Electrical behavior of polypropylene composites melt mixed with carbon-based particles: Effect of the kind of particle and annealing process

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A B S T R A C T

Polypropylene (PP) composites with different carbon-based fillers such as graphite (G), thermally reduced graphene oxide (TrGO), and carbon nanotubes (CNT) were prepared by the melt mixed method and the effect of the kind of particle and the annealing process on the electrical behavior was analyzed. Our results show that the electrical conductivity of the resulting composites strongly depends on the filler used. The lowest electrical percolation threshold is obtained when CNT is used as filler whereas when TrGO is used this threshold increases by a factor of two. Noteworthy, composites based on G-microparticles present a percolation process at concentrations one order of magnitude higher than those based on CNT. By annealing the composites at the melt state, the electrical conductivity can be improved several orders of magnitude although depending on the carbon-based particle and its concentration. In particular, composites at concentrations of CNT and G around the percolation threshold are largely affected by the annealing process. The electrical conductivity can also be increased by adding CNT particles to PP/TrGO composites having as consequence a decrease in its percolation threshold.

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1. Introduction

Polymer nanocomposites have yielded novel advanced functional materials with improved properties such as electrical conductivity, mechanical, barrier and thermal stability [1,2], among others, that can be used in many fields from electronics to aerospace applications [3]. From the different types of nanoparticles used as filler, carbon-based materials are highlighted, especially carbon nanotubes (CNTs) having outstanding properties such as thermal stability (>700 °C in air), strength (~50 GPa), high aspect ratio (~1000) and electrical conductivity (~10^6 S/m) [1]. CNTs are mainly used to develop electrical conductive polymer composites by changing the insulating nature of the matrix through a phenomenon known as electrical percolation. However, CNTs present a major drawback related with its high cost explaining the large interest during the last years in polymer composites based on other less expensive carbon nanostructures such as those derived from graphite. Graphite (G) is the most stable carbon form at standard conditions [4]. It is a low-cost natural material with a current annual global production of around 1.15 million tons and a value around U\$ 1150/ton in 2011 [5]. Because of the large

number of delocalized π electrons in its structure [6], G is a good electrical conductor although is not often used as filler in polymers because of the high incorporations of standard micrometer G-particles (20–50 μm) needed to achieve good conductivities [7–11]. However, during the last years nanoparticles based on modified G, such as graphene or its derivatives, have appeared as filler that could replace expensive CNTs [12]. Graphene has extraordinary properties such as a Young's modulus of 1 TPa and a tensile strength of 130 GPa, becoming the most resistant materials measured. Graphene has also an electrical conductivity of ~6×10^5 S/m that is not affect by chirality as in CNTs. These properties along with its extremely high specific surface area (around 2630 m^2/g) and impermeability to gases, show the great potential of graphene derivatives as filler for improving the properties of polymers [13].

Although there are several methods to obtain graphene, from the scotch-tape to chemical vapor deposition, those based on chemical solution are stressed by its practical approach to scale up the production. These top-down methods breaks the sp^2 bonds of G by using strong oxidizing agents (Hummers process) forming new bonds with functional groups within the structure and producing exfoliated graphite oxide (GO) particles [14]. GO consists of intact graphitic regions interspersed with both sp^3-hybridized carbons containing hydroxyl and epoxide functional groups on

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the top and bottom surfaces of each sheet and sp^2-hybridized carbons containing carboxyl and carbonyl groups mostly at the sheet edges [15]. The presence of the functional groups largely reduces the thermal stability and the electrical conductivity of GO [13,16], even though by a reduction process these properties can be restored reaching conductivities around $\sim$10^3–10^4 S/m [17]. This process can be accomplished by using reducing agents such as hydrazine monohydrate or sodium borohydride, in a suitable medium producing chemically reduced graphene. Another route to reduce GO is by a thermal shock at high temperatures in inert atmospheres such as Ar or N, producing thermally reduced graphene oxide (TrGO) [15,18]. These processes remove the functional groups while exfoliate even more the structure increasing the surface area [16,19]. Because of its extraordinary features, TrGO can be considered as an ideal filler for the development of functional polymeric nanocomposites. TrGO or GO have been successfully dispersed in polar polymers such as poly(acrylonitrile) (PAN), poly(acrylic acid) (PAA), polyester, epoxy resin, thermoplastic polyurethane (TPU), poly(vinyl alchol) (PVA), and poly(methyl methacrylate) (PMMA), using solution-mixing techniques [13, 20–22]. Despite polyolefins, such as polypropylene (PP) and polyethylene (PE), represent more than 50% of the market, its nanocomposites with TrGO have been less developed. Kim et al. [23] successfully create PE/TrGO nanocomposites achieving an increase of four orders of magnitude in electrical conductivities as compared with pure PE by either solution-mixing or melt blending techniques. PP/TrGO nanocomposites have also been prepared by melt blending [15,24], although other techniques such as in situ polymerization are further reported [25,26]. PP/TrGO nanocomposites exhibit increased electrical conductivity compared with pure PP by more than six orders of magnitude, with improved mechanical and thermal properties [15,24–26].

The addition of either a second particle or the annealing process are two novel methodologies able to improve the electrical conductivity (or decrease the percolation threshold) of polymer/CNT nanocomposites. By adding a second particle to polymer/CNT composites, resulting in a hybrid material (one matrix and two fillers), the space between conductor nanofillers is reduced forming a percolated structure more easily and lowering the electrical percolation threshold. This theory is known as free volume theory [4,27–31]. Examples of these hybrid materials are polymer/CNT with inert filler: calcium carbonate (CaCO$_3$) [30], montmorillonite (Cloisite 15A) [28], SiO$_2$ [28], and GO [31]; or with conductive particles: silver (AgNP) [27], copper (CuNP) [28], carbon black (CB) [29] nanoparticles and stainless steel microparticles [4]. The final electrical conductivity of the hybrid compounds does not depend on the conductive/insulating nature of the second particle but of its aspect ratio [28]. On the other hand, it is well known that the conductivity of polymer/CNT composites can be increased by annealing at temperatures higher than the melting temperature of the matrix [32,33]. These changes in conductivity are related with the non-equilibrium state of CNT in high viscous matrices under these quiescent conditions [34] driven by either the entropic forces of self-organization [35] or the high attractive interparticle potential [36–39] overcoming its limited Brownian motion. These processes, together with the filler rearrangements due to relaxation of polymer chains at high temperatures, can form conductive agglomerates from the initially dispersed CNT [33,38,40,41]. Independent of the mechanism, under annealing the mean distance between CNT, or its clusters, decreases causing enhanced conductivities [32]. The effects caused by this heat treatment on hybrid nanocomposites have been confirmed in mixtures of PP/CNT/CuNP, PP/CNT/Cloisite 15A and PP/CNT/SiO$_2$ [28]. In this article, we analyze how the type of carbon-based fillers can tune the geometrical electrical percolation of nanocomposites. The effect of an annealing process on the percolation threshold of the composites prepared is also discussed through the article.

2. Experimental section

2.1. Materials

A commercial grade polypropylene from Petroquim S.A. (Chile) (PH0130) with a melt flow rate of 1.7 g/10 min (2.16 kg/230 °C) (Norm ASTM D-1238/95) was used as matrix. G (graphite fine powder extra pure) with a particle size <50 μm, sulfuric acid (98.08%, H$_2$SO$_4$), potassium permanganate (99%, KMnO$_4$), Hydrochloric acid (32%, HCl), and sodium nitrate (99.5%, NaNO$_3$) were obtained from Merck (Germany) and used as received. Hydrogen peroxide (5%, H$_2$O$_2$) was purchased from Kadus S.A. The Multiwalled carbon nanotubes (MWCNT) were obtained from Bayer Material Science AG (Germany) (Baytubes C150P). Based on the datasheet information provided by Bayer, they are characterized by a purity higher than 95 wt.%, number of walls between 2 and 15, an outer mean diameter of 13–16 nm, an inner mean diameter of 4 nm, length between 1 and >10 μm, and a bulk density around 150 kg/m^3.

2.2. Preparation TrGO

TrGO was prepared in a two-step oxidation/thermal reduction process using G as raw material. The graphite oxidation process of Hummers and Offeman was employed [14]. The first step is an oxidation of G with KMnO$_4$ and NaNO$_3$ in concentrated sulfuric acid. This oxidation was carried out using 250 ml of concentrated sulfuric acid as dispersion medium per 10 g of G. To the stirred dispersion, 5 g of NaNO$_3$ were added and after 30 min of stirring it was cooled down to $\sim$0 °C using an ice water bath. Then 30 g of KMnO$_4$ were added during 4 h. When the addition was completed, the resulting dispersion was stirred at room temperature for 1.5 h. The reaction was quenched by pouring the dispersion into 0.5 L of ice water and adding 450 mL of H$_2$O$_2$ (5 wt.%) until the excess of KMnO$_4$ was reduced. The GO was filtered off and washed with aqueous HCl and subsequently washed with water. The purified brown GO was dried under vacuum to 110 °C for 10 h. In a second step, the dry GO was thermally reduced to afford TrGO in a nitrogen atmosphere by rapidly heating GO up to $\sim$600 °C during 40 s using a quartz reactor heated in a vertical tube furnace. TrGO was obtained as a black powder of very low bulk density. The thermal shock is the prime requirement to achieve exfoliation of graphene sheets.

2.3. Melt compounding

The composites were prepared by using a Brabender Plasticorder (Brabender, Germany) internal mixer at 190 °C and a speed of 110 rpm. Filler content ranges from 0 to 12.5 vol% for TrGO or CNT, and from 0 to 25 vol% for G. First, a half of polymer and an antioxidant were added to the mixer operated at 110 rpm. After 2 min approximately for melting the polymer, the filler was added during 3 min. Finally, the rest of polymer pellets was added and the speed of the mixer was held at 110 rpm for 10 min. Therefore, the total mixing time was around 15 min. For the hybrid materials, first the polymer was added to the mixer followed by the proper amount of TrGO (1 and 2 vol%) as above explained and afterwards, the desired amount of the CNT (from 0 to 2 vol%). In this case, the same process conditions of the binary mixtures were used and the total time for the mixing was also around 15 min.

2.4. Characterizations

X-ray diffraction (XRD) analysis was performed on a Siemens D-5000 diffractometer with scintillation detector diffraction system and Bragg–Brentano geometry operating with a Cu Kα$_1$ radiation

source filtered with a graphite monochromator (λ = 1.5406 Å) at 40 kV and 30 mA in the 2θ range of 2–80° at the scan rate of 0.02°/s. The morphology of nanocomposites was analyzed using a scanning electron microscope (SEM, FEI Quanta 250). The morphology and microstructure of the nanocomposites were determined by transmission electron microscopy (TEM) in a Tecnai F20 FEG-S/TEM operated at 120 kV, equipped with an Energy Dispersive X-ray analysis system (EDS). Ultrathin sections of about 70 nm were obtained by cutting the samples with a Sorvall Porter-Blum MT2-B ultra-microtome equipped with a Diatome diamond knife. For the electric resistivity, different meghommeters (Megger BM11 with a highest voltage of 1200 V and AEMC 1060 with a highest voltage of 5000 V) were used depending on the conductivity of the samples. With this set-up, the standard two-points method was used. For each electrical value displayed in this contribution, at least four samples were prepared and four measurements for each one were carried out. In general, differences around one order of magnitude were detected in the non-percolated samples having low conductivity values ($\sim$10^{-9} S/cm). For percolated samples, otherwise the experimental error for conductivities was less than 50%. For annealing tests, the samples were putted in a hot-press at 190 °C for 30 min without pressure. For these tests, samples of 40 × 16 mm^2 and a thickness of 2 mm were used.

3. Results and discussion

3.1. Graphitic derivatives

In order to obtain TrGO, G was treated by an oxidation (to obtain GO) and afterward by a thermal reduction process. Fig. 1 (right side) shows that the GO (in a quartz reactor) significantly expands its volume, exfoliating the structure during rapid thermal treatment as reported previously [13,15,23]. This exfoliation process takes place when high pressure is generated by the gas (CO$_2$) released by the decomposition of the epoxy and hydroxyl sites of GO, producing gas pressures that exceed the Van der Waals forces between the graphene oxide sheets [13,18].

X-ray diffraction (XRD) allows us to detect the interlayer distance between graphene sheets and therefore confirm the

exfoliation state of TrGO. Fig. 2 shows that G possesses a (0 0 2) diffraction sharp peak at 2θ = 26.44°, corresponding to an interlayer spacing of 3.4 Å. After oxidation this peak is reduced significantly and changed to 2θ = 10.98°, indicating that the interlayer distance is increased up to 8.1 Å and disordered due to the intercalation by oxygen containing groups or absorbed moisture [20,22,23,42]. After rapid thermal reduction, the disappearance of the diffraction peak of GO indicates a successful exfoliation of the TrGO [20,23,43]. The changes in the interlayer distance, and therefore in the morphology, are confirmed by SEM images displayed in Fig. 3. Both the unmodified G and GO particles have very similar stacking layered structures. However, a relevant volume expansion due to thermal shock is observed in TrGO resulting in accordion like morphology and in wrinkled structure [15,16].

3.2. Electrical properties of the PP nanocomposites

Carbon-based fillers are excellent candidates for preparing electrically conductive PP composites [15,24–26,28]. The high electrical conductivity of these carbon-based fillers (either micro or nanofillers) changes the insulating nature of the polymeric matrix when a percolation threshold is reached. Fig. 4 shows the electrical conductivity plotted against the different carbon fillers at different concentrations, leading to the conclusion that the percolation threshold strongly depends on the structure of the carbon particles. Composites with the lowest percolation threshold and the highest electrical behavior are those having CNT as filler. At concentrations higher than 2 vol% of CNT, a drastic increase in the conductivity of the composite is displayed because of the presence of a continue conduction path of electrically conductive fillers (as shown in Fig. 5(a)) through which electrons travel along the polymer matrix [28]. G composite materials otherwise require high percentages of incorporation in order to achieve significant changes in electrical conductivity. The percolation threshold is reached at concentrations around 13 vol% of filler and the electrical conductivity of composite at 25 vol% of G was lower than the conductivity achieved for the composites of PP with only 5 vol% of CNT. Noteworthy, TrGO emerges as a promising alternative as the percolation process is similar to those achieved using CNT. In the case of TrGO the percolation threshold is at concentrations around 3 vol% of filler, which indicates that both CNT and TrGO nanofillers easily transferred electrical conductivity to PP [15]. Composites with concentrations of CNT and TrGO above 10 vol% do not show a significant increase in the electrical conductivity as the filler is increased because they are already percolated with a formed network. Generally, excess of conductive particles is not necessary if the conductive particle content is above the threshold region [44].
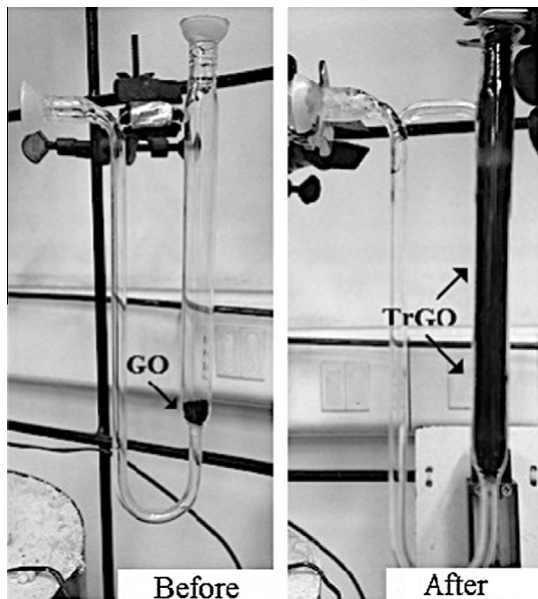

Fig. 1. Thermal reduction of GO forming TrGO. GO (in a quartz reactor) before (left) and after (right) flash heating at 600 °C.
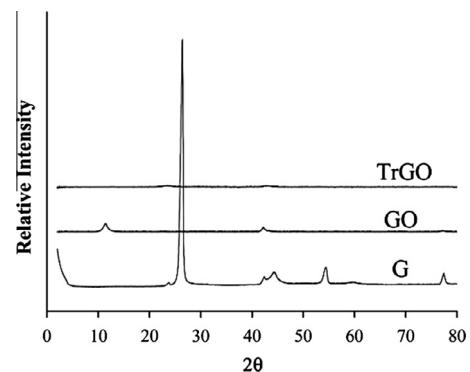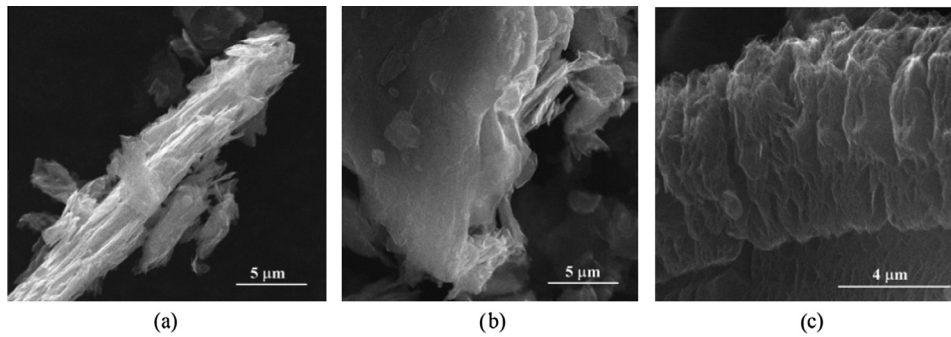

Fig. 2. XRD patterns of the G, GO and TrGO.

Fig. 3. SEM images of graphite and its modifications. (a) G; (b) GO; and (c) TrGO.
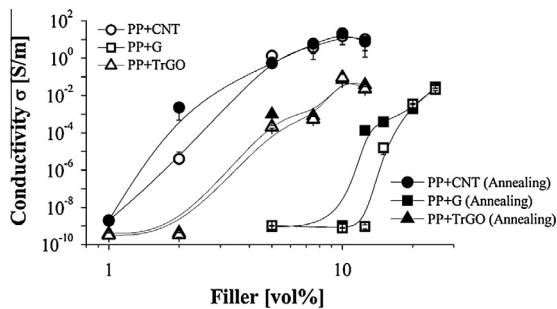

Fig. 4. Effect of carbon-based fillers and annealing (30 min at 190 °C) on the electrical conductivity of polypropylene composites.

Our results of conductivity for PP composites with CNT are very similar to those reported in other studies where the percolation threshold is below 3 vol% of CNT and the electrical conductivity is around 10^{-3} S/m [28,29,45–47]. For polypropylene/TrGO composites, our results of conductivity are better than those reported in other studies where the percolation threshold is below 5 vol% for TrGO [15,24,42]. Our composites prepared with concentrations higher than 7.5 vol% of TrGO exhibit electrical conductivity around 10^{-2} S/m or 10^{-1} S/m when the filler concentration is 10 vol%. Previous publication reaches electrical conductivities around 10^{-4} S/m for PP/TrGO nanocomposites although larger conductivities have also been reported such as 10^{-3} S/m in by Li et al. [46] and Milani et al. [26] with concentrations of about 7.5 vol% and 10 vol% of TrGO, respectively. For G based composites, the maximum electrical conductivity achieved has been $\sim 10^3$ S/m at 90 wt.% or concentrations higher at 60 vol% as reported by other studies [7,10,48]. Our composite with 25 vol% of G has an electrical conductivity of 10^{-2} S/m.

In the classic theory of percolation, the composite conductivity depends on the filler conductivity and its volume fraction, critical filler volume fraction at which percolation takes place, and the critical index of conductivity that relates with the dimensionality of the filler. This theory predicts a power-law correlation between these parameters by assuming physical contact between particles. However, polymer compounds based on carbon filler are more complex systems as the electrical conductivity cannot be fully predicted with this theory [49,50]. In polymer composites the conductive particles are separated by energy barriers (polymer molecules) and the tunnel effect becomes relevant modifying the percolation model. Based on this, the composite conductivity depends on the filler conductivity and its volume fraction, and a tunnel parameter that varies according to the dimensionality of the particle [49,51,52]. Under this model, the effect of the carbon-based filler on the percolation threshold is rather explained considering the average interparticle distance related with the probability of contact between conductive particles [51]. This interparticle distances depends on both the aspect ratio of the particles and its sizes. The introduction of these parameters can explain the different electrical behavior found in these polymer composites from a sharp increase in the conductivity reaching a plateau to a broad percolation curve with a growing conductivity [52]. PP/G composites display a broad percolation process as the conductivity increase with the filler content above the percolation threshold. This behavior can be due to a progressive reduction of the energy barrier between conductive particles as the concentration of filler increase similar to the reported in other polymer composites based on G [7,49,51]. Composites based on TrGO and CNT otherwise reached a plateau in the conductivity at high filler concentration showing a narrower percolation process. Under the tunnel model therefore, we can state that the in our PP composites the contact between nanoparticles is better than in microparticles.

The conductivity of the composites increases with increasing the aspect ratio of fillers [46], as occurs in our composites prepared with elongated particles as CNT and TrGO with narrower interparticle distances because of the entangled structures. However, a
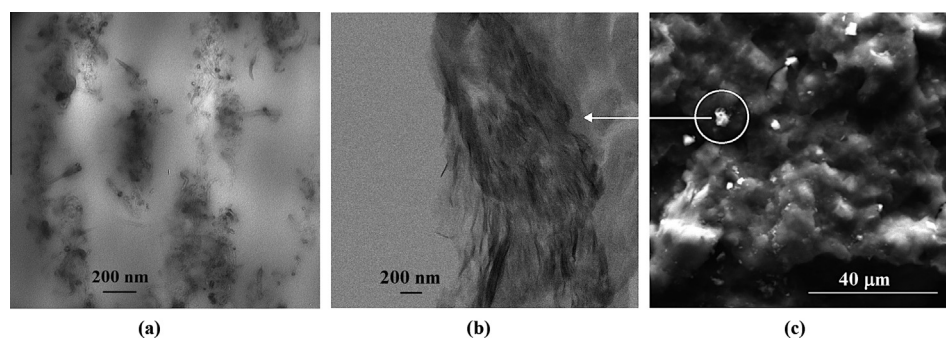

Fig. 5. Representative images of PP nanocomposites. (a) TEM of PP/CNT 5 vol%; (b) TEM y (c) SEM of PP/TrGO 5 vol%.
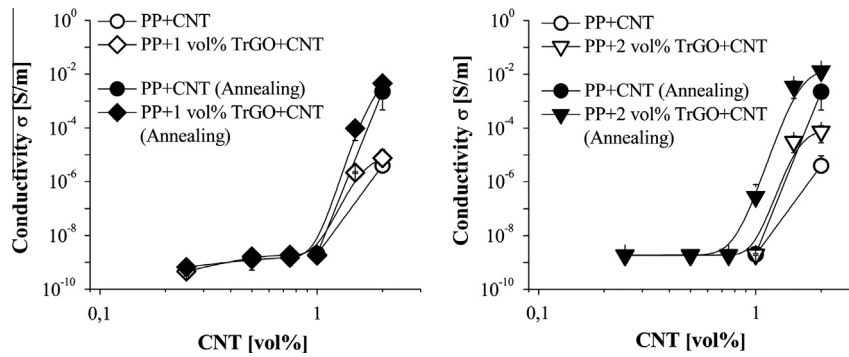
Fig. 6. Effect of CNT and annealing (30 min at 190 °C) on the electrical conductivity of PP/TrGO/CNT hybrid composites. Hybrid composites with 1 vol% of TrGO (left) and hybrid composites with 2 vol% of TrGO (right).

possible agglomeration of the TrGO in PP matrix compromised the effect of high aspect ratio. Thus, the percolation threshold of the PP/TrGO composites is slightly larger than the composites made with CNT. Fig. 5(b and c) shows the presence of agglomerates in PP composites with 5 vol% of TrGO.

3.3. Annealing effect on the electrical properties

As discussed earlier, polymer/CNT composites recover or increase the electrical conductivity by annealing [28,32]. Fig. 4 displays the effect of annealing at 190 °C for 30 min on the electrical behavior of the different composites. As expected, the percolation threshold is reduced by ~50% after annealing for PP/CNT composites [28]. Percolation threshold is also reduced by ~25% after annealing for PP/G composites. However, PP/TrGO composites do not change its percolation threshold. The PP/carbon-based fillers nanocomposites are typically non-Brownian systems on account of the high viscosity of the matrix and extended geometry of the nanoparticles [33]. However, although translational and rotational diffusions can be limited, the particles are able to reorient themselves because of the viscoelasticity of the polymer matrix [33] and the attraction potential (Lennard–Jones) between the carbon nanofillers [39]. The relaxation of the polymer chains at high annealing temperatures facilitate the reorganization of nanofillers dispersed, decreasing the mean distance between CNT [28,32,33] and increasing the conductivity. Therefore, a reduction in percolation threshold is obtained by annealing as has been observed in polymer/CNT composites [28,33]. Although this behavior is well known in polymer/CNT composites, the effect of annealing in PP/TrGO and PP/G composites has not been reported. One possible explanation to the absence of annealing effect in PP/TrGO samples may be related with the wrinkled structure [15–17,23] and more exposed surfaces (contact area) having layered structure hindering the nanofillers reorganization within the PP matrix. A similar effect was reported by Cipriano et al. where a highly rough structure of the fillers incorporated in a polymer matrix produces a substantial increase in resistance to the re-orientation during annealing [33]. PP/G composites otherwise show a small reduction of the percolation threshold after annealing because the micron-size of G particles hinders the rearrangement but should be considered that quasi-spherical geometry favors rearrangement of the particles generating less resistance to move within the viscoelastic matrix [53].

3.4. Hybrid nanocomposites

The effect of adding a second nanoparticle (CNT) in PP/TrGO composites was studied by evaluating the electrical behavior based on previous results showing an improvement in the electrical conductivity of hybrid nanocomposites [4,27–31]. Fig. 6 shows a set of hybrid nanocomposites (one matrix and two fillers) containing two concentrations of TrGO (1 and 2 vol%) and CNT (from 0 to 2 vol%) to make certain that the concentrations of TrGO and CNT lie below the percolation threshold of nanocomposites. The simultaneous presence of both carbon nanofillers is able to increase the conductivity of the composites compared to pure polypropylene and to reduce the percolation threshold even below the threshold of PP/CNT composites. In hybrid nanocomposite with 2 vol% of TrGO and concentrations higher than 1 vol% of CNT, the conductivity is higher than the hybrid nanocomposites with 1 vol% of TrGO at equal concentrations of CNT. In general, hybrid nanocomposites show an improvement in the electrical conductivity on account of the free volume theory [30], since the incorporation of a second nanoparticle reduces the space available between the nanofillers forming a percolated structure with ease, achieving electrical conductivity and lower percolation threshold. In our case the conductive nature of both fillers causes that CNT acts as bridges among TrGO nanoparticles, thus facilitating the formation of conductive paths in the PP/TrGO/CNT hybrid composites as reported by Liang et al. for PP/Ag/CNT hybrid composites [27]. Another possible explanation for the improvement in conductivity could be because of the better dispersion of the TrGO nanoparticles caused by CNT fillers [28]. Fig. 7 shows the improvement in the dispersion of TrGO, and the bridge effect (indicated by arrows) between conductive nanofillers.
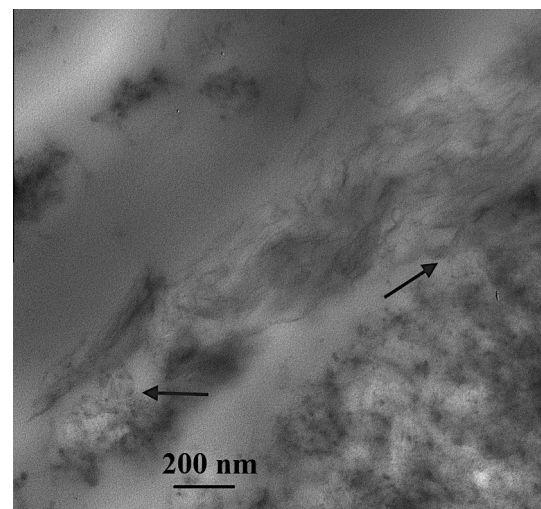

Fig. 7. TEM image of PP/TrGO/CNT hybrid composites with 2 vol% of TrGO and 2 vol% of CNT. The arrows indicate areas where the bridging effect between the conductive nanoparticles occurs.

The effect of annealing in PP/TrGO/CNT hybrid composites on its electrical behavior has not been reported. The electrical conductivity of our hybrid composites changes after annealing. The conductivity is higher in the annealed hybrid composites with 2 vol% of TrGO than with 1 vol% of TrGO. Moreover, the percolation threshold of annealed hybrid composites is lower than the annealed composites of PP/CNT. Hybrid composites with 1 vol% of TrGO and 1 vol% of CNT do not change its electrical conductivity and the insulation state is remained after annealing. However, the hybrid composites with 2 vol% of TrGO and 1 vol% of CNT showed that after annealing the conductivity can increase three orders of magnitude. Therefore, annealing is able to change the insulation nature of these nanocomposites saving the consumption of expensive CNT. Just as in binary mixtures, the relaxation of the polymer chains at high annealing temperatures facilitate the reorganization of nanofillers dispersed, promoting the formation of conduction paths and decrease the percolation threshold.

4. Conclusions

PP nanocomposites containing different carbon-based fillers were prepared by melt mixing method. The effect of the kind of particle added to the polypropylene matrix and annealing process on the electrical behavior of PP/TrGO materials was studied. The carbon-based filler aspect ratio has a very significant impact on the electrical conductivity behavior. Elongated nanoparticles as CNT and TrGO could form a percolated network in the matrix at a lower loading than G. The annealing effect on PP/CNT and PP/G composites shows relevant increases in the electrical conductivity. However, the PP/TrGO nanocomposites do not show any change in the conductivity by annealing, possibly related with the wrinkled structure that produces a substantial increase in resistance to the re-orientation during annealing. By adding a second carbon structure (CNT) to PP/TrGO composites, a relevant increase in the conductivity can be further observed. In particular, the addition of 1 vol% of CNT to PP composites with 2 vol% of TrGO can have electrical conductivities of $\sim 10^{-4}$ S/m, having as consequences a save of $\sim 50\%$ in the use of CNT.

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