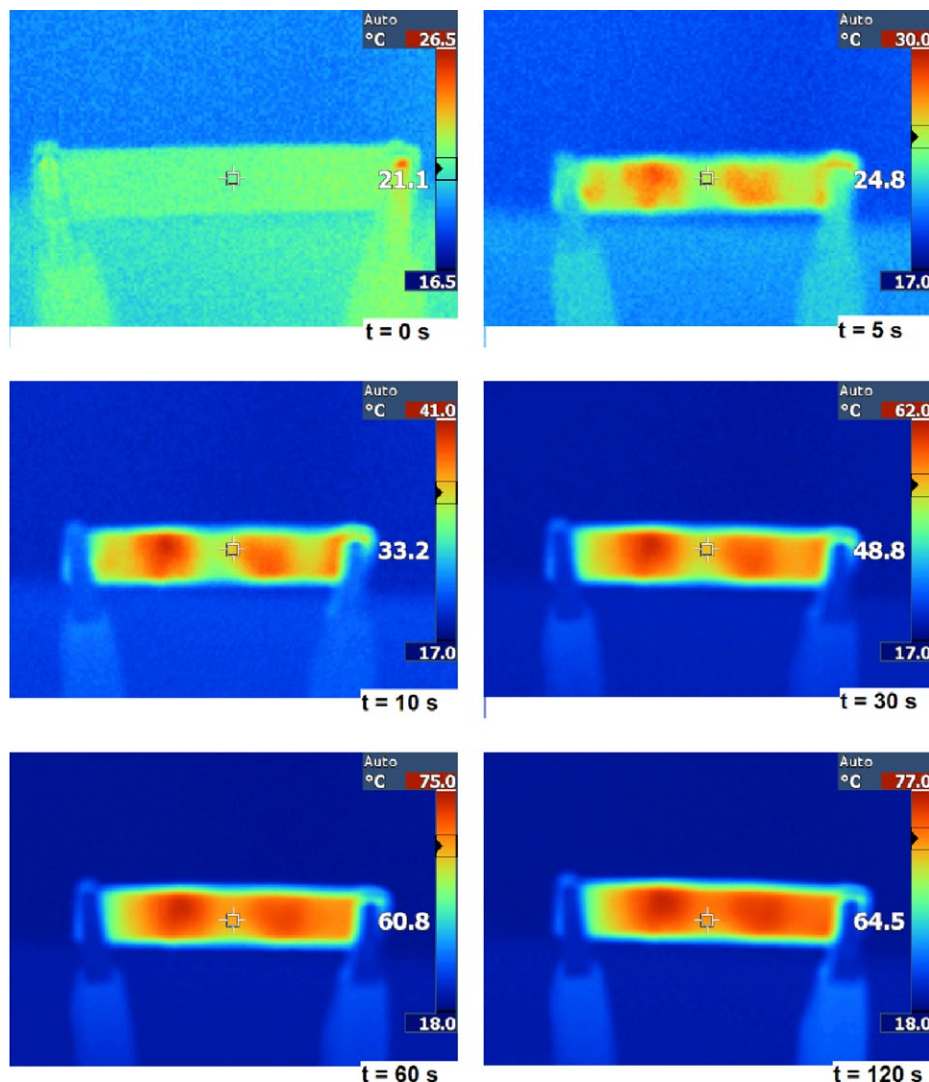
FIGURE 5 Evolution of the surface temperature upon voltage application of PBT-CNT-4-CB-2 sample at an applied voltage of 12 V. CNT, carbon nanotubes; CB, carbon black; PBT, polybutylene terephthalate [Colour figure can be viewed at wileyonlinelibrary.com]

the material reaches a temperature plateau after 60 s. This aspect is very important for the final application of these materials as filters, because the thermal degradation of the materials for prolonged voltage application times should be avoided.

4 | CONCLUSIONS

Novel electrically conductive nanocomposites based on PBT, filled with different amounts of CB and CNTs masterbatches were investigated. FESEM micrographs demonstrated that a good nanofiller dispersion was achieved both by adding CB and CNT, while the processability of the nanocomposites was impaired at elevated filler amounts. CNT addition slightly increased the glass transition temperature of the materials and promoted an interesting nucleating capability of the PBT matrix, with an impressive enhancement of the crystallization temperature and the crystallinity degree.

Nanofiller addition above the percolation threshold allowed to considerably improves the electrical conductivity of the samples. Electrical resistivity values of about $10^2 \, \Omega$ cm were obtained for nanocomposites with a total filler amount of 6 wt% and a CNT/CB relative ratio equal to 2:1. With this composition, it is possible to obtain a rapid surface heating through Joule effect even at applied voltages of 2 V.

Further efforts will be made in the future to improve the electrical conductivity of the prepared materials, by adding different kinds of carbonaceous nanofillers at various concentrations. Moreover, nanofiller surface functionalization will be performed to further improve its dispersion within the matrix.
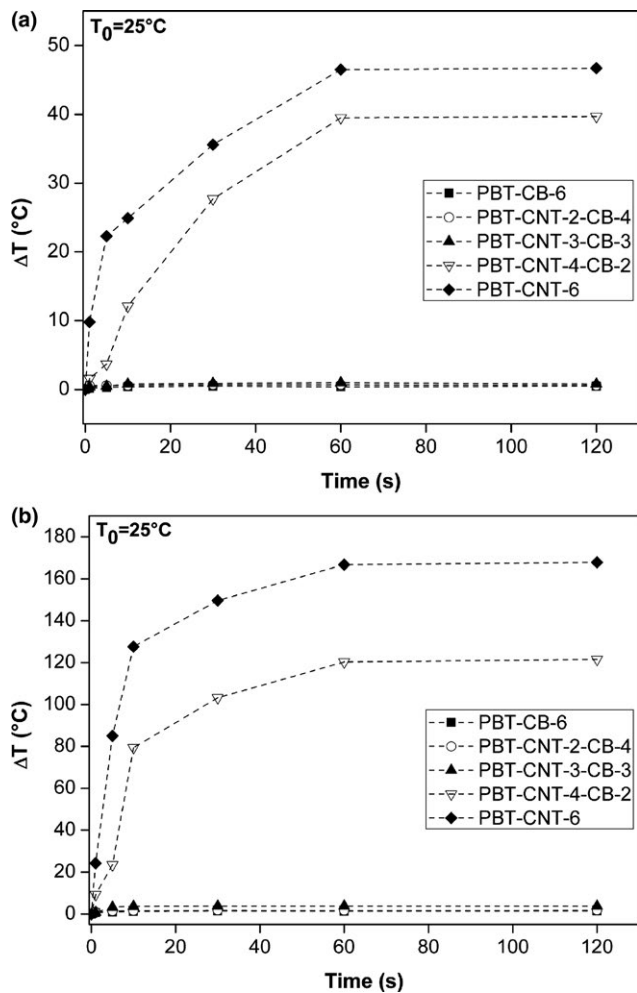
FIGURE 6 Evolution of the surface temperature of bulk nanocomposite samples: (a) applied voltage 12 V and (b) applied voltage 24 V

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