Nucleation activity of polyaniline coated short glass fiber towards isotactic polypropylene

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Polyaniline (PAn) is an intrinsically conductive polymer increasingly being used in new thermoplastic-based composites for applications in electrostatic discharge or electromagnetic shielding [1, 2]. However, blends of PAn with thermoplastics usually led to a decrease of mechanical properties of the resulting composites. To overcome this problem, PAn-coated fibers have been developed as an electrically conducting reinforcement. These types of materials were designed to combine the electrical properties of PAn with the strengthening effect of high modulus fibers. Short glass fiber (SGF) is a highly used reinforcement in thermoplastics, thus PAn-coated SGF [3] has become one of the most promising electrically conductive reinforcement, because of its inexpensive synthetic route, good mechanical properties, and relatively high electrical conductivity. Although some studies have addressed the mechanical and electrical properties of PAn blends with thermoplastics [4] and thermosets [5], less effort has been put into studying the influence of this conductive polymer on the thermoplastics thermal behavior. Besides the technological relevance of this issue, the factors that lead to nucleation and transcrystallization in reinforced thermoplastics are not completely understood and may be useful to predict the mechanical performance of these composites. As part of a broader study, we have investigated the effect of the PAn-coated SGF on the crystallization behavior of isotactic polypropylene (iPP).

Accordingly, PAn-coated SGF was prepared using the method reported by Li and Ruckenstein [3]. SGF of deep green color with a coating degree (as examined by optical microscopy) close to 100% was obtained. The PAn-coated SGF was treated with an alkaline solution for 48 hr and thoroughly washed to remove the chlorine doping agent. The resulting dark blue fiber was redoped using a 4.0% wt *p*-toluensulfonic acid solution which, unlike chlorine, is a thermally stable doping agent for PAn up to 200 °C [6]. Excess *p*-toluensulfonic acid solution was exhaustively removed from the fiber before drying. The resulting fiber had a bulk electrical conductivity of 5×10^{-4} S/cm, high enough so the SEM image could be taken without using a conductive coating (Fig. 1). The morphology of the PAn-coating on the fiber consists of a smooth thin film with irregular particles attached to the surface. While the smooth film is expected to be chemically grafted to the glass surface [3], the particles are most likely polymerized in the reaction media and finally deposited on the PAn film, in agreement to the mechanism reported by Sapurina *et al.* [7]. PAn-coated SGF was thermally blended with isotactic polypropylene homopolymer (*Valtec HP423M*, MFI 3.8, density 0.9 g/cm^3) in a batch mixer (*Brabender Plasticorder PL2000*) at different concentrations (60 rpm for 12 min at 200 °C). The resulting composites were compression molded into flat plaques of 2.6 mm thickness at 200 °C under 2.45 MPa for 10 min.

Dynamic scanning calorimetry (DSC) measurements were performed in a *TA Instruments 2920* equipment using a heating/cooling rate of 10 °C/min. A first scanning was done from ambient temperature to 200 °C and the samples were held 5 min in molten state to erase previous thermal history, then the samples were cooled to room temperature and heated again to 200 °C. A crystal heat of fusion of 209 J/g [8] was employed in the calculation of the crystalline fraction of iPP. The crystallization temperatures T_c for the composites are shown in the Table I. T_c of pure iPP is of 112.2 °C, and after the addition of 10% weight of PAn-coated SGF increased to 122.4 °C indicating that the surface modified fiber acts as nucleating agent. A much lower impact on crystallization temperature was achieved with further addition of PAn-coated SGF, indicating that there was no additional crystallite nucleation, probably because there are enough fiber present at 10 wt% to provide sufficient surface area to nucleation in order that crystal growth became rate-limiting. On the other hand, a slight, yet significant increment in the crystalline fraction was achieved at higher weight fractions of the reinforcement, suggesting that fiber-induced crystallization propagates to the melt. Although nucleation is not necessarily accompanied by an increase in the crystalline degree of the matrix, similar results

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TABLE I Crystallization temperature (T_c), melting temperature during the second heating (T_m) and crystalline fraction (X_c) of the iPP/PAn-coated SGF composites

IPP/PAn-coated SGF	T_c (°C)	T_m (°C)	X_c
100/0	112.2	164.8	0.45
90/10	122.4	164.9	0.47
80/20	123.6	165.1	0.49
70/30	123.9	164.6	0.51

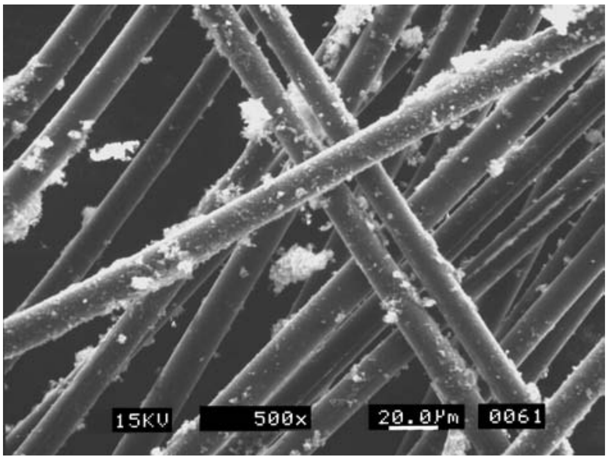

Figure 1 SEM image of the PAn-coated SGF.

have been obtained in iPP reinforced with SGF with different surface treatment [9]. Melting temperatures (T_m, Table I) scarcely changed (±0.5 °C) and just a slight sharpening in the melting peaks was appreciated after addition of the PAn-coated SGF, which can be attributed either to crystal perfection or narrowing of the crystal thickness distribution, both phenomena associated to the presence of a nucleating agent [10].

The nucleation activity of PAn-coated SGF towards iPP was confirmed by observation in a polarized light microscope (*Olympus BX90* equipped with a *TX90 metler-toledo* hot-stage thermal control). Model composites were prepared embedding a few PAn-coated SGF in melted iPP. The samples were rapidly heated to 200 °C, held 5 min and then cooled at a 5 °C/min rate. During cooling, uncoated SGF showed no nucleation activity (Fig. 2a), in agreement with results obtained by Bogoeva-Gaceva *et. al.* [11], in contrast, a transcrystalline layer was formed on the PAn-coated SGF, as seen in Fig. 2b. Neither fiber pulling nor stress was applied during these observations. Transcrystalline zones results from the high nucleating effect of the fiber surface for iPP crystallization [11]. Regarding to the effect of transcrystallization on the matrix−fiber adhesion, some studies have found improvement in interfacial adhesion [12, 13] while others have found no difference [14, 15], therefore, the effect may be dependent of the fiber−matrix pair, among other factors. However, nucleation activity of a fiber results in time reduction in injection cycles, which is of technological importance.

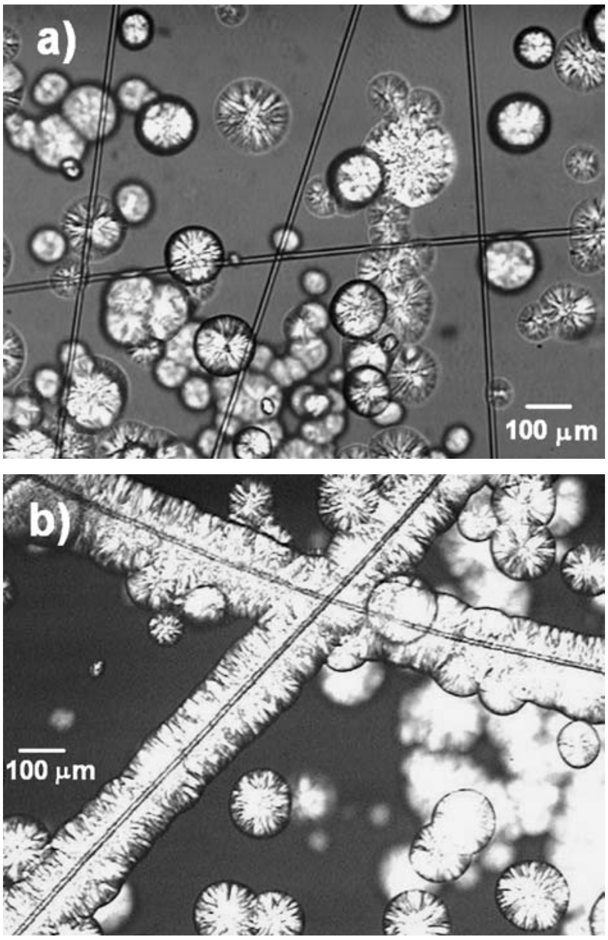

Figure 2 Polarized light microscopy images of non-isothermal iPP crystallization in quiescent melt; (a) uncoated short glass fiber, (b) growth of transcrystalline zone on the surface of PAn-coated SGF.

Since it has been reported that certain fibers, such as aramid fibers, induce polymorphs in iPP [16], a WAXD study (*Siemens D-5000 X*-Ray Diffractometer with a Cu-K$_\alpha$ radiation source, (intensity 25 mA, 35 kV acceleration voltage) was done to investigate the crystal structure of the transcrystalline regions. All the samples displayed the characteristic reflections (not shown) at 2θ angles of 14.2°, 17.0°, 18.7°, 21.3°, and 22.0°, corresponding to the lattice planes of the of the α-type (monoclinic) crystal [17]. These results confirm that both the transcrystalline regions and the matrix consist of α-type crystal of iPP. Although several types of fibers have been investigated as nucleating agents of iPP [18], the literature concerning nucleating activity of conductive polymers is brief. Genetti *et al.* [19] found that polypyrrole coated nickel flakes act as nucleating agent of low-density polyethylene, although in that case, the large difference in thermal conductivity between the filler and the matrix may also contribute to the nucleating activity of the filler [20]. Since model composites with both coated and uncoated SGF were prepared under similar conditions, the chemical surface composition seems to play a key role in the nucleating process. Besides the PAn, *p*-toluensulfonic acid, the doping agent ionically bonded to the PAn, account for the chemical composition and physical properties of the PAn, therefore different thermal behavior may be expected by changing the doping agent. Thus, the results shown here must be considered specific for *p*-toluensulfonic acid doped PAn.

In conclusion, we reported the nucleation activity of PAn-coated SGF towards iPP. Transcrystalline layers of the α-type (monoclinic) crystal of polypropylene were formed around the fiber during non-isothermal crystallization. A more detailed study on the morphology, mechanical properties and electrical conductivity of the composites is in progress.

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