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Structure and Properties of Melt-Spun PET/MWCNT Nanocomposite Fibers

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Polyethylene terephthalate (PET) melt-spun fibers were modified with multiwall carbon nanotubes (MWCNT) to obtain conductive microfibers smaller than 90 μm in diameter. Physical properties such as crystallinity and orientation of as-spun fibers were studied by X-ray diffraction, Raman spectroscopy, and microscopy techniques at different draw ratios (DR) and MWCNT concentrations. Morphological and orientation analysis of MWCNT after melt-spinning process showed agglomerates formation and highly oriented CNTs. The study of the orientation of PET crystalline phase in drawn fibers proved that the addition of nanoparticles decreases the orientation of crystalline units inside the fibers. The orientation of MWCNT as well as that of PET chains was studied using Raman spectroscopy at different DR and a high degree of CNT orientation was observed under high DR conditions. Mechanical and electrical properties of as-spun fibers were also investigated. Our results showed that it was possible to achieve conductive fibers at a MWCNT concentration of 2% w/w, and more conductive fibers using higher DR were also obtained without increasing the MWCNT concentration. Mechanical properties results showed interestingly high value of maximum tensile strain at break (ϵ_{max}) of nanocomposite fibers, up to three times more than pure PET fibers. *POLYM. ENG. SCI.*, 50:1956–1968, 2010. © 2010 Society of Plastics Engineers

INTRODUCTION

Specific properties of polyethylene terephthalate (PET) such as high drawability have made this polymer one of the most important polymers in textile industry, as demonstrated by the large body of literature devoted to PET fiber production and properties [1–3]. Different techniques

have been used to modify PET fibers properties and most particularly its electrical conductivity, using carbon nanotubes (CNTs) [4–11]. The maximum orientation of CNTs in CNT nanocomposites is of considerable interest because orientation considerably enhances mechanical and electrical properties even for low concentration of CNTs. However, only very few address the issue of improving drawability and conductivity of PET fibers by using nanofillers such as nanoclay and CNTs, respectively [12–14].

Physical and rheological properties of PET/CNT nanocomposites have been studied by different groups [7, 15–20]. Anand et al. studied the crystalline structure of single wall carbon nanotube (SWCNT)/PET nanocomposites [15]. Their analysis proved the role of SWCNT as a nucleating agent during crystallization in addition to inducing oriented crystalline formation through preorientation of SWCNT in PET matrix [15]. Dispersion of CNT in nanocomposite was found as one of the main controlling parameters of their final properties [16]. Jin et al. could modify the dispersion through chemical surface modification of CNT such that they could considerably enhance the mechanical properties [16]. Hu et al. studied the rheological and electrical conductivity of PET/multiwall carbon nanotubes (MWCNT) systems [21]. They showed that dispersion and aspect ratio are the most important determining factors for rheological and electrical percolation. They obtained a low percolation threshold at 0.6 wt% of MWCNT for rheological properties and 0.9 wt% of MWCNT for electrical conductivity [21]. However, no detailed analysis of the structure and morphology of the nanocomposite fibers were performed in terms of dispersion, orientation, etc. of the matrix and nanoparticles.

Conductive polymer fibers from polypropylene/carbon nanofiber (CNF) nanocomposites were studied by Kumar et al. for the first time [22]. Their results showed an enhancement of the mechanical and electrical properties by adding 5% CNF [22]. In the earliest studies available on polyester fibers conductivity modification, Ma et al.

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TABLE 1. Average diameter (μm) of produced fibers at different processing conditions and MWCNT concentrations.

	Pure PET	1% MWCNT	3% MWCNT	4–7% MWCNT
DR = 112 (20% of DR_{max})	97 ± 14	97 ± 14	97 ± 14	Only nondrawn rod-like fibers 200–800
DR = 202 (40% of DR_{max})	66 ± 14	66 ± 14	66 ± 14	
DR = 291 (60% of DR_{max})	57 ± 7	57 ± 7	57 ± 7	
DR = 380 (80% of DR_{max})	Impossible to produce	50 ± 9	50 ± 9	
DR = 470 (DR_{max})	Impossible to produce	48 ± 9	48 ± 9	

surveyed polyester/CNF nanocomposite fibers produced by melt spinning [23]. They studied the processing, structure, and properties of the composite compared with pure PET [23]. They showed that tensile strength is considerably increased as compared with pure PET only if there is a good dispersion of the nanoparticles. In a recently published paper on PET/CNT, Li et al. investigated the microstructure of PET/CNT conductive nanocomposite fibers in more details [13]. They added 4 wt% of CNT to PET and they detected considerable changes in electrical properties above percolation (4 wt%). They also investigated other properties of PET/CNT system such as viscosity, crystallinity, and CNT dispersion homogeneity along fiber axis using techniques such as scanning electron and optical microscopy [13].

In this work, we produce melt-spun PET/MWCNT nanocomposite fibers with a precise morphological characterization and control of processing conditions. We focus mainly on studying the effect of two important material and process parameters: MWCNT concentration and draw ratio (DR). The crystalline structure and the effect of MWCNT on final crystallinity are studied by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Orientation of crystalline phase and polymer chains is also studied in details using XRD, Fourier transform infrared (FTIR), and Raman spectroscopies. Morphological study and dispersion modification before and after fiber formation are investigated in details in this article. The orientation and morphology of CNTs are studied by high resolution scanning electron microscopy (HR-SEM) and transmission electron microscopy (TEM) in addition to Raman spectroscopy. Finally, electrical and mechanical properties of the nanocomposite fibers are measured and the role of MWCNT on the drawability of the nanocomposite fibers is evaluated. Therefore, the effect of CNTs dispersion and processing conditions on the mechanical and electrical properties of the fibers are assessed here.

EXPERIMENTS

Polymer Mixing and Melt-Spinning Process

The extrusion grade PET used in this work was a Sellar 7086 polymer obtained from DuPont Co. A commercial PET/CNT masterbatch (MB-6815-00), composed of PET

mixed with 15% multiwall carbon nanotube (MWCNT), was purchased from Hyperion Catalysis Co. We used a melt mixing method for masterbatch dilution and CNT dispersion. Mixing was conducted using a lab-scale twin-screw extruder (Leistritz Group Co.; with 1.78 mm diameter and length of 40D) at controlled temperature and speed. The appropriate amount of MWCNT masterbatch was first mixed with PET pellets and then fed into the extruder for CNT dispersion in PET matrix. We used this procedure to optimize CNT dispersion in the matrix and to obtain optimal dispersion at different CNT concentrations. The best condition for CNT dispersion were obtained at 200 rpm screw speed using a temperature profile along the extruder ranging from 300°C at the first zone after hopper to 270°C at the die end.

A capillary rheometer (Rosand) combined with a take-up device was used to produce single fibers under controlled pressure and temperature profiles. The fibers were produced using a barrel temperature of 270°C and ambient air cooling. Various DR were used. We used diluted PET/CNT compounds to obtain fibers at different CNT concentrations (containing up to 3 wt% MWCNT) and DR. Above 3 wt% of CNT, the brittle behavior of the nanocomposite decreased the drawability of the fibers. Therefore, only rods were extruded from the nanocomposites with more than 3% MWCNT. The dimensions of the fibers produced in this work at different processing conditions (different DR) and MWCNT concentrations are given in Table 1. The values of DRs are given in proportion to maximum DR ($\text{DR}_{\text{max}} = 470$) of the nanocomposite fibers (DR_{max} of the fibers with 1% or 3% MWCNT) through the text and in the figures.

Morphological Analysis and Dispersion Evaluation of CNTs

Two microscopy techniques were used to study and evaluate the distribution and dispersion condition of CNTs in PET matrix: Scanning electron microscopy (HR-SEM) and TEM. A HR-SEM (Hitachi S-4700) on microtomed platinum-coated samples was used to investigate the CNTs distribution in PET matrix. TEM (JEOL, JEM-2100 F) was the technique used after HR-SEM observations to study and optimize the CNTs dispersion in PET matrix. A similar characterization was conducted on the resulting fibers after the processing step.

Crystalline Characteristics (DSC and XRD)

Differential scanning calorimetry (DSC, Q1000; TA Instruments) and X-ray diffraction (XRD, Discover, D8, Bruker) were used to study the crystalline behavior of PET/CNT nanocomposites. The effect of CNT addition on crystalline structure and behavior of drawn fibers as compared with molded samples was first studied by DSC. The tests were performed in nonisothermal conditions using a heating/cooling/heating cycle with the rate of 10°C/min. XRD technique was used in addition to DSC to characterize the crystalline structure of the system and to evaluate the orientation in final melt-spun and drawn fibers. We used an X-Ray goniometer, which was accompanied with a Hi-STAR two-dimensional area detector. The generator voltage and current were 40 kV and 40 mA, respectively, and a copper Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) was selected by a graphite crystal monochromator. The fibers obtained were examined using a wide angle X-ray diffraction (WAXD) method and the orientation was determined using a pole-figure accessory. The orientation is reported in terms of the Herman orientation function and is given by [24]:

$$f = \frac{(3 \cos^2 \theta - 1)}{2} \quad (1)$$

where θ is the angle between the unit crystalline cell axes (a , b , and c) and the reference axis that is machine direction (MD). Details about the calculations have been given elsewhere [25].

Orientation Determination (Raman and FTIR Spectroscopy)

Raman and Fourier transform infrared (FTIR) spectroscopy techniques were used for CNT and PET orientation determination respectively. A Nicolet Magna 860 instrument from Thermo Electron Corp. (DTGS detector, resolution 4 cm⁻¹, accumulation of 128 scans) was used for all FTIR experiments. Raman spectra were recorded on a Renishaw spectrometer equipped with an inVia Raman microscope. The samples were tested using a NIR laser (785 nm) with a grating of 1200 g/mm in a regular mode and use of a 20 $\times$ microscope. Orientation of MWCNTs and PET chains was obtained through comparing the spectra in parallel and perpendicular directions to the laser beam for Raman and FTIR spectroscopy, respectively.

Electrical Conductivity

Electrical conductivity of three types of samples was measured using various conductivity measurement instruments and test fixtures. The electrical conductivity of single rods and fibers at different DR was measured and compared with the electrical conductivity of molded samples. Molded samples were shaped as a disk after com-

pounding and before fiber formation. Below percolation and for materials with low conductivity (insulators), a KEITLEY 6517, high resistance meter was used and in the conductive range and above electrical percolation a combined set-up of KEITHLEY 6620 as a current source and Agilent 34401 A (6 1/2 Digit Multimeter) as voltage source were used. We used a two-probe technique with various test fixtures, compatible with the three types of samples below the percolation threshold. Above percolation, the experiments were performed using a four-probe technique.

Mechanical Properties

The mechanical properties of samples produced at different processing conditions were obtained employing a micro tester 5548 (Instron). First, the mechanical properties of single rods were measured at different CNT concentrations to assess the effect of CNT addition on single rods. For rod-like fibers, the tensile test was performed using a 2 kN load cell and speed of 50 mm/min. The mechanical properties of single fibers up to 3% MWCNT were evaluated at various CNT concentrations and drawing conditions. For the fibers below 100 μm , we used the tensile test load cell of 5N and a speed of 50 mm/min.

RESULTS AND DISCUSSIONS

Morphological and Dispersion Analysis

A proper initial dispersion of CNTs in polymer matrix is an important parameter for controlling the electrical and mechanical properties of the fibers. In this work, a CNT masterbatch was diluted to reach the desirable final concentration in the nanocomposite. Screw rotation speed, temperature profile along screw, and volumetric flow rates (residence time) were changed during the experiments to identify the processing conditions for the optimal dispersion of the CNT. The results showed that the screw speed was the most important parameter influencing the state of dispersion of the nanoparticles. Figure 1 shows the resulting dispersion state of the CNT in the diluted masterbatch for: (a) a poorly dispersed sample produced at 150 rpm screw rotation speed and (b) a sample produced at a rotation speed of 200 rpm. When comparing these two samples at different magnifications leads to the conclusion that CNT (3 wt%) are reasonably well distributed in the PET matrix (Fig. 1b). Even though the crystalline structure of compression molded PET matrix (method used to prepare the initial samples for morphological studies and dispersion modification) is the main reason that prevents obtaining a perfect distribution of CNT, the nanocomposites obtained with our optimal processing conditions (Fig. 1b) exhibit a reasonably well-dispersed morphology.

A similar dispersion analysis but this time using TEM is reported in Fig. 2, again showing a poorly dispersed

FIG. 1. HR-SEM images of PET/3% MWCNT at different distribution condition. (a) Poor distribution and (b) good distribution; the best distribution condition obtained at 200 rpm twin-screw extruder.

sample (Fig. 2a) produced at 150 rpm, and an optimized sample mixed at 200 rpm (Fig. 2b). As it is shown in these images, in the optimized dispersion conditions (Fig. 2b), CNTs have been mostly individually dispersed in PET matrix with no agglomeration. Therefore, it is expected that interactions of CNTs with PET matrix will help to improve both mechanical properties and electrical conductivity.

The best dispersion conditions were chosen for CNT masterbatch dilution and PET/CNT composite fiber preparation at different concentrations. TEM images of drawn fibers at 20% of DR_{max} (112) and DR_{max} (470) along fiber axis, in addition to cross section of fiber at DR_{max} are shown at different magnifications in Figs. 3 and 4. A comparison of these figures suggest that more aggregations are observed by increasing DR to DR_{max} during fiber formation. In addition, the TEM results at DR_{max}

(Fig. 4) show agglomerates both along fiber axis and at fiber cross section.

In the case of the maximum DR, the fiber diameter is small ($\sim 50 \mu m$). Therefore, the nanotubes are brought closer to each other and they are subjected to a high deformation rate and confined in a small volume. This strongly oriented flow field favors the formation of clusters. Therefore, as it is shown (Figs. 3 and 4), more CNTs aggregates are observed because of less volume and shorter time available for CNTs to reorganize themselves under the high-elongation flow rate of fiber spinning at higher values of DR.

Crystalline Behavior

The effect of CNT on the crystalline structure of nanocomposite melt-spun fibers also determine, to a large

FIG. 2. TEM images of PET/3% MWCNT at different dispersion condition. (a) Poor dispersion, and (b) good dispersion; the best dispersion condition obtained at 200 rpm twin screw.

FIG. 3. TEM images of PET/3% MWCNT and CNT orientation at 20% of DR_{max} along fiber axis at two different magnifications.

extend, their properties of interest. The role of CNT addition on X-ray patterns of PET/MWCNT nanocomposite was studied in a first step, followed by thermal analysis using DSC method.

X-Ray Diffraction Characteristics

XRD analysis was performed on compounded nanocomposites, where all the samples were prepared under identical molding conditions. X-ray patterns of PET/MWCNT at different concentrations after compounding is compared to the trace of a pure PET in Fig. 5 [12]. Clearly, the presence of CNT enhances the crystallinity as expected if one acknowledge the nucleating effect of these nanoparticles. Moreover, a sharp peak around $2\theta = 26^\circ$ (d_{002}) is obtained when CNT is added, as compared with pure PET. The intensity of this peak increases con-

siderably with increasing CNT concentration, and more agglomerates are found. A similar behavior has been reported previously for polycarbonate and polyethylene carbon nanotube nanocomposites [26, 27]. This is indicated by the fact that the related XRD peak ($2\theta = 26^\circ$) is more enhanced at high CNT concentrations and agglomerations [27]. This peak is located at the same position as that for PET (100) reflection (Fig. 5). As pointed out previously, DSC results (not reported here) show that adding CNTs as a nucleating agent causes an increase in the PET matrix crystallinity. Both CNT aggregate formation and high-crystalline structure formation at 15 wt% CNT concentration could be the reason for the enhancement of sharpness observed in this peak.

XRD analysis of nanocomposite melt-spun fibers showed totally amorphous structure for nanocomposite fibers at different processing conditions with CNT content

FIG. 4. TEM images of PET/3% MWCNT and CNT orientation at DR_{max} along fiber axis and at fiber cross section at two different magnifications.

FIG. 5. X-ray diffraction pattern of PET/MWCNT nanocomposite of molded samples prepared at the same condition at different MWCNT concentrations: Pure PET, PET/3% MWCNT, and PET/15% MWCNT.

up to 3 wt%. We also prepared XRD samples of drawn melt-spun nanocomposite fibers annealed at 160°C for 24 h. Annealing was mainly used to study the effect of carbon nanotube on crystallinity and orientation. The XRD

patterns obtained from the melt-spun annealed fibers at different DR and CNT concentrations are shown in Fig. 6. It is possible to detect, from the WAXD patterns, the crystalline planes and their orientation in the melt-spun and annealed fibers [12]. Increasing the CNT concentration at different DR causes a decrease of orientation. We used the pole-figure accessory to analyze the results obtained from XRD on annealed samples (see Table 2). The details of calculations have been given elsewhere [24]. The a and b axes orientation functions $f_{a,MD}$ and $f_{b,MD}$ were obtained by the pole-figure analysis of the (100) plane ($2\theta = 17^\circ$), and (010) plane ($2\theta = 25^\circ$) respectively. $f_{c,MD}$ was obtained by using the following orthogonality equation [25]:

$$f_{a,MD} + f_{b,MD} + f_{c,MD} = 0 \quad (2)$$

These measurements and calculations were all performed in GADDS (GADDS stands for “General Area Detector Diffraction System”) (transmission) mode for both drawn and nondrawn fibers. The contribution of CNT peaks here is almost zero contrary to reflection mode of XRD used for molded samples, because the sig-

FIG. 6. XRD pattern of PET/MWCNT melt-spun annealed fiber CNT concentrations and DRs: (a) Pure PET, 20% DR_{max}, (b) PET/1% MWCNT, 20% DR_{max}, (c) PET/3% MWCNT, 20% DR_{max}, (d) pure PET, 60% DR_{max}, (e) PET/1% MWCNT, 60% DR_{max}, (f) PET/3% MWCNT, 60% DR_{max}, (g) PET/1% MWCNT, Max DR_{max}, and (h) PET/3% MWCNT, DR_{max}.

TABLE 2. Orientation function ($f_{c,MD}$) at different DR and CNT concentrations.

	20% DR _{max} (112)	60% DR _{max} (291)	DR _{max} (470)
Pure PET	0.14	0.12	Not possible to be produced
1 wt% CNT	-0.08	0.04	0
3 wt% CNT	-0.07	-0.03	-0.03

nals related to CNT are quite weak in GADDS mode considering the shorter exposure time. Therefore, the analyses are only made over the peaks under the effect of PET crystals and not CNT. It is shown that maximum orientation is obtained in the case of pure PET fibers at different DR. Addition of carbon nanotube decreases the orientation and causes an increased drawability of the fibers.

It is known that CNTs can act as a nucleating agent therefore accelerate the nucleation process [15]. However, nucleation and quiescent crystallization are not the only determining factor. The kinetics of crystallization especially at the high pace of a melt spinning process must also be considered. To investigate the effect of the crystallization rate, we looked at the XRD results of as-spun fibers at very low-DR and different MWCNT concentrations without the postannealing step (Fig. 7). As it is shown, at lower end of the DR range, the crystalline behavior is not in accordance with previous observations (Fig. 6). The addition of CNT at low DR (10% of DR_{max}) enhances the crystallinity and at 3% w/w, fibers with high crystalline structures are obtained. At low rate of solidification and fiber formation, the nucleation and quiescent crystallization (and not the crystal growth) are the determining steps of the overall kinetics, which explains why more crystalline structures are obtained by increasing the CNT concentration, due to the nucleating effect of the particles.

FIG. 7. WAXD patterns of fibers at 10% DR_{max} and different CNT concentrations.

DSC Results

The values of ΔH used in the different calculations needed for interpreting the DSC curves have been corrected for nanoparticles content by the following equation, to have the data purely related to the polymer weight:

$$\Delta H_{i,corrected} = \Delta H_{i,Experiment} / (1 - w_{CNT}) \quad (3)$$

Then, the degree of crystallinity was calculated by the equation [14]:

$$X_c = (\Delta H_f - \Delta H_{rc}) / \Delta H_f^0 \quad (4)$$

where ΔH_f is the enthalpy of fusion, ΔH_{rc} is the enthalpy of recrystallization occurring during heating cycle, and ΔH_f^0 is the enthalpy of fusion of perfectly crystalline structure of PET at equilibrium thermodynamic melt temperature E_m^0 and was taken as 140 J/g [28].

The results obtained from heating and cooling cycles of rod-like fibers at different carbon nanotube concentrations are summarized in Table 3. As expected, the addition of CNTs causes an increase in the crystallization temperature T_m because of the nucleation role of CNTs. In addition, the CNTs addition changes the cooling cycle and crystallization behavior of the system. The results show that the crystallization starts at a higher temperature in the samples containing CNTs as compared with pure PET rod-like fibers. Moreover, the overall crystallinity and peak of crystallinity are all higher in the samples containing CNTs.

Rate and kinetics of crystallization are important factors in final structure of PET and its CNT nanocomposites. The time required to reach 50% relative crystallinity ($t_{1/2}$) is usually reported to compare the rates of crystallization of different samples. It is calculated by using the following equation [14]:

$$X_r = \frac{\int_{T_0}^T qdT}{\int_{T_0}^{T_\infty} qdT} \quad (5)$$

where X_r is the relative crystallinity, q is the heat flow at temperature T , T_0 and T_∞ are the initiation and termination crystallization temperature, respectively. The time related to each temperature is obtained from the heating cycle.

TABLE 3. Thermal parameters of rod-like fibers at different CNT concentrations.

	T_m (°C)	ΔH_f	ΔH_{rc}	X_c (%)	T_c (°C)	T_0 (°C)	T_∞ (°C)	ΔH_c
Pure PET	252.7	38.3	26.3	8.6	206.9	218.3	177.5	41.0
3% CNT	252.6	40.7	5.2	25.4	222.3	243.9	181.3	43.5
5% CNT	252.7	42.7	2.0	29.1	225.4	248.3	186.9	45.9
7% CNT	252.3	44.5	0	31.8	227.2	247.6	191.5	46.0

FIG. 8. Relative crystallinity (%) as a function of time at different carbon nanotube loading during cooling cycle.

The crystallization curves as a function of time during the cooling cycle are reported in Fig. 8. As the results show, the samples containing CNTs have higher values of $t_{1/2}$ (half-time of crystallization) as compared with pure samples. Therefore, the overall crystallinity is more rate controlled and the final crystalline content is reduced followed by adding CNTs as reported previously [29].

The crystalline content of the as-spun fibers at different carbon nanotube concentrations and DRs up to 3 wt% MWCNT concentrations is given in Table 4. The crystalline content is reduced when CNT content is increased. This might be the most important reason for the increase in drawability of the fibers. Addition of CNTs increases the amorphous phase of the nanocomposite in as-spun fibers. Amorphous phase has the most important role in energy dissipation under tension. Addition of CNTs accelerates the initiation of crystallization; therefore, the system of nanocomposite fibers is expected to contain many crystals of small sizes that connect the amorphous regions next to each other. This causes the enhancement of mechanical properties and the drawability of nanocomposite fibers.

CNT and Molecular Orientation

Pure PET Fibers Orientation (FTIR and Raman Spectroscopy). Herman orientation equations were used for evaluating the orientation function. For an uniaxially oriented sample, the dichroic ratio D is defined as:

TABLE 4. Crystallinity (%) as a function of DR and MWCNT concentration.

	20% DR _{max} (112)	60% DR _{max} (291)	DR _{max} (470)
Pure PET	17.2	23.5	Not possible to be produced
1% CNT	16.2	15.8	15.4
3% CNT	16.3	15.4	14.7

$$D = \frac{A_{\parallel}}{A_{\perp}} \quad (6)$$

where A is the absorbance of a specific band parallel or perpendicular to the IR polarizer [30]. Then, the Herman orientation function is obtained according to [25]:

$$f = \frac{D - 1}{D + 2} \cdot \frac{2}{3 \cos^2 \alpha - 1} \quad (7)$$

where α is the angle between the dipole moment of a particular vibration and the chain axis. Based on the vibration frequency selected in the IR test, it is possible to use the Herman orientation function for estimating the orientation of the amorphous or crystalline phase. PET shows very characteristic absorption bands in the IR. The most important ones are: 973 cm⁻¹: CH₂ vibration of trans conformation with $\alpha = 32^\circ$; 1340 cm⁻¹: CH₂ wagging mode of glycol segment in trans conformation with $\alpha = 21^\circ$; 1370 cm⁻¹: the vibration related to gauche conformation; and 1020 cm⁻¹: absorption band attributed to in-plane vibration of C—H group of benzene with $\alpha = 20^\circ$ [30, 31].

We selected the 1020 cm⁻¹ band for our calculations because it is not related to either crystalline or amorphous structures [30], and thus, it provides an overall idea about the orientation. All the results were normalized by the intensity of the band located at 1410 cm⁻¹ [30] (it is not sensitive to anisotropy). The FTIR analysis results show almost the same trend as XRD orientation for crystalline phase orientation (Fig. 9). At DR_{max} and 3% MWCNT concentration, a reduction in the orientation function is clearly observed. The polymer chains can be trapped during crystal initiation occurring at high CNT concentrations. It is likely that at 3 wt% MWCNT, the chains are immobilized by small crystal nuclei and they cannot be stretched as freely as compared with 1% MWCNT condition.

FIG. 9. Herman orientation function obtained from FTIR analysis at different CNT concentrations and DRs: f_{1020} normalized related to $\lambda = 1410 \text{ cm}^{-1}$.

FIG. 10. Raman spectra of as-spun fibers of pure PET at different draw ratio: (a) Fibers parallel to polarized light and (b) fibers perpendicular to polarized light.

The Raman characteristics peaks of molded a PET sample were compared with those obtained from oriented fiber structures at different DR, both in parallel and perpendicular directions with respect to the axis of oriented fibers (Fig. 10). As the results show, the peaks parallel (Fig. 10a) to the laser beam are more intense than to the ones observed in the perpendicular (Fig. 10b) direction, which is indicative of orientation. The change in the intensity of other characteristic peaks are also significant. These peaks include: 1310 cm^{-1} related to C—C stretching of the ring in the backbone, 1610 cm^{-1} relative to the stretching of the $\text{C}_1\text{—C}_4$ and 1730 cm^{-1} related to stretching of C=O band [14, 32, 33]. All the characteristic peaks of orientation signals are observed here. The most important one is the peak at 998 cm^{-1} , which is related to existence of trans conformations in chain axis [33]. This peak is not observed in Raman spectra of molded samples; in addition, there is not such a peak in the Raman spectra of the fibers in perpendicular direction to the beam. This peak comes from the stretching of O—CH₂ and C—C of the trans conformation of ethylene glycol unit in PET backbone. Existence of this peak in

parallel direction shows the orientation of PET chains in crystalline cells or in amorphous region because they are indicative of trans conformation structures [14, 32, 33]. The results of FTIR spectra also prove both the existence of molecular orientation and change into trans conformation during the drawing process as confirmed the correlation with DR.

CNT Orientation Study (Raman Spectroscopy). The same conditions mentioned previously for Raman measurements on pure PET fibers were also used for the characterization of nanocomposite fibers with 1% (Fig. 11) and 3% MWCNT (Fig. 12) concentrations. The results are given both in parallel (a) and in perpendicular polarization direction (b). In all samples, the Raman spectra are compared with molded samples. Three different characteristic peaks related to CNTs can be easily observed in the Raman spectra. Two strong peaks are located at 1580 cm^{-1} (G) and 1350 cm^{-1} (D) [34–37]. A weak peak is also detected at around 2700 cm^{-1} (G'), which is not sensitive to orientation. G and D peaks are two important peaks related to MWCNT structure. The intensity of the peaks due to the presence of MWCNT in parallel direction is quite high and they could cover almost all the characteristic peaks of PET, especially in the samples containing 3% MWCNT. The intensity of D and G bands are dependant on the DR and the spectra obtained in the parallel direction are quite different from those in the perpendicular axis. This could indicate a high level of CNT orientation in the samples as also shown previously by the morphological study. For the case of fibers containing 3% MWCNT, the orientation is quite high at the maximum DR (Fig. 12a).

Another interesting point is the change in the orientation characteristic peaks of PET in PET/MWCNT nanocomposite fibers. At high DR for 1% MWCNT nanocomposite fibers, the peaks related to PET orientation appear in the parallel direction (Fig. 11a). This is clearly shown for the absorption band at 1730 cm^{-1} . However, no peak could be found at the position of the spectrum in 3% MWCNT nanocomposite fiber (Fig. 12a). This could be an evidence of the effect of CNT on orientation and crystallinity. As mentioned previously, the results from Raman spectroscopy prove that adding CNT to PET melt-spun fibers decreases the degree of both orientation and crystallinity. Similar results and behavior have been reported in a recent study on a PET/nanoclay system [14]. In our results, addition to the reduction in crystallinity and increased drawability by adding carbon nanotube, we also detected a reduction in PET chains orientation. Likewise, this has been previously observed in some fibers from polymer blends and PET/clay fibers [14, 38, 39]. When nanoparticles are added, modified flow conditions develop around the nanoparticles. Because it is possible to consider the melt-spinning system as an iso-strain system; the applied elongation field on the pure polymer phase is reduced by converting a fraction of the elonga-

FIG. 11. Raman spectra of as-spun of PET/1% MWCNT nanocomposite fibers at different draw ratio: (a) Fibers parallel to polarized light and (b) fibers perpendicular to polarized light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIG. 12. Raman spectra of as-spun PET/3% MWCNT nanocomposite fibers at different draw ratio: (a) Fibers parallel to polarized light and (b) fibers perpendicular to polarized light. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tional flow into a shear component at the nanoparticle/polymer interface [14, 38, 39]. This reduction in the strength of the elongational flow imposed on the polymer melt could explain the decrease of the overall degree of orientation as compared with pure PET fibers [14, 38, 39].

Electrical Conductivity Measurement

The conductivity of different types of samples was measured to study the effect of composition and processing on their final properties. At the beginning, compounded samples were molded into disk-like shapes and their conductivity was measured. The results obtained from their conductivity measurements are compared to those from rod-like fibers in Fig. 13. Both types of samples show percolation threshold at 2 wt% MWCNT con-

FIG. 13. Electrical conductivity as a function of MWCNT concentrations.

FIG. 14. Electrical conductivity of fibers at different draw ratios.

centration. As it can be observed, forming the compound to rod-like fibers causes an increase in conductivity compared with molded samples at the same MWCNT concentration. Rod-like fibers show higher conductivity especially above the percolation threshold and after the network formation (Fig. 13). Higher conductivity of rod-like fibers is the result of partial orientation of MWCNT along fiber axis. Moreover, rod-like fibers reach a plateau region almost at 3 wt% MWCNT concentration. High enough conductivity (0.01 S/cm) is likely obtained because of the good dispersion of CNTs within the PET matrix.

Moreover, we measured the conductivity of fibers of 1% MWCNT (below percolation) and 3% MWCNT (above percolation) in the same way as the other experiments. The conductivity of fibers obtained at different DR is compared with rod-like fibers and molded samples and is presented in Fig. 14. As expected, the conductivity of fibers increased with the DR. This effect is clearer in 1% MWCNT and below the percolation threshold. The conductivity of fibers at 20% of DR_{max} has increased about one order of magnitude compared with rod-like fibers at the same concentration (1%). At 3%, there is still a slight increase in the conductivity at higher DR; however, the effect is not as significant when compared with observations at 1% MWCNT concentration. At 3%, the nanocomposite is above percolation and the conductivity reaches a plateau toward its ultimate value; therefore, further increasing DR cannot affect considerably the final conductivity.

Mechanical Properties Characteristics

At first, mechanical properties of rod-like fibers at different MWCNT concentrations were measured. All the fibers were in the same range of diameters (200–400 μm). Addition of MWCNT decreased the strength, elongation at break, and it caused the development of a brittle behavior. The moduli of the fibers at different MWCNT concentrations are given in Table 5. As it is shown, the addition of MWCNT does not considerably affect the modulus considering experimental uncertainties. A slight increase is observed in the modulus below percolation, whereas above percolation, the modulus decreases. Aggregate formation above percolation and the difficulty of dispersing the MWCNT in a PET matrix reduces the sample homogeneity. Inhomogeneity could cause stress concentration and weakening of the nanocomposite. Moreover, rod-like fibers have enough time for the development of a crystalline structure during solidification. Therefore, the addition of MWCNT reduces the amorphous phase concentration. This might be another reason for the observed brittle behavior and the reduction in elongation at break, from 500% (pure PET) to about only 4% in composites (PET/7% MWCNT).

Mechanical properties of as-spun fibers at different MWCNT concentrations were studied for 1 wt% and 3 wt% MWCNT concentrations. The mechanical results obtained at different DRs are given in Fig. 15. As the results show, changing the MWCNT concentration and DR does not significantly affect the modulus (Fig. 15a) and strength (Fig. 15b) values. Addition of MWCNT up to 3 wt% slightly increases the modulus of the fibers obtained at different DR, which might be due to the role of MWCNT as a reinforcing particle in the melt-spun fibers. Mechanical test results show that adding MWCNT does not cause a weakening of the mechanical properties within the studied range of DR. All the fibers at different MWCNT concentrations and DR show a tough behavior and stress hardening was observed in all the samples during the mechanical testing experiments.

The results reported here are in complete agreement with those obtained during fiber spinning. Increasing the MWCNT concentration causes an increase in drawability. As the results show that the addition of MWCNT to 1% and 3% concentrations increased drawability up to three times compared with pure PET fibers, because the fibers containing MWCNT are less crystalline. In this way, the fibers produced are in the conductive range, whereas they have better mechanical properties and significant drawability which is of considerable practical interest.

TABLE 5. Tensile modulus of rod-like fibers as a function of CNT concentration.

	Pure PET	1% MWCNT	2% MWCNT	3% MWCNT	4% MWCNT	5% MWCNT	7% MWCNT
Modulus (MPa)	2327 $\pm$ 513	2150 $\pm$ 409	2607 $\pm$ 186	1859 $\pm$ 111	1982 $\pm$ 434	2008 $\pm$ 567	2084 $\pm$ 460

FIG. 15. Final mechanical properties of fibers at different draw ratios and MWCNT concentrations: (a) Modulus, (b) tensile strength, and (c) tensile elongation.

CONCLUSIONS

Various morphological and physical properties of PET melt-spun nanocomposite fibers at different MWCNT concentrations and DR were studied in this work. Microscopy observations and Raman spectroscopy measurements showed a high degree of MWCNT orientation after fiber spinning. Moreover, it was found that the addition of MWCNT decreases both the crystalline content and polymer chain orientation. DSC results showed that MWCNT caused increase the half-time of crystallization, which is the main reason for the reduction of crystalline phase formation during melt spinning upon increasing MWCNT concentration. Conductivity of single fibers showed that it was possible to reduce the percolation threshold by both dispersion modification and changes in the processing conditions. Mechanical test results proved the weakening of properties after percolation because of poor dispersion and stress concentration. However, addition of MWCNT could considerably increase the drawability of as-spun fibers and the elongation at break in mechanical test. This

was because of the role of MWCNT in the reduction of crystalline formation, which favors the dissipation of energy by the amorphous phase, whereas the adhesion and wetting of polymer chains to MWCNT nanoparticles is adequate due to a proper control of the factors affecting the dispersion of CNT in the PET matrix.

NOMENCLATURE

α	The angle between dipole moment of particular vibration and chain axis (FTIR)
ΔH	Enthalpy (DSC)
θ	The angle between the unit crystalline cell axes (XRD)
A	Absorbance (FTIR)
f	Herman orientation function (FTIR, XRD)
q	Heat flow (DSC)
T	Temperature
w	Weight fraction
X	Crystallinity fraction

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