

Effect of the Kind of Carbon-Based Nanofiller on the Electrical Conductivity and Rheological Melt Behavior of Polypropylene Composites

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ABSTRACT

Polypropylene (iPP) 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. The rheological results under oscillatory shear conditions at melt state showed that the liquid material experienced a solid-like transition at a threshold concentration that strongly depends on the filler used, for instance: ~5 vol% for CNT, ~4 vol% for TrGO, and ~20 vol% for graphite.

Keywords: polymer–matrix composites (PMCs), carbon-based fillers, hybrid composites, electrical properties, mechanical properties

1 INTRODUCTION

Recent interest in the use of nanoparticles for the manufacture of polymer composites has arisen due to the striking improvements in some properties achieved at lower loadings compared to micrometer fillers. In particular, derivatives of graphite (G), such as sheets of graphene and thermally reduced graphene oxide (TrGO), emerge to replace expensive carbon nanotubes (CNT). G-based particles are used today as a filler in various polymer matrices due to its amazing electrical transport properties and low cost, achieving a significant improvement in electrical properties at low percentages of incorporation (0.5-5.0 wt. %) [1]. Moreover, these structures are able to dramatically change the melt behavior of the polymer matrix, especially when a network is developed through the nanocomposite (percolation process). In the present study, the effect of type of carbon structure (TrGO, G, and CNT) on the electrical conductivity and the melt behavior of polymer nanocomposites prepared by melt-mixing was analyzed.

2 EXPERIMENTAL SECTION

2.1 Materials

A commercial grade isotactic polypropylene (iPP) 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), $M_w = 360$ kg/mol, $M_n = 70$ kg/mol, and melting point of 160 °C was used as matrix. Graphite (graphite fine powder extra pure) with a particle size <50 μm , sulfuric acid (98.08%, H_2SO_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_2O_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/m³.

2.2 Preparation TrGO

TrGO was prepared in a two-step oxidation/thermal reduction process using graphite as raw material. The graphite oxidation process of Hummers and Offeman was employed [1], with KMnO_4 and NaNO_3 as oxidants in concentrated sulfuric acid, as described in ref [2]. In a second step, the dry GO was thermally reduced to afford TrGO in a nitrogen atmosphere by rapidly heating GO up to ~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 too hard to determine, and therefore the density of graphite (2.2 g/cm³) for the preparation of composites was used. The thermal shock is the prime requirement to achieve exfoliation of graphene sheets.

2.3 Melt Compounding

The composites were prepared 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 graphite. First, a half of polymer (~13 g) and an antioxidant

were added to the mixer operated at 110 rpm. After 2 minutes by melting the polymer, the filler was added during 3 minutes. Finally, the rest of polymer pellets was added and the speed of the mixer was held at 110 rpm for 10 minutes. Therefore, the total mixing time was around 15 minutes. For the hybrid materials, first the polymer was added to the mixer followed by the proper amount of TrGO (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 mixing time was also around 15 minutes.

2.4 Characterizations

The morphology of nanocomposites was analyzed using a scanning electron microscope (SEM, FEI Quanta 250). For the electric resistivity, different megohmmeters (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 minutes without pressure. For these tests, samples of $40 \times 16 \text{ mm}^2$ and a thickness of 2 mm were used. Rheological measurements were run on a ARES-G2, TA-Instruments rheometer with 25mm parallel plate geometry doing isothermal frequency sweep at 190 °C with $\omega = 100\text{--}0.01 \text{ rad s}^{-1}$. All measurements were run in the linear regime, with deformation amplitudes $\gamma_0 = 3\%$, and under nitrogen atmosphere to avoid oxidative degradation.

3 RESULTS AND DISCUSSION

In order to obtain TrGO, G was treated by an oxidation (to obtain GO) and afterward by a thermal reduction process. The changes in the interlayer distance, and therefore in the morphology, are confirmed by SEM images displayed in Figure 1.

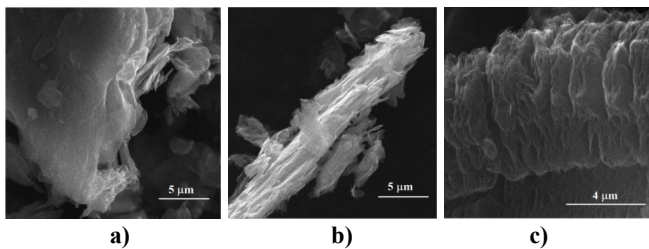


Figure 1: SEM images of graphite and its modifications. a) G; b) GO; and c) TrGO [2].

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 [3,4].

Our results show that the electrical conductivity and the melt behavior (complex viscosity) 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 (Figure 2 a)). Noteworthy, composites based on G-microparticles present a percolation process at concentrations one order of magnitude higher than those based on CNT. The conductivity of the composites increases with increasing the aspect ratio of fillers [5], as occurs in our composites prepared with elongated particles as CNT and TrGO with narrower interparticle distances because of the entangled structures. However, a possible agglomeration of the TrGO in iPP matrix compromised the effect of high aspect ratio. Thus, the percolation threshold of the iPP/TrGO composites is slightly larger than the composites made with CNT.

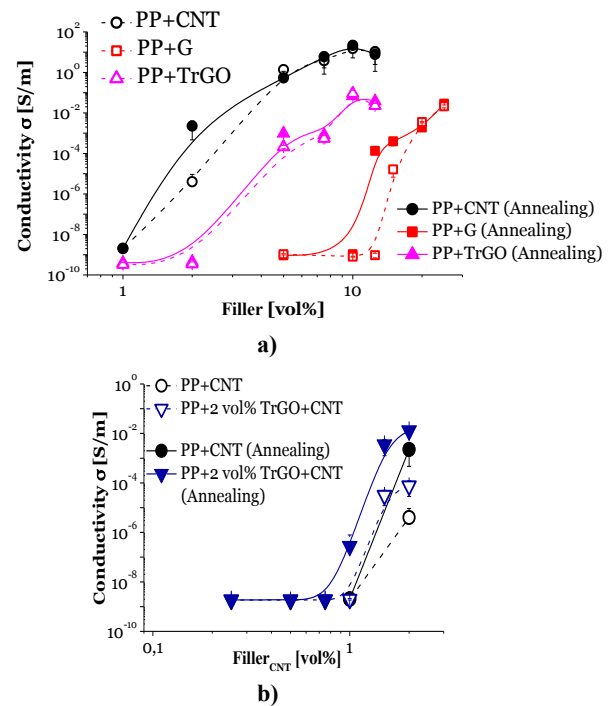


Figure 2: a) Effect of carbon-based fillers and annealing (30 minutes at 190 °C) on the electrical conductivity of a) iPP composites, and b) iPP/TrGO/CNT hybrid composites with 2 vol% of TrGO [2].

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 iPP/TrGO composites (Figure 2 b)) having as consequence a decrease in its percolation threshold [2].

While iPP melt and composites with low filler content behave as traditional viscous liquid material, composites with high content show an elastic solid-like behavior due to the rheological percolation process [3]. Viscosity (η) at low frequencies reveals information about the interactions between the particles, resulting in the formation of a rigid network above some value (concentration) threshold. Figure 3 shows the variation of the complex viscosity (measured at 0.01 rad/s and 190 °C), with increased concentration of carbon-based fillers. Clearly (Figure 3) iPP composites with CNT, the rheological percolation threshold is ~ 5 vol%, showing a marked increase in viscosity, whereas iPP composites with G the rheological threshold percolation is achieved only at high concentrations exceeding 20 vol%. The rheological results under oscillatory shear conditions at melt state showed that the liquid material experienced a solid-like transition at a concentration threshold that strongly depends on the filler used, for instance: ~ 5 vol% for CNT, ~ 4 vol% for TrGO, and ~ 20 vol% for graphite. Furthermore, compared with the iPP, composites having low concentrations (1 and 2 vol%) of TrGO have a lower viscosity. This decrease in viscosity is due to the interlayer sliding in the iPP/TrGO composites because of low surface friction (or delamination) of graphite [5]. However, when the 2 vol% of TrGO is exceeded, it can reach the rheological percolation threshold, increasing dramatically (by several orders of magnitude) the viscosity. Figure 3 show that the hybrid composites despite having 2 vol% of TrGO, adding ~ 1 vol% CNT is capable of modifying the viscoelastic behavior, counteracting the low viscosity of binary mixtures of iPP/TrGO at same concentrations, reaching percolation threshold along with a continuous increase in its viscosity.

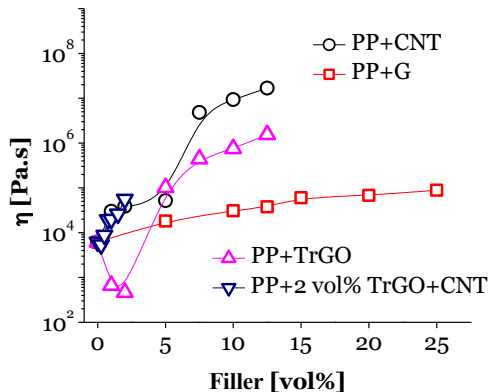


Figure 3: Complex viscosity of PP composites with carbon-based fillers measured at 0.01 rad/s and 190 °C.

In the present study, the iPP composites with carbon-based fillers, have slightly a rheological percolation greater than the electrical percolation, probably because of the state

of inhomogeneous dispersion where both macroscopic aggregate as the dispersed nanofillers contribute as has been reported in other studies [6].

4 CONCLUSIONS

iPP 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 iPP/carbon-based fillers composites was studied. The carbon-based filler aspect ratio has a very significant impact on the electrical conductivity and rheological 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 iPP/CNT and iPP/G composites shows relevant increases in the electrical conductivity. However, the iPP/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 iPP/TrGO composites, a relevant increase in the conductivity can be further observed. In particular, the addition of 1 vol% of CNT to iPP 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.

The viscoelastic behavior of polymeric composites strongly depends on the filler used. The viscosity of iPP/TrGO at low filler concentration was lower than neat iPP in the whole frequency range studied, due to the iPP/TrGO interlayer slipperiness caused by the low surface friction of graphite. By adding a second carbon structure (CNT) to iPP/TrGO composites, a relevant increase in the rheological behavior can be further observed.

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