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Preparation, processing and analysis of physical properties of Calcium Ferrite-CNTs/PET nano-composite

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Abstract

The present work is focused on the preparation of composites based on Poly(ethylene terephthalate) (PET) and novel nano-hybrid filler compo of Calcium Ferrite (CF)-Carbon Nanotubes (CNTs), obtained by direct growth of CNTs on CF based iron catalysts. The carbon content in the hybrid filler was 76 wt%. Composites loaded with 1.0, 1.5, 2.0, 3.0 wt% of filler were obtained by melt compounding and processed by thin-wall injection molding. Unfilled Poly(ethylene terephthalate) was processed using the same techniques. Structural characterization and physical properties (thermal, mechanical and electrical) were analyzed and correlated to the hybrid filler loading, and to the percentage of carbon nanotubes.

Keywords: A: hybrid; A: Physical Properties; D: Thermal Analysis; E: Chemical vapour deposition (CVD)

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most used polyester resin in conventional industry because of its low cost, good mechanical properties, high transparency, processability, and moderate recyclability. Thus, PET holds a potential for industrial application, including industrial bottles, films, fibers, and engineering plastics [1-2]. To this regard, considerable research work has been performed to develop commercial applications of this polyester or its composites, being such a high performance polymer. Although promising, however, insufficient mechanical properties and thermal stability of PET have hindered its practical application in a broad range of applications. Nanocomposite science and technology has been proved to be an efficient way to improve physical properties of polymers by using several nanofillers, such as carbon nanotubes and nanofibers [3-7], graphene [8-10], clay [11-14], silica [15-17], etc. From both an economic and industrial perspective, the major challenges for high performance polymer nanocomposites are to obtain the materials with low costs and to facilitate large scale-up for commercial applications. Furthermore, it

is well known that the morphological organization, and thus the physical properties of polymeric manufactures, are the result of the parameters imposed during the processing conditions [18-21]. The complex thermo-mechanical history experienced by a polymer during the processing can generate a large anisotropy of the final physical properties, in particular with semicrystalline polymers filled with particles of large aspect ratio. The increasing development of microsystem technologies has opened up new applications for polymer nanocomposites. Thin-wall injection molding is one of the most suitable process for producing small parts cheaply and with high precision. As for the conventional injection molding technique, the physical properties of manufactures obtained by thin wall injection molding are strongly influenced by the processing parameters. However, due to the characteristics of thin wall injection molding, such parameters and their effects are strictly correlated to the materials characteristics (i.e. polymer, type and/or amount of filler, degree of filler dispersion). In this paper we report the morphological organization and physical properties (thermal, mechanical, electrical) of nano-hybrid Calcium Ferrite-CNTs (CF-CNTs) composites prepared by microinjection molding using a twin screw extruder. CF-CNTs (CNT content 76 wt%) were prepared by direct growth of CNTs over CF based catalysts [22-23]. The effect of filler load, in the range 1.0 - 3.0 wt%, was investigated. The physical properties of PET composite were compared with those of un-filled PET submitted to the same thermo-mechanical history.

Experimental

1.1 Materials

PET, supplied by M&G Polimeri Italia S.p.A, is commercially named CLEARTUF P76 (intrinsic viscosity is 0.74 dL/g).

CF-CNTs nano-hybrid were prepared by catalytic chemical vapor deposition (CCVD) of isobutane with 15 wt% Fe supported on CF catalyst, accordingly to a procedure reported elsewhere [22]. Briefly, catalyst (0.5 g) was placed in a quartz boat inside the reactor, located in a horizontal electric furnace and fluxed with 120 sccm of H₂+He mixture (volume ratio 1:1). Temperature was then raised up to 700 °C then He was replaced with 60 sccm of i-C₄H₁₀. After 2 h the reaction was stopped and the product was cooled down to room temperature under H₂+He flow.

2.2 Composite preparation

The composites were obtained by melt compounding adopting a twin screw counter-rotating intermeshing mixer (HAAKE Minilab II) which allows for recycling in order to improve the dispersion and distribution of the filler within the polymer. The well dried polymer and a weighted amount of filler were starve-fed until a complete filling of the mixer was reached. The mixing conditions applied during the compounding were: temperature 280°C; screws rotation speed 200 rpm; recycling time 4 mins; fed mass 7 g. PET composites were prepared using different weight percent of CF-CNTs: 1.0, 1.5, 2.0 and 3.0 wt%. Also the pure PET was processed following the same procedure as the composites, and taken as reference. In the following samples will be coded as PET/CF-CNTsX where X is the hybrid filler amount (wt%/wt). Immediately after compounding, the composites were injection molded by adopting a HAAKE MiniJet in a rectangular mold 60 mm long, 10 mm wide and 500micron thick. The molding conditions are summarized in Table 1. It is worth noting that injection temperature and pressure of PET composites were lower than unfilled PET since they showed a higher fluidity. In particular, it was not possible to process pure PET in the conditions adopted for composites, since it did not completely fill the cavity. On the other hand, a considerable flash was obtained when composites were processed in the conditions adopted for PET. This behavior would suggest that at high shear rates, those of interest for injection molding, the presence of filler could decrease the viscosity of the polymer. This effect has been reported in the literature for CNTs/PET [6] and was attributed to the fact that CNTs might have property of shearing thinning effect similar to polymer because of their one-dimensional chain structure. Therefore, at high shear rates CNTs can orient and induce a rapid decrease of the viscosity of the composites.

In order to verify if physical (mechanical and electrical) properties of PET loaded with the nano-hybrid filler resulted better than the composites filled with separate component of the nano-hybrid, we prepared two composites with the same percentage of CNTs and Calcium Ferrite present in the 2 wt% of nanocomposite PET+Hybrid filler (i.e. 1.52 wt% of CNTs and 0.48 wt% of CF). The processing conditions were the same reported in Table 1. These composites will be named CF0.48 and CNT1.52. CNTs used in CNT1.52 sample were obtained after a purification treatment in concentrated HCl to eliminate calcium ferrite. C deposits were then washed in distilled water and finally dried at 110 °C. As demonstrated in Figure 1, XRD diffractogram of the product after purification showed the only peak of graphite ($2\theta = 26^\circ$).

1.2 Methods

X-ray Diffraction measurements (XRD) were performed with a Bruker diffractometer (equipped with a continuous scan attachment and a proportional counter) with Ni-filtered Cu K α radiation ($\lambda=1.54050 \text{ \AA}$).

Thermogravimetric Analysis (TGA) was carried out with a Mettler TC-10 thermobalance. Samples were heated from 25°C to 1000 °C at 10 °C/min heating rate under air flow. The mass loss was recorded as function of temperature.

High Resolution Transmission Electron Microscopy measurements (HRTEM) were carried out on a 200 kV JEOL JEM 2010 analytical electron microscope (LaB6 electron gun), equipped with EDX analyzer.

Differential Scanning Calorimetry (DSC) analysis was carried out on samples with a mass ranging between 10 and 12 mg. The tests were carried out by means of a DTA Mettler Toledo (DSC 30) under nitrogen atmosphere. Samples were heated from 25°C to 280°C at 10°C/min, cooled from 280°C to 25°C at 10°C/min and re-heated from 25°C to 280°C at 10°C/min.

The crystallization kinetics was assessed by measuring the heat flow during isothermal tests. In particular, the samples were heated to 280°C at a rate of 10°C/min, and then rapidly cooled, at 60°C/min, to the crystallization temperature at which they were kept for 120 minutes.

The parameters of crystallization kinetics were calculated following a previously reported procedure [22]. According to this method, the heat flow dQ/dt (in W/g, after baseline subtraction) during isothermal test was directly correlated to the evolution of crystallization kinetics:

$$\frac{dQ}{dt} = \Delta H_{\infty} \exp[-k(t-t_0)^n] nk [k(t-t_0)^{n-1}] \quad (1)$$

in which ΔH_{∞} is the total heat generated up to the end of the crystallization process, n and k are the Avrami index and the kinetic constant, respectively, and t_0 is the starting time of the isothermal test. The parameters ΔH_{∞} , n , k and t_0 were found by a best fitting analysis of the calorimetric curves by adopting eq. (1). Once n and k are known, the crystallization half time can be calculated as

$$t_{0.5} = (\ln 2)^{1/n} / k \quad (2)$$

Dynamic Mechanical properties were evaluated using a DMA TAQ800. Measurements were conducted at the constant frequency (1Hz) and amplitude (5 μ m). The temperature was varied between 30°C and 150°C at 3°C/min.

Electrical conductivity

In order to carry out electrical measurements, thin films were obtained from composites using a Carver Laboratory Press. Compounded composites were heated at 260°C and quickly quenched at 0°C in an ice-water bath, to ensure the amorphous organization of PET and composites' structure. The specimens were about 0.0100 cm thick (as determined by means of a micrometer), about 2 cm wide and 4 cm long. The electrical conductivity was measured in the voltage range -10÷10V and the data were averaged on three strips. The electrical conductivity of unfilled PET, as taken from literature [24], was considered as reference. A Keithley Model 8009 was used to test the electrical conductivity of the composites. The electrical conductivity, σ (S/cm), of all the samples was obtained by using the basic equation:

$$\sigma = \frac{L}{\tau W} \frac{1}{R} = \frac{L}{\tau W} \frac{I_{\text{measured}}}{V_{\text{applied}}} \quad (3)$$

where $R(\Omega)=V_{\text{applied}}/I_{\text{measured}}$, τ (m), W (m), and L (m) are the resistance, the thickness, the width and the length of the specimens respectively.

2. Results and discussions

2.1 CF-CNTs nano-hybrids morphology

Figure 2 (a) shows the SEM analysis of raw products. The copious formation of long filaments covering CF (rounded shape light spots) is clear from pictures. It is worthy noticing that upon CF elimination, by washing with diluted HCl, filaments appeared highly entangled then much less dispersed than in nano-hybrids (Figure 2 (b)). Higher magnification TEM images revealed that filaments are mainly constituted by multi walled CNTs (2 (c)), formed by ordered graphitic layers constituting the tube walls. Raman analyses of purified CNTs and the crystalline quality indicator ($IG'/ID=1.5$) fully confirm the goodness of CNT crystalline quality [22].

2.2 XRD analysis

Figure 3 reports the x-ray diffraction patterns of PET, CF-CNTs and composites at different nano-hybrid loading. The CF-CNT spectrum shows three main diffraction peaks raising from graphitic CNT structure at $2\theta=25.8^\circ$ (JCPDF 25-0284) and calcium ferrite $CaFe_4O_7$ (JCPDF 12-0145) at $2\theta=17.6^\circ$ and 34.2° . PET spectrum displays a broad signal typical of amorphous structures. XRD spectra of composites show the same features, regardless the filler load, namely the wide signal of amorphous PET and a weak signal at $2\theta = 25.8^\circ$ coming from CNT graphitic structure whose intensity increases with the filler content. $CaFe_4O_7$ peaks at $2\theta= 17.6^\circ$ were not visible because of

the low amount. The fact that all the materials are amorphous indicates that the different processing conditions adopted for pure PET and composites do not induce different morphological properties in the molded parts.

2.3 DSC analysis

2.4 Non isothermal analysis

The DSC thermograms collected during heating at 10°C/min (Figure 4 (a)) shows that the glass transition temperatures, T_g , of pure PET and the composites are not very different, in agreement with the literature [24]. A better determination of T_g was carried out in the following by DMA, which is a more sensitive technique for T_g determinations of filled polymers. The cold crystallization peak present for all the samples confirms the fact that all samples are essentially amorphous. The thermograms collected during cooling at 10°C/min (Figure 4 (b)) clearly show the nucleating effect of the filler: the crystallization peak moves from about 195°C for pure PET to about 220°C for the PET with 1wt% of CF-CNTs. The crystallization peak keeps increasing on increasing the amount of filler but the largest part of the effect seems to be reached already with 1%. During the following heating step, all the samples show nearly the same behavior (Figure 4 (c)). Calorimetric data, as recorded from the described three non-isothermal scans are reported in Table 2.

2.5 Isothermal analysis

The thermograms collected during isothermal tests, some of which are reported in Figure 5, show that the crystallization kinetics of pure PET and composite samples are on completely different scales. Indeed, at the temperatures at which the crystallization kinetics of PET was measurable by DSC (namely at temperatures close to 230°C) the composites crystallize so fast that most of crystallization takes place during cooling. Vice-versa, PET crystallization is not measurable at the temperatures at which the kinetics of composites can be assessed (namely in the range 240-245°C). The results of the kinetics parameters found after the regression procedure are reported in Table 3. It can be noticed that, while PET presents Avrami index in the range 2-3, the compounds present much lower Avrami indexes, thus indicating that the growth is far from being spherulitic. The crystallization half times are reported in Figure 6. It is evident that the composite PET/CF-CNTs3.0 presents crystallization half times more than one order of magnitude lower than those of pure PET. At the same temperature (244°C) the crystallization half times decrease on increasing the filler content.

2.6 Thermogravimetric (TGA) analysis

Figure 7 shows the TGA curves of pure PET and the nanocomposites with different CF-CNTs content, obtained in air flux. Curves show the degradation of PET and its composites in two steps. The first one is due to the decomposition of the starting materials, the second step is attributed to the consumption of char under the air atmosphere [25-26]. Typical thermo-oxidative degradation temperatures for 5%, 50% and 90% of weight loss under air flux are also summarized in Table 4. The enhancement in the thermal stability of PET/CF-CNTs nano-hybrids can be attributed either to a barrier effect of the nano-filler dispersed into the PET matrix, respect to the volatile decomposed products, as well as the air gases permeating through the nanocomposites, or to an effect of the trap action exercised by CNTs on the polymer peroxy radical that prevents their recombination [27-28].

2.7 Dynamic Mechanical Analysis

Figure 8 (a) reports the storage modulus for PET and composites, as function of temperature. The drop of modulus, in the range $70 \div 90^{\circ}\text{C}$ is evident of the glass transition temperature of all samples. The increasing of the modulus with increasing the temperature is due to thermal crystallization of PET occurred during the heating scan. In correspondence of the drop in modulus it is evident a strong dissipation band (Figure 8 (b)). The maximum of $\text{Tan } \delta$ allows to define the glass transition temperature of each sample. It can be observed that the intensity of $\text{Tan } \delta$ is lower in the composites. These lower values are indicative of two structural characteristics of the composites: the amount of the amorphous phase and its molecular mobility. Such behavior can be attributed either to a reduced molecular mobility of the amorphous phase, or to a segregation of an amorphous phase having reduced mobility. The effect on mechanical properties of the synergic hybrid filler was evaluated considering the composite PET/CF-CNTs2.0 and the correspondence “counterparts” (CF0.48 and CNT1.52). Figure 9 (a) and (b) reports the dynamic mechanical parameters of PET/CF-CNTs2.0, CF0.48 and CNT1.52, versus temperature. Figure 10 (a) reports the T_g ($^{\circ}\text{C}$) as a function of filler content. It is evident an increase of T_g , indicating a stiffening of the amorphous phase with the introduction of the filler. The T_g values of composites filled with 0.48 wt% of CF and 1.52% of CNTs are lower than the T_g of the sample PET/CF-CNTs2.0, indicating a synergistic effect of the hybrid filler in reducing the molecular mobility. Figure 10 (b) reports the modulus evaluated at 40°C as a function of filler content. Such parameter increases with filler content, reaching a value for 3 wt% of filler about 22% higher than that of pure PET. Also for this parameter the synergistic effect of the hybrid filler is evident. The moduli of the composites filled with the

“separated” components are lower than the modulus showed by the composites filled with 2 wt% of CF-CNT. Table 5 summarizes the experimental data reported in Figure 10.

2.8 Electrical properties

Electrical performances of the different PET/CF-CNT nano-hybrids, were measured in the voltage range $-10 \div 10$ V. From the I-V measurements, the contact geometry and the measured sample thickness, the electrical conductivity, σ (S/cm) was determined, using equation (3). Being the carbon nanotubes the conducting nanoparticles, the current flow and the percolation threshold is attributed to their loading and degree of dispersion. Figure 11 shows the electrical conductivity, σ (S/cm), as a function on CNTs (wt%) into the composites. PET matrix shows an insulating behaviour with an electrical conductivity around 1×10^{-17} S/cm [24]. Increasing the filler (CNTs) loading, the electrical conductivity increased reaching a plateau value for about 1.0 wt% of CNTs. At already at 1.0 wt% of nano-hybrid (i.e. 0.76 wt% of CNTs) the electrical conductivity resulted improved of about seven orders of magnitude. According to the Electronic Industry Association (EIA) standards, conductive materials have a surface resistivity of less than 10^5 Ohm/sq, dissipative materials have a surface resistivity from 10^5 Ohm/sq to 10^{12} Ohm/sq and insulative materials have a surface resistivity greater than 10^{12} Ohm/sq. For many articles in electrostatic discharge protected environments, such for instance computer housings or exterior automotive parts, the optimal surface resistivity is in the range of 10^6 - 10^9 Ohm/sq. For our samples, the measured conductivity is about the reciprocal of the resistivity in Ohm/sq and thus it can be stated that the addition of the fillers confers to PET electrostatic dissipative properties [29]. According to classical percolation theory the dependence of conductivity of composite materials on the conductive filler content can be described by the following equation [30]:

$$\sigma_{comp} \propto (x - x^*)^\tau \quad (4)$$

where τ is the critical exponent, x (wt%) is the weight fraction of filler, x^* (wt%) is the percolation threshold. This equation is valid when $x > x^*$ and $(x - x^*)$ is much smaller than 1. Usually, x^* and τ can be determined experimentally by fitting the experimental points from Figure 10. Using Equation (4) the best fitted values of x^* and τ can be obtained. In the inset of Figure 10 we also report the Pearson's correlation coefficient (which tends to 1 if the points are on a straight line) of the linear regression between $\ln(\sigma_{comp})$ and $\ln(x - x^*)$ as a function of different values of x^* . It can be noticed that the best correlation was obtained for values of x^* falling in a very narrow range to show that the parameters found by regression are indeed quite reliable. The percolation threshold resulted to

be equal to 0.65 wt%, the value τ was 0.62. The analysed systems has a complex morphology in which conductive nanotubes are growth on CF particles and separated by regions of the insulating PET matrix. Hence, electrical conductivity is limited by tunnelling between potential barriers within conductive regions [31-32]. As already demonstrated in the literature [33-34] using hybrid fillers based on inorganic clay as catalytic sites for the growth of CNTs, such an improvement of electrical performances with the low percolation threshold could be attributed to the synergic effect of the carbon nanotubes and calcium ferrite particles. The latter should prevent re-agglomeration during the processing (either blending or injection moulding). The physical network created by the well dispersed CNTs enhanced contact resistance on areas where nanotubes are in contact each other, justifying the higher measured electrical conductivity. We measured also the electrical conductivity of the sample filled only with 1.52 wt% of CNTs (as in the 2 wt% of CF-CNTs filled composite). The electrical conductivity resulted lower than the one exhibited by the composite with the same CNTs percentage growth over CF, namely about 1.5×10^{-12} S/cm. We recall that the role of carbon-ferrite is just catalytic for the growth of nanotubes. This result demonstrated the efficiency of the hybrid filler in dispersing the CNTs, limiting re-agglomeration during the processing.

3. Concluding remarks

Novel Poly(ethylene terephthalate) (PET) composites were obtained by melt compounding and microinjection processing using a nano-hybrid filler based on Carbon Ferrite (CF) used as catalyst for the growth of multi walled carbon nanotubes (CF-CNTs). The CNTs content into the filler was 76 wt%. The filler percentages adopted were 1.0, 1.5, 2.0, 3.0 wt%. It was found that the introduction of novel nanofillers into PET can strongly modify the processing parameters of such polymer, even at low loading, allowing the use of milder process conditions.

Structural characterization and analysis of physical (thermal, mechanical, electrical) properties were carried out and correlated to the hybrid filler amount, and carbon nanotubes loading.

- X-ray analysis on composites showed that with the used processing conditions PET showed a morphological organization with macromolecular chains in the amorphous state. This structure was retained in the composites, at any filler loading.
- The DSC analysis revealed that the presence of CNTs enhanced the crystallization kinetics of more than one order of magnitude. Furthermore, while PET presents Avrami index in the range 2-3, the compounds present much lower Avrami indexes, thus indicating that the growth is far from being spherulitic.

- The thermal stability of PET/CF-CNTs nano-hybrids, evaluated through TGA analysis, resulted enhanced. This was attributed either to the barrier effect of the filler dispersed into the PET matrix respect to the volatile low molecular weight products, or to the presence of CNTs, entrapping free radicals produced during the thermal scan, hindered the thermo-oxidation of PET.
- Dynamic mechanical analysis showed a stiffening of amorphous PET phase. This has been demonstrated either observing an improvement in the elastic modulus, or an increasing of glass transition temperature with filler loading. The synergistic effect of the hybrid filler was demonstrated
- Electrical conductivity was evaluated and correlated to CNTs content. Already at 0.76 wt% of CNTs the electrical conductivity increased of about seven orders of magnitude. With increasing CNTs loading the conductivity slightly incremented, reaching a plateau value for about 1.0 wt% of CNTs, where it resulted eight orders of magnitude higher than the one showed by the unfilled PET matrix. The percolation threshold was found to be 0.76 wt% of CNTs. Such result was attributed to the CF particles that favored the CNTs dispersion into the PET matrix, preventing any re-agglomeration of the nanotubes during the processing. The electrical conductivity of the composites filled with crude nanotubes was lower than the one filled with CF-CNTs at the same CNTs loading, demonstrating the efficiency of the hybrid filler in preventing nanotubes re-agglomeration during the processing. The obtained electrical conductivity enlightens a promising application in electrostatic dissipative field.

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