The Role of $\alpha$, $\gamma$, and Metastable Polymorphs on Electrospun Polyamide 6/Functionalized Graphene Oxide

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Keywords: electrospinning, PA6, nitroxide functionalized graphene oxide, polymorphs, tensile stress.

Abstract. The present paper describes the addition of nitroxide-functionalized graphene oxide (GOFT) into polyamide 6 (PA6) micro- and nanofibers, which were obtained through electrospinning. SEM micrographs demonstrated the presence of fibers. Tensile testing presented an unexpected and non-obvious behavior, in which the Young’s modulus, tensile strength, and elongation simultaneously and remarkably increased compared to the pristine polymer nanofibers. GOFT induces the hydrogen bonding between the NH group from PA6 with the functional groups, thus promoting higher crystallinity of the polymer matrix. Nonetheless, deconvoluted DSC curves revealed the presence of two quasi-steady polymorphous ($\beta$ and $\delta$ phases) contributing to 46% of the total crystallinity. This evidence suggests that their presence and high-ratios are responsible for the unexpected and simultaneous enhancement of tensile properties.
Polyamide 6 (PA6 or Nylon 6) is a semicrystalline polyamide that can be processed into films, plastics and fibers,[1] it finds applications in the automotive, food packaging, sports, and textiles industries. Fibers of this polymer are used in parachutes,[2,3] automobiles and aircraft tire cords.[4,5] Holmes recognized in 1955 that Nylon 6 presented different crystal structures,[6] which are now identified as the α phase (thermodynamically preferred) and the γ phase. The α crystal is monoclinic and forms hydrogen bonds between antiparallel fully extended chains, while the γ crystal is also monoclinic but the hydrogen bonds are established between parallel pleated chains.[7,8] It is common to encounter both crystalline phases coexisting, but a phase can be favored under proper processing conditions. For example, the α crystal is obtained from solution crystallization or slow cooling from the melt, while the γ crystal is obtained with I2/KI treatment.[9,10] Interconversion of these phases is also possible under annealing or drawing conditions.[11–13] In addition to these phases, mesomorphic crystal forms (β or δ phases) have been observed experimentally and predicted by MSXX force field. Although there is disagreement in the literature as to the existence of one or several of these metastable phases, it is recognized that intermediate crystal structures that present intermediate conformational features between the α or γ crystals occur.[14–16] Identification of these intermediate polymorphs is elusive by X-ray diffraction patterns and FTIR spectra because these are similar to the more stable α and γ phases, and their interconversion into the latter structures further complicates their analysis.

Electrospinning is the most studied fiber forming technique that produces micro- and nanofibers. It consists of placing a polymer solution in a syringe equipped with a needle or capillary tube attached to a high-power source, which generates a high voltage difference between the needle and a grounded target, usually in the range 5-30 kV. As the polymer solution is ejected from the syringe, the electrical charges on the polymer and the solvent induce evaporation of the latter, simultaneously promoting a charge repulsion that elongates and creates a thin polymer fiber. Finally, the dry polymer fiber travels to deposit on a grounded target.[17,18]
Nanotechnology and the acknowledgement that smaller fiber diameters offer high aspect ratio and enhanced mechanical properties\(^{[19]}\) is the driving force for the interest in this technique.\(^{[20]}\) On the other hand, graphene is a single layer of sp\(^2\) hybridized carbon atoms forming a two-dimensional hexagonal lattice. Its outstanding properties has attracted enormous attention for scientific studies and technological developments.\(^{[21]-[23]}\) However, one of the biggest challenges is its tendency to aggregate, so its properties cannot be fully displayed unless it is exfoliated and dispersed. Graphene, graphene oxide (GO) and derivatives can be exfoliated and dispersed in solvents\(^{[24]}\) and polymer matrices\(^{[25]}\) by physical and chemical methods,\(^{[26]}\) and can be produced from graphite at larger amounts, presenting an area of opportunity to develop a new generation of materials.\(^{[27]}\) The pioneering work of Avila-Vega et al.,\(^{[28]}\) disclosed the functionalization of GO with bulky nitroxide moieties (GOFT), which serve to exfoliate and slow down re-aggregation of the nanomaterial in certain solvents. GOFT was then added to PA6 solutions and electrospun, resulting in composite submicron fibers with enhancements in the Young’s modulus (73%), tensile strength (93%) and tensile strain (78%).\(^{[28]}\) This paper correlates the significant enhancement on tensile testing with polymer molecular changes, and crystalline phases to understand the origin of this effect.

The chemical structure of GO, contains oxygen centered functional groups consisting of hydroxyl, carboxylic acids, ketone and epoxy along their surface and edges,\(^{[29]}\) and their distribution strongly depends on the oxidation pathway used.\(^{[30]}\) A proposed functionalization mechanism of GO with oxoammonium salts (Br-TEMPO) to produce nitroxide-functionalized graphene oxide (GOFT) has been reported by our work group before (Figure S1, Supporting Information).\(^{[28,31]}\)

**Figure 1a** shows a high-resolution transmission electron microscopy (HRTEM) micrograph of natural graphite wherein hundreds of layers were observed. **Figure 1b** demonstrates GO layers exhibiting many wrinkles on their surface owing to the presence of several oxygen-centered functional groups, which promotes their exfoliation. **Figure 1c** illustrates a single-layer of
GOFT. Subsequently, GOFT was added (0.1, 0.5 and 1.0 wt. % with respect to the polymer) to a solution of PA6/HFIP to obtain electrospun composite mats. Figure 1d shows a HRTEM micrograph of a PA6/GOFT 0.1% electrospun fiber, demonstrating a GOFT layer embedded within the polymer matrix. Figure 1e shows the scanning electron microscopy (SEM) micrograph of electrospun PA6, which demonstrate mostly defect free fibers with a diameter of 1.80 ± 0.91 µm. Figure 1f-h present SEM micrographs of PA6 fibers containing: 0.1 wt.% of GOFT with an average fiber diameter of 0.83 ± 0.36 µm; 0.5 wt.% of GOFT with an average fiber diameter of 0.97 ± 0.48 µm, and 1.0 wt.% GOFT with an average fiber diameter of 1.19 ± 0.98 µm, respectively. Micrographs of these fibers (not shown) demonstrate regions of dense defect free non-woven micro- and nanofibers, but there are also regions (Figure 1f-h) where it is evident that these fibers contain beads defects and even ruptured areas. Furthermore, the histograms for these PA6/GOFT composite (Figure S2a-c, Supporting Information) demonstrate the variability of the fiber diameters when the functional-nanomaterial is added. PA6 fibers had a median of 1.69 µm, while at 0.1 wt.% fibers presented a 0.78 µm median, but more variations in fiber diameters occurred at 0.5 wt.% with a 0.85 µm median, and ultimately many small diameter fibers are produced along with a few big fiber diameters when 1.0 wt.% additive is added, resulting in a 0.83 µm median. The observation of these defects suggests that the capacity to form homogeneous fibers by the polymer solutions has been being modified. There are reports on the influence of salts and carbon nanotubes\cite{32-34} addition to polymer solutions, in which it has been found that an increase in the electrical conductivity due to the salts or the nanomaterials has promoted thinner and more uniform fibers. In this study, addition of GOFT promoted the formation of electrospun fibers thinner than the pristine polymer with enhanced tensile properties, but fiber quality was reduced by formation of beads, broken fibers, and as the additive concentration increased, larger variability and average fiber diameters. Therefore, optimization of the processing conditions and further improvements in tensile properties should be possible. The Young’s modulus (Figure 2) of PA6 micro- and nanofibers
increased significantly (73%) upon addition of GOFT at 0.1 wt.%. Addition of GOFT at 0.5 wt.% also caused a significant increase (67%), while incorporation of 1.0 wt.% of GOFT promoted only a modest modification (7%) of this property. Tensile stress (Figure 2) was similarly improved on the composite fibers when compared to PA6 fibers, and presented the same behavior observed for the Young’s modulus with an increase of 93% (0.1 wt.% GOFT), 66% (0.5 wt.% GOFT), and 47% (1.0 wt.% GOFT). Tensile strain (Figure 2) in these fibers was also augmented at all concentrations of GOFT’s, showing an increase of 78% at 0.1 wt.%, 67% at 0.5 wt.%, and 19% at 1.0 wt.% GOFT. Therefore, it is observed that an enhancement on Young’s modulus, tensile stress and tensile strain is attained (Table S1, Supporting Information), and although improvements on the mechanical properties are obtained at all GOFT concentrations, their effect becomes less pronounced as their concentration increases. The fact that the fibers obtained presented beads and broken up mats upon addition of GOFT, and that these defects increased with higher concentration of GOFT (see Figures 1 e-h), explains that the highest possible mechanical properties were presented at 0.1 wt.%. Nonetheless, the mechanical properties of the composite fibers containing 0.1 and 0.5 wt.% of GOFT are similar if the standard deviations of the measurements are considered (see Table S1, Supporting Information); so additional improvements in the tensile properties should be evaluated by optimizing the electrospinning process and minimizing fibers defects. Regardless, the resulting composite fibers are stiffer, withstand higher loads to break, and deform more than pristine PA6 fibers. Further, the addition of GO and a silica derivative to PA6 through other dispersion techniques and melt mixing processing has also resulted in enhancements of elastic modulus, tensile strength, stiffening, strengthening, and toughening from 100 % to 210 %, reporting the authors that these modifications are due to high interfacial adhesions and reactions with the functional groups of the polymer.[35–38]

In order to understand the effect that GOFT is imparting on the polymer matrix at the molecular level, FTIR spectra of the pristine PA6 micro- and nanofibers and their corresponding
composite fibers PA6/GOFTs were obtained and are presented in Figure 3. It can be observed that the NH stretching region for PA6 is composed of a typical broad and intense peak for a polyamide, with a maximum at 3439 cm$^{-1}$ and a subtle shoulder at 3303 cm$^{-1}$. However, this band splits into two well defined peaks in the composite fibers, indicating GOFT interaction with the hydrogen of the amide bond. Hence, deconvolution of the area was performed with the objective to identify and quantify the components of this band (Figure S3, Supporting Information), demonstrating that it is formed by two peaks, which are assigned to free NH (3449 cm$^{-1}$) and hydrogen bonded NH (3252 cm$^{-1}$) stretching vibrations.$^{[39,40]}$ The small peak at 3088 cm$^{-1}$ is attributed to asymmetric and symmetric stretching of CH$_2$ in the polymer and is not considered in this analysis. This result indicates that most of the pristine PA6 fibers do not present intra- or intermolecular hydrogen bonding between the NH bonds and C=O bonds. Figure S3 shows the deconvolution of the 0.1% GOFT in PA6 fibers, and it can be observed that the bonded NH peak increases significantly when compared to pristine PA6. Further addition of GOFT to 0.5 wt.% resulted in an additional increase of the hydrogen bonded peak, and as the concentration of the nanoparticles was increased to 1.0 wt.%, the hydrogen bonded peak decreased slightly, but was still higher than for PA6 nanofibers. The quantitative contribution of the individual peaks to the broad NH band is presented (Table S2, Supporting Information) suggesting that the maximum modification of the PA6 fibers hydrogen bonding, which was promoted by the addition of GOFT, occurred at 0.5 wt.%. The spectra also showed that the C=O band is affected. The amide I band maximum (1637 cm$^{-1}$) shifts slightly to higher wavenumbers (Figure 3) when GOFT is added to the system, and the relative intensity of this C=O bond in the composite fibers increased, evidencing that this bond is also interacting with the nanosheets, increasing its dipole moment and becoming stiffer. It is also observed that the amide II band (1543 cm$^{-1}$), is split into two peaks in PA6, but it converges into a single peak for the composite fibers. Hence, the data suggests that the GOFT nanosheets are dispersed in
between individual macromolecules and establishing hydrogen bonding with the NH bond, and π–π or π–n interactions with the C=O.

Differential scanning calorimetry was used to investigate the melting behavior and crystallinity of PA6 and the corresponding composite micro- and nanofibers. It is expected that the electrospinning process will have an impact on the macromolecular alignment, packing, and crystallinity, and as such, it is important to investigate the properties of these samples as obtained from the process in the first heating cycle. **Figure 4** shows the thermograms of PA6 and the samples containing GOFT. PA6 showed a broad melting peak with two shoulders and a melting temperature of 221°C. PA6/GOFT_0.1% presented a relatively flat region with two subtle melting peaks contained within this area. In contrast, the fibers obtained from PA6/GOFT_0.5% had two well defined melting temperatures at 218°C and 221°C. However, PA6/GOFT_1.0% resembled the behavior of PA6 fibers without nanoparticles, showing a broad peak with a single melting temperature at 221°C.

Melting temperatures, heats of fusion and percent crystallinity of the fibers obtained here are disclosed. The results indicate a 36.5, 40.1, 39.7 and 37.2% crystallinity corresponding to PA6, PA/GOFT_0.1%, PA/GOFT_0.5% and PA/GOFT_1.0% fibers, respectively (**Table S3**, Supporting Information). This is similar to the trend observed in tensile testing, where the maximum in properties was achieved at 0.1 wt.%. Therefore, one can conclude that the nanoplatelets are nucleating agents, which results in higher crystallinity. However, this observation does not explain the significant and simultaneous enhancement in Young’s modulus, tensile strength, and tensile strain. To understand these effects, we have to analyze the role of each PA6 phase. The density of 100% crystalline α is 1.235 g/cm³, melting enthalpy is calculated at 230 J/g, and melting temperature of 223°C. Meanwhile, the density of 100% crystalline γ is 1.190 g/cm³, and melting temperature of 214°C.[41,42] The calculated Young’s modulus in the chain direction is 295 GPa for α, 135 GPa for γ, and 253 GPa for β.[16] Hence,
the properties of films, fibers and plastics prepared from Nylon 6 must be dependent upon total crystallinity, and the relative ratios of their crystalline phases, since higher Young’s modulus and tensile strength are associated with the thermodynamically stable α phase, while elongation is associated with the kinetically favored γ phase.\(^\text{[12]}\) Figure 4 shows the deconvolution of the crystalline phases, and (Table S4, Supporting Information) presents the relative ratios calculated from these curves. The deconvolution analysis confirms reports that the γ phase is obtained in higher ratios (42.6 %) than the α phase (26.1 %) during electrospinning, but it also reveals that the β and δ metastable phases contribute 31.3 % of the total crystallinity. It is more significant that upon addition of GOFT, these intermediate phases increase their relative ratio to 45, 46.7 and 36.3 % corresponding to 0.1, 0.5 and 1.0 wt.% GOFT, respectively.

In conclusion, the data presented herein confirms that electrospinning results in the formation of the γ phase,\(^\text{[43]}\) which is the most stable crystalline phase, but addition of GOFT induces hydrogen bonding between the NH bond of PA6 and the nanoplatelets, promoting higher crystallinity of the polymer matrix, and higher tensile properties. However, the formation and relatively high relative ratios (0.1% and 0.5% wt. GOFT) of the β and δ polymorphs play a relevant role on the simultaneous enhancement of the stress, strain and Young’s modulus.

**Acknowledgements**

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[7] J. R. Ueyoko, Kiyoshi; Boehlefeld, Reduced Weight Aircraft Tire **2013**.
[34] D. M. Chipara, J. MacOssay, A. V. R. Ybarra, A. C. Chipara, T. M. Eubanks, M.

Figure 1. HRTEM of a) natural graphite; b) GO; c) GOFT; d) fiber of PA6/GOFT_0.1%; e-h illustrate SEM micrographs of electrospun fibers of PA6, PA6/GOFT_0.1%, PA6/GOFT_0.5%, and PA6/GOFT_1.0%, respectively.
Figure 2 Tensile properties of PA6, and composite PA6/GOFT electrospun fibers
Figure 3. FTIR of pristine PA6 and PA6/GOFT fibers at different additive concentrations
Figure 4. DSC deconvoluted melting curves in the first heating cycle corresponding to electrospun fibers of: a) PA6, b) PA6/GOFT_0.1%, c) PA6/GOFT_0.5%, d) PA6/GOFT_1.0%.
β/δ metastable crystalline phases, induced by the presence of functionalized GO on electrospun PA6 nanocomposites fibers, promote the simultaneous and unexpected increase on the tensile stress, tensile strain and Young’s Modulus.

**Keyword** electrospinning, PA6, functionalized graphene oxide, polymorphs, tensile stress.

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**The Role of α, γ and Metastable Polymorphs on Electrospun Polyamide 6/Functionalized Graphene Oxide**
Supporting Information

The Role of $\alpha$, $\gamma$ and Metastable Polymorphs on Electrospun Polyamide 6/Functionalized Graphene Oxide

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Experimental Section

Functionalization and exfoliation of graphene oxide with TEMPO moieties (GOFT). Briefly, the exfoliation and functionalization reaction of graphene oxide to obtain graphene oxide single-layers functionalized with TEMPO groups (GOFT) was performed in a glass reactor equipped with a cooling jacket, a condenser and a magnetic stirrer. To obtain GOFT, 0.5 g of graphene oxide (which was previously obtained using an improved Hummer’s method), 2.6 g (0.025 mol) of triethylamine and 60 mL of N,N-dimethylformamide (DMF, was used to improve the graphite oxide dispersion) were placed into the glass reactor and then the mixture was sonicated during 30 min at 150 W. Then, the dispersion was vigorously stirred and a solution of 2.5 g of Br-TEMPO (0.010 mol) in 40 mL of DMF was added dropwise. The reaction time was 4 h, at 2 °C under N$_2$ atmosphere. Nitroxide functionalized graphene oxide layers (GOFT) were washed with fresh DMF and filtered using a nylon-membrane of 0.2 μm under vacuum, followed by drying overnight at room temperature prior characterization.

Electrospinning of non-woven mats of PA6/GOFT nanocomposites. A solution of PA6 (7.5 wt.-%) / 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was prepared dissolving the polymer overnight. PA6/GOFT dispersions were prepared by placing 0.1, 0.5 or 1.0 wt.% (with respect to the polymer) of GOFT in the PA6/HFIP solution and sonicated using an ultrasonic processor operating at 20 KHz with amplitude of 20 % for 1 h. PA6/GOFT dispersion were placed in a 10 mL syringe and were electrospun immediately after dispersion using a peristaltic pump.
(KDS 210) with an applied voltage of +15 kV in the needle tip, while the negative electrode was set to a voltage of -15 kV in the rotating collector (mandrel). A 15 cm distance between the needle tip and the mandrel was used to obtain the nanofibers, which were dried under vacuum for 24 h in the presence of P$_2$O$_5$ for removing any traces of residual moisture and solvents.

**Materials.** Polyamide 6 (PA6, Zytel 7301 NC010, $\overline{M}_w = 33,300$ Da) was donated from DuPont, natural graphite (GN, OCF97) were purchased from Superior Graphite and was reacted to obtain graphene oxide (GO) by an improved Hummer’s method, 2,2,6,6-tetramethylpiperidine-1-N-oxyl (TEMPO, C$_9$H$_{18}$NO, M.W. = 156.25 g/mol, 99%), bromine (Br$_2$), carbon tetrachloride (CCl$_4$), dimethylformamide (DMF), dichloro-methane (CH$_2$Cl$_2$), and N,N,N-triethylamine (Et$_3$N, M.W. = 101.19 g/mol, 99.5%) were purchased from Sigma–Aldrich and were used without further purification. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 99.5%) was acquired from ACROS.

**Instrumentation.** FTIR–ATR spectra were recorded with a Nexus 470 Spectrometer at 4000–500 cm$^{-1}$ using 32 scans and 4 cm$^{-1}$ of resolution. High-resolution Transmission Electron Microscopy (HRTEM) experiments were performed in the National Laboratory of Nanotechnology at CIMAV using a JEOL JEM-2200FS equipped with a spherical aberration corrector in the condenser lens, and operated at an accelerating voltage of 200 kV. Under these conditions, no visible sample damage was observed during HR-TEM image acquisitions. Scanning electron microscopy (SEM) using an EVO® LS10 (Carl Zeiss Microscopy) was utilized to investigate the electrospun nanofibers morphology. The samples were coated with a thin layer of silver-palladium for 180 s at 45 mA with a Desk II Denton Vacuum Cold Sputter. After coating, the micrographs were taken at an accelerating voltage of 10.75 kV. Fiber diameters were determined using 50 random fibers from images utilizing the SEM micrographs with 1,000 X magnification. Image J 1.50g was utilized for these determinations. A 500-watt ultrasonic processor (Sonics Vibra-cell model VCX 500) operating at 20 kHz with an amplitude
of 20% was used for the dispersion of functionalized graphene layers with TEMPO moieties in the polymer solution. Thermal transitions of new composites polymer/functionalized graphene were studied using a differential scanning calorimetry (DSC) for each experimental sample, using a TA Instruments DSC Q200. Typically, 1-2 mg of sample was added into an aluminum pan (Tzero®) and under nitrogen flux (100 mL/min) was undergoing to the follow thermal treatment: 1) A heating at 10 °C/min over the range of 10 °C up to 250 °C; 2) 250°C isothermal for 1 min; 3) A cooling at 10 °C/min over the range of 250 °C up to 10 °C; 4) 10°C isothermal for 1 min; 5) A heating at 10 °C/min over the range of 10 °C up to 400 °C. A custom-made electrospinning chamber consisting of a 10 mL glass syringe with a 22 needle gauge (0.7 mm OD and 0.4 mm ID) at a flow rate of 0.02 mL/min, which was controlled using a KDS 210 pump (KD Scientific Holliston, Inc., MA). High power voltage supplies (ES30P-5W and ES30 N-5W for positive and negative voltages, respectively) were purchased from Gamma High Voltage Research (Ormond Beach, FL). The mechanical behavior of the nanofiber mats was investigated using an INSTRON® tensile tester 5943 with a 25 N maximum load cell.
**Figure S1.** Schematic representation of functionalization mechanisms of GO with the o xoammonium salt (Br-TEMPO). (A colour version of this figure can be viewed online.)
Figure S2. Histograms corresponding to: a) PA6, b) PA6/GOFT_0.1 wt.-%, c) PA6/GOFT_0.5 wt.-%, and d) PA6/GOFT_1.0 wt.-%.
Figure S3. NH stretching region and deconvolution for pristine PA6 and composite fibers
**Table S1.** Tensile properties of micro- and nanofibers based on PA6, and PA6 reinforced with GOFT1 at 0.1 wt.%, 0.5 wt.% and 1.0 wt.%. 

<table>
<thead>
<tr>
<th>Tag</th>
<th>Tensile stress (MPa)</th>
<th>Tensile strain (mm/mm)</th>
<th>Young's modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA6</td>
<td>9.79 ± 0.37</td>
<td>0.63 ± 0.07</td>
<td>46.2 ± 2.06</td>
</tr>
<tr>
<td>PA6/GOFT_0.1%</td>
<td>18.9 ± 0.98</td>
<td>1.12 ± 0.17</td>
<td>80.1 ± 6.79</td>
</tr>
<tr>
<td>PA6/GOFT_0.5%</td>
<td>16.2 ± 1.87</td>
<td>1.05 ± 0.16</td>
<td>77.1 ± 2.52</td>
</tr>
<tr>
<td>PA6/GOFT_1.0%</td>
<td>14.4 ± 1.39</td>
<td>0.75 ± 0.04</td>
<td>49.5 ± 4.48</td>
</tr>
</tbody>
</table>

**Table S2.** Relative ratios of free and bonded hydrogen in NH.

<table>
<thead>
<tr>
<th>Bonding type</th>
<th>PA6</th>
<th>PA6/GOFT_0.1%</th>
<th>PA6/GOFT_0.5%</th>
<th>PA6/GOFT_1.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH free (3449 cm⁻¹)</td>
<td>79.58%</td>
<td>76.01%</td>
<td>60.17%</td>
<td>70.49%</td>
</tr>
<tr>
<td>NH bonded (3252 cm⁻¹)</td>
<td>17.70%</td>
<td>20.98%</td>
<td>33.52%</td>
<td>26.70%</td>
</tr>
</tbody>
</table>

**Table S3.** Melting temperatures, heats of fusion and crystallinity determined by DSC for electrospun fibers.

<table>
<thead>
<tr>
<th>Tag</th>
<th>PA6</th>
<th>PA6/GOFT_0.1%</th>
<th>PA6/GOFT_0.5%</th>
<th>PA6/GOFT_1.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st melting peak or shoulders</td>
<td>214°C, 217°C</td>
<td>218°C</td>
<td>218°C</td>
<td>217°C</td>
</tr>
<tr>
<td>2nd melting peak</td>
<td>221°C</td>
<td>221°C</td>
<td>221°C</td>
<td>221°C</td>
</tr>
<tr>
<td>ΔHf</td>
<td>63.97 J/g</td>
<td>70.33 J/g</td>
<td>69.53 J/g</td>
<td>65.04 J/g</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>36.5%</td>
<td>40.1%</td>
<td>39.7%</td>
<td>37.2%</td>
</tr>
</tbody>
</table>

\[ \Delta H \text{ 100% crystalline PA6} = 175 \text{ J/g}^{[41]} \]

**Table S4.** Relative ratios of phases for PA6 and PA6-GOFT fibers deconvoluted from DSC.

<table>
<thead>
<tr>
<th>Phases</th>
<th>PA6</th>
<th>PA6/GOFT_0.1%</th>
<th>PA6/GOFT_0.5%</th>
<th>PA6/GOFT_1.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>42.6%</td>
<td>30.7%</td>
<td>24.5%</td>
<td>37.6%</td>
</tr>
<tr>
<td>β</td>
<td>21.4%</td>
<td>29.8%</td>
<td>29.4%</td>
<td>11.9%</td>
</tr>
<tr>
<td>δ</td>
<td>9.9%</td>
<td>15.2%</td>
<td>17.3%</td>
<td>24.4%</td>
</tr>
<tr>
<td>α</td>
<td>26.1%</td>
<td>24.3%</td>
<td>28.8%</td>
<td>26.2%</td>
</tr>
<tr>
<td>γ + α</td>
<td>68.7%</td>
<td>55%</td>
<td>53.3%</td>
<td>63.8%</td>
</tr>
<tr>
<td>β + δ</td>
<td>31.3%</td>
<td>45%</td>
<td>46.7%</td>
<td>36.3%</td>
</tr>
</tbody>
</table>