Melt Spinning and Drawing of Polyethylene Nanocomposite Fibers with Organically Modified Hydrotalcite

Luca Fambri,1,2 Izabela Dabrowska,1 Alessandro Pegoretti,1,2 Riccardo Ceccato1,2
1Department of Industrial Engineering, University of Trento, via Mesiano 77, 38123, Trento, Italy
2National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121, Firenze, Italy
Correspondence to: L. Fambri (luca.fambri@unitn.it).

ABSTRACT: Fibers of high density polyethylene (HDPE)/organically modified hydrotalcite (LDH) were produced by melt intercalation in a two-step process consisting of twin-screw extrusion and hot drawing. The optimum drawing temperature was 125°C at which the draw ratios up to 20 could be achieved. XRD analysis revealed intercalation with a high degree of exfoliation for the composites with 1–2% of LDH. Higher thermal stability of nanofilled fibers was confirmed by TGA analysis. DSC data indicated that dispersed LDH particles act as a nucleating agent. Crystallization kinetics of the HDPE matrix in the composite fibers is characterized by two transition temperatures, that is, for Regimes I/II at 123°C and for Regimes II/III ranging between 114–119°C as a function of the nanocomposite composition. Fibers with 1–2% of LDH show for the drawing ratios up to 15 a higher elastic modulus, 9.0–9.3 GPa (with respect to 8.0 GPa of the neat HDPE), maintain tensile strength of 0.8 GPa and deformation at break of 20–25%. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2014, 131, 40277.

KEYWORDS: fibers; polyolefins; nanoparticles; nanowires and nanocrystals; mechanical properties; properties and characterization

INTRODUCTION
Polymer fibers are widely used for various textile applications, such as automotive, carpets, geotextile, sail, or as reinforcements in composite materials. The most common polymers used for melt spinning are polypropylene, polyethylene, polyamides, or polyethylene terephthalate. The interest in the production of oriented polymers with high stiffness and strength dates back to 1960–1970. In the case of polyethylene drawn films Treloar estimated the Young's modulus of about 200 GPa and tensile strength of about 3 GPa.1 However, molecular alignment achieved after melt spinning and drawing was much lower than predicted, as described by White et al. and in references therein.2 The development of high modulus polyethylene fibers was presented in the pioneer research of Andrews and Ward, where a direct correlation between the draw ratio and modulus was established.3 For instance, after increasing draw ratio from 7 to 13, Young modulus of cold-drawn fibers rose from 4 GPa to 20 GPa. Capaccio and Ward comparing the drawing behavior of several commercial polyethylene fibers observed the best results for polymers with low molecular weight and narrow distribution, analogously to the conclusions of White and coworkers.2,4 Nowadays polyolefins for fiber spinning have reached an extensive application, not only for economic reason but also for easy processability, excellent melt dyeability, and low moisteres absorption.5–7

Along with melt spinning, polyolefin fibers were produced by other processing and drawing methods, for example, solid-state hot drawing, solid-state extrusion, gel-spinning of UHMWPE.8–10 Solid-state deformation was used by Ward and coworkers, who succeeded in stretching polymers in the solid state at temperatures sufficient to permit molecular mobility of polyethylene; thus, they obtained Young’s moduli of 70 GPa and tensile strength of 1.5 GPa at very high draw ratios (greater than 30).11 Melt spinning remains widely used processing method despite of the fact that that mechanical properties of produced fibers are lower than those of the gel-spun fibers.3

The challenge to produce stronger, tougher, light-weight materials continues apace, being driven by demands for property improvements, economy, and material availability. In order to improve polymer properties, the introduction of small amount of inorganic nanofillers in polymer matrices is an interesting method, as it is evident that nanocomposites offer similar or better properties at significantly lower filler loading levels than materials with conventional fillers. The addition of nanofillers to polymers makes possible to produce composite materials with improved mechanical and barrier properties, flame retardancy, electrical conductivity, and so on.12

Recent literature evidences a lot of progress in the nanofilled bulk materials; on the contrary, there are relatively a few
ered silicates were reported. Owing to the alignment of the含钙碳酸盐，碳纳米管，二氧化硅，和lay-fibers and drawing at 100°
thermo-mechanical, flame retardant, barrier and rheological easily be melt dispersed into a polymer and exfoliated forming
If properly processed, the organically modified hydrotalcite can
decreased interaction between platelets to facilitate dispersion.29
distance of the pristine clay, increased hydrophobic nature and
num hydroxides. In this article we have used organically modi-
lishers, for example, layered silicates, carbon nanotubes, and mont-
materials can find applications where the chemical purity is
since the chemical composition can be precisely controlled, these
articles can find applications where the chemical purity is
required, for example in food, medical, and microelectronic industries.33 In general, LDH has a layered structure similar to
silica clays, but the layers positively charged with an anionic
layer interlayer gallery can be exchanged by bulk organic anions; when
the interlayer distance is increased, polymer chains can intercalate
into the gallery and thus nanocomposites with an intercalated
and/or exfoliated morphology can be obtained.26,27,29,34
Commercially available grades are based on magnesium alumi-
nium hydroxides. In this article we have used organically modi-
hydrotalcite characterized by the enlarged interlayer
distance of the pristine clay, increased hydrophobic nature and
decreased interaction between platelets to facilitate dispersion.29
If properly processed, the organically modified hydrotalcite can
easily be melt dispersed into a polymer and exfoliated forming
a true nanocomposite resulting in improved properties such as
thermo-mechanical, flame retardant, barrier and rheological
(better thermoforming properties).28–32
In our previous paper we have described the compounding of
hydrotalcite with HDPE (either internal mixing or mixing in
full-screw extruder) and the preliminary melt spinning of
fibers and drawing at 100°C.35 In this article, the production of
polyethylene/organically modified hydrotalcite fibers was de-
veloped and detailed on a wider scale. In particular, the effects of
the drawing temperature (between 100 and 140°C) and of the
draw ratio (up to 20) are reported. The effects of the fiber com-
position and of the drawing ratio on resulting morphology
(SEM) and level of intercalation/exfoliation (XRD) have been
studied. Mechanical and thermal measurements of the fibers
have been used to evaluate the beneficial effects of hydrotalcite
with regard to its concentration and processing procedure.

### Table I. Designation and Composition of the HDPE Nanocomposite Fibers

<table>
<thead>
<tr>
<th>Material</th>
<th>Hydrotalcite [%]</th>
<th>HDPE [%]</th>
<th>Compatibilizer HDPE-g-MA [%]</th>
<th>Screw speed [rpm]</th>
<th>Output [g/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>5</td>
<td>140</td>
</tr>
<tr>
<td>LDH-0.5</td>
<td>0.5</td>
<td>99</td>
<td>0.5</td>
<td>4.5</td>
<td>141</td>
</tr>
<tr>
<td>LDH-1</td>
<td>1</td>
<td>98</td>
<td>1</td>
<td>5</td>
<td>142</td>
</tr>
<tr>
<td>LDH-2</td>
<td>2</td>
<td>96</td>
<td>2</td>
<td>4</td>
<td>137</td>
</tr>
<tr>
<td>LDH-3</td>
<td>3</td>
<td>94</td>
<td>3</td>
<td>3</td>
<td>138</td>
</tr>
</tbody>
</table>

Recently many articles on synthetic layered double hydrotalcite (LDH) have been published. LDH is a synthetic clay pro-
duced in a broad range of chemical compositions. Moreover,
since the chemical composition can be precisely controlled, these
materials can find applications where the chemical purity is
required, for example in food, medical, and microelectronic industries. In general, LDH has a layered structure similar to
silica clays, but the layers positively charged with an anionic
layer interlayer gallery can be exchanged by bulk organic anions; when
the interlayer distance is increased, polymer chains can intercalate
into the gallery and thus nanocomposites with an intercalated
and/or exfoliated morphology can be obtained.26,27,29,34

Commercially available grades are based on magnesium alumi-
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studied. Mechanical and thermal measurements of the fibers
have been used to evaluate the beneficial effects of hydrotalcite
with regard to its concentration and processing procedure.

**Experimental**

**Materials**

Fine powder of high density polyethylene HDPE Eltex® A4009
(melt flow rate 0.85 dg/min at 190°C/2.16 kg; density 0.96
g/cm³) was supplied by BP Solvay (Brussels, Belgium).

Masterbatch pellets at 12% by weight of synthetic hydrotalcite organically modified with fatty acid, Perkalite F100
(Akzo-Nobel, CAS number 39366-43-3 and 67701-03-5; density
1.35–1.40 g/cm³) and containing 12% by weight of maleated polyethylene HDPE-g-MA as compatibilizer, was provided from
Clariant Masterbatches S.p.A.-Italy. Masterbatch was dried for
24 h in vacuum oven at 90°C before processing. Nanocompo-
sites were designated as hydrotalcite abbreviation (LDH) and
the filler content. As an example, LDH-1 indicates a nanocom-
posite sample filled with 1 wt % of hydrotalcite.

**Fiber Spinning**

Monofilament fibers were produced by means of Thermo Haake
PTW16 intermeshing corotating twin screw extruder (screw
diameter 16 mm, L/D ratio 25, rod die diameter 1.65 mm) that
performed both compounding and spinning (the composition is
given in Table I). The temperature profile along the screw was
gradually increased (T1 = 130°C, T2 = 200°C, T3 = 210°C,
T4 = 220°C) up to the rod die (T5 = 220°C). The spun fibers
were fast cooled in water at room temperature in order to elim-
inate orientation and drawing of the fibers immediately after
the extrusion, and wrapped around a rotating cylinder (40 mm
diameter) rotating at 67 rpm. To obtain fibers with diameter of
500 μm, the screws rotation speed was fixed in the range 3–5
rpm depending on the material composition.

**Fiber Drawing**

As spun fibres were drawn in a hot-plate drawing apparatus 1.4
m length (SSM-Giudici srl, Galbiate, LC, Italy). Three different
temperatures 100°C, 125°C, and 140°C, a constant feeding rate of
1.2 m/min and various collecting rates were selected. Drawn
fibers were distinguished in dependence on the draw ratio (DR)
that is defined as the ratio between the cross section of the ini-
tial (S₀) and final fiber (Sₖ) according to eq. (1)

\[
DR = \frac{S₀}{Sₖ} = \left(\frac{D₀}{Dₖ}\right)^2
\]

where \(D₀\) and \(Dₖ\) are the initial and final diameter of the fiber.
The diameter of the fiber was measured by using an optical
microscope connected to image processing software (ImageJ).

![Materials Views](WWW.MATERIALSVIEWS.COM)

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Fiber Characterization
Thermogravimetric analysis (TGA) was performed by using thermobalance Mettler TG 50 on as-spun fibers of about 15 mg in air flow (100 mL/min) at a heating rate of 10°C/min in the range 50–600°C. The temperatures at 2% and 5% of mass loss, the onset temperature (intersection between the tangent at 200°C and the tangent at the inflection point), and the temperature of the inflection point were evaluated.

Differential scanning calorimetry (DSC) analyses were performed by using a Mettler DSC30 calorimeter. The experiments were performed on fiber samples of about 15 mg in crucible of 50 mg formed by using a Mettler DSC30 calorimeter. The experiments were performed on fiber samples of about 15 mg in crucible of 50 mg in air flow (100 mL/min) at a heating rate of 10°C/min in the range 50–600°C. The temperatures at 2% and 5% of mass loss, the onset temperature (intersection between the tangent at 200°C and the tangent at the inflection point), and the temperature of the inflection point were evaluated.

Table II. TGA Data of the Neat and Nanofilled HDPE Fibers

<table>
<thead>
<tr>
<th>As spun fiber</th>
<th>Onset temperature [°C]</th>
<th>Temperature of 2% mass loss [°C]</th>
<th>Temperature of 5% mass loss [°C]</th>
<th>Max degradation rate [%/°C]</th>
<th>Inflection point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>356 ± 2.0</td>
<td>276 ± 2.0</td>
<td>333 ± 2.0</td>
<td>1.38</td>
<td>423</td>
</tr>
<tr>
<td>LDH-0.5</td>
<td>358 ± 1.0</td>
<td>268 ± 1.0</td>
<td>332 ± 3.0</td>
<td>1.16</td>
<td>456</td>
</tr>
<tr>
<td>LDH-1</td>
<td>365 ± 1.0</td>
<td>298 ± 3.0</td>
<td>344 ± 2.0</td>
<td>1.18</td>
<td>460</td>
</tr>
<tr>
<td>LDH-2</td>
<td>377 ± 5.0</td>
<td>294 ± 2.0</td>
<td>347 ± 1.0</td>
<td>1.22</td>
<td>460</td>
</tr>
<tr>
<td>LDH-3</td>
<td>392 ± 6.0</td>
<td>276 ± 3.0</td>
<td>377 ± 3.0</td>
<td>1.61</td>
<td>442</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

As-spun Fibers
All composition were easy to spun in single monofilaments of 500 micron diameter, with a linear density of about 190 tex, as described in the previous paper. Thermogravimetric analysis of fibers evidenced a shift of the degradation curve at higher temperature after introduction of LDH, as shown in Figure 1. Various comparative parameters such as the temperature of the selected mass loss, inflection point are summarized in Table II. As the most representative parameter appears the onset temperature of thermogram that proportionally increased from 356°C for the neat HDPE fiber up to 392°C for the fiber with 3% of LDH. Moreover, the inflection point is shifted from 423°C up to 442–460°C after incorporation of 0.5–3% of hydrotalcite, confirming the higher thermal stability of LDH-nanocomposite fibers.

SEM Analysis
SEM micrographs of the fracture surface of the fibers are reported in Figure 2. It could be seen that for LDH-1 [Figure 2(a,b)] and LDH-2 [Figure 2(c,d)] the dispersion of hydrotalcite was uniform. Mainly LDH particles clusters of about 0.25 μm are visible; however, single larger clusters in the range of 1.2–1.5 μm are also observed. At a higher magnification, the nanofiller particles seem to evidence a random distribution because of the irregular shape and the low aspect ratio. In contrast, the fracture surfaces of undrawn LDH-3 fibers reveal many clusters of microcracks.
aggregates hydrotalcite particles with a mean size around 1.5–2 μm [Figure 2(e)]. It is known that for a low organoclay content a good dispersion of small size particles can be achieved, frequently at nanoscale, whereas higher loadings result in large size domains and less uniform distribution. Similar behavior was already observed by D’Amato et al. in the case of the HDPE-nanosilica composite fibres.23

![Image](a) LDH-1 (1000x); (b) LDH-1 (2000x); (c) LDH-2 (625x); (d) LDH-2 (3200x); (e) LDH-3 (1600x); (f) LDH-3 (5000x).

Figure 2. ESEM micrographs of LDH nanocomposite as-spun fibers (fracture surface). (a) LDH-1 (1000x); (b) LDH-1 (2000x); (c) LDH-2 (625x); (d) LDH-2 (3200x); (e) LDH-3 (1600x); (f) LDH-3 (5000x).

Nonisothermal Crystallization Kinetics
In order to collect complementary information on the effect of crystallization temperature during drawing, a deeper investigation on the crystallization kinetics of HDPE nanocomposites analysis was performed. DSC results of the nonisothermal crystallization at different cooling rate between −0.3°C/min and −40°C/min are summarized in Table III. Higher crystallization

Table III. Crystallization Temperature (Tc) of the neat HDPE and HDPE Nanocomposites at Different Cooling Rate in DSC

<table>
<thead>
<tr>
<th>Material</th>
<th>0.3°C/min</th>
<th>0.5°C/min</th>
<th>1°C/min</th>
<th>2°C/min</th>
<th>5°C/min</th>
<th>10°C/min</th>
<th>20°C/min</th>
<th>40°C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>124.3</td>
<td>123.8</td>
<td>122.6</td>
<td>120.7</td>
<td>117.6</td>
<td>111.3</td>
<td>107.5</td>
<td>99.8</td>
</tr>
<tr>
<td>LDH-0.5</td>
<td>124.3</td>
<td>123.6</td>
<td>122.2</td>
<td>119.7</td>
<td>115.8</td>
<td>112.2</td>
<td>102.5</td>
<td>91.1</td>
</tr>
<tr>
<td>LDH-1</td>
<td>124.2</td>
<td>123.6</td>
<td>122.7</td>
<td>121.3</td>
<td>118.6</td>
<td>112.4</td>
<td>110.0</td>
<td>101.3</td>
</tr>
<tr>
<td>LDH-2</td>
<td>123.9</td>
<td>123.3</td>
<td>122.3</td>
<td>121.3</td>
<td>118.7</td>
<td>113.0</td>
<td>110.0</td>
<td>101.2</td>
</tr>
<tr>
<td>LDH-3</td>
<td>123.9</td>
<td>123.5</td>
<td>122.6</td>
<td>121.1</td>
<td>118.4</td>
<td>115.1</td>
<td>110.0</td>
<td>103.7</td>
</tr>
</tbody>
</table>
temperatures of the LDH nanocomposites seem to confirm a nucleating effect of hydrotalcite.\textsuperscript{28, 35}

The experimental data in three selected temperature intervals were fitted with straight lines whose slopes express the activation energy determined by using the Kissinger approach:

\[
\ln C = \ln C_0 - \left( \frac{E_{\text{act}}}{R} \right) \frac{1}{T_c}
\]

where \(C_0\) is a pre-exponential factor, \(T_c\) is the peak temperature and \(R\) is the universal gas constant.\textsuperscript{37} Figure 3 evidences the case of HDPE and LDH-2 for which the three straight lines could be related to the different mechanisms of the crystallization regimes I, II, and III of the Hoffman theory, and their intersection is related to the transition temperature between different regimes. For linear polyethylene, transition temperatures of 127°C and 119°C for regime I/II and regime II/III, respectively, were reported.\textsuperscript{38} In our case, both transition temperatures and the activation energies of the regimes are summarized in Table IV. The transition temperatures for the neat HDPE \( (T_{\text{I/II}} = 123.8°C \text{ and } T_{\text{II/III}} = 117.5°C) \) are slightly lower in comparison to literature data. In the case of HDPE/LDH nanocomposites \( T_{\text{III}} \approx 122°C \), whereas the temperature transition between regime II and III was found at 119.0°C for LDH-1 and LDH-2. Moreover, the neat HDPE activation energies of 894, 410, and 140 kJ/mol for regime I, II, and III were calculated, respectively; whereas the calculated activation energies of regime I (about 1050 kJ/mol) and regime II (about 500 kJ/mol) of nanocomposites with 1–3% of LDH are higher than those of the neat HDPE. Such higher activation energy could be related to lower molecular mobility in the LDH nanocomposites, whereas a higher crystallization temperature could be attributed to the heterogeneous nucleation of hydrotalcite particles. Similar results were previously observed for the HDPE/BaSO\(_4\) nanocomposites.\textsuperscript{39} Thus, two different roles could be attributed to the LDH nanoparticles: first, they acted as nucleating agents and promoted the crystallization process of HDPE; second, they simultaneously acted as physical hindrances, thus retarding crystal growth of HDPE.\textsuperscript{39}

**Drawing Process**

In our previous work, a preliminary drawing temperature 100°C was selected.\textsuperscript{35} A deeper study on three drawing temperatures is presented in this paragraph; in particular both LDH-2 and HDPE fibers were drawn at 100°C, that is, the temperature of regime III crystallization, and at two higher temperatures, 125°C and 140°C, in the regime of crystallization type II and I.

Both elastic modulus and stress at break of fibers drawn at various temperatures are compared in Figures 4 and 5. The elastic modulus of the neat HDPE fibers with DR = 10 was found 3.0 GPa and 5.0 GPa after drawing at 140°C and at 100°C, respectively, whereas a value of 5.2 GPa was reached for drawing

<table>
<thead>
<tr>
<th>Composition</th>
<th>( T_{\text{I/II}} ) [°C]</th>
<th>( T_{\text{II/III}} ) [°C]</th>
<th>( E_{\text{act I}} ) [kJ/mol]</th>
<th>( E_{\text{act II}} ) [kJ/mol]</th>
<th>( E_{\text{act III}} ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>123.8</td>
<td>117.5</td>
<td>894 ± 132</td>
<td>410 ± 25</td>
<td>140 ± 31</td>
</tr>
<tr>
<td>LDH-0.5</td>
<td>122.2</td>
<td>114.4</td>
<td>734 ± 77</td>
<td>320 ± 16</td>
<td>77 ± 5</td>
</tr>
<tr>
<td>LDH-1</td>
<td>122.7</td>
<td>119.0</td>
<td>1046 ± 30</td>
<td>496 ± 20</td>
<td>137 ± 25</td>
</tr>
<tr>
<td>LDH-2</td>
<td>122.2</td>
<td>119.0</td>
<td>974 ± 56</td>
<td>551 ± 30</td>
<td>131 ± 35</td>
</tr>
<tr>
<td>LDH-3</td>
<td>122.7</td>
<td>117.5</td>
<td>1175 ± 156</td>
<td>486 ± 42</td>
<td>149 ± 8</td>
</tr>
</tbody>
</table>

**Table IV.** Transition Temperatures \( (T_{\text{I/II}} \text{ and } T_{\text{II/III}}) \) and Activation Energy of Crystallization \( (E_{\text{act}}) \) Found for Regimes I, II, and III for Neat HDPE and HDPE-LDH Composites.
temperature of 125°C (Figure 4). In the case of LDH-2 fiber the same tendency was observed, with elastic modulus of 3.1 GPa after drawing ten times at 140°C, 5.8 GPa at 100°C and 6.9 GPa at 125°C.

Figure 5 shows similar trends for stress at break. For DR = 10, the neat HDPE fibers show the highest stress at break (640 MPa) for drawing temperature of 125°C; slightly lower values were found at 100°C (590 MPa) and 140°C (480 MPa). The trends observed for the LDH nanofilled fibers are quite analogous, (660, 470, 530 MPa, respectively).

The dependence of fiber mechanical properties on drawing temperature could be interpreted in term of crystallization-induced-orientation, and also taking into consideration the different crystallization forms and regimes, as briefly summarized by the description of Hoffman and coworkers.38 In regime I, secondary nucleation rate is slow allowing for completion of the nucleated layer before the next event of the secondary nucleation; in the regime II, their rates are comparable to allow multiple nucleation; finally, during III regime surface spreading is lower than the nucleation rate. Hence, fibers drawn at the lower temperature (100°C) could developed further crystallization according to crystallization regime III, where the nucleation rate is slow, and thus, accounting for a lower crystallinity content. Moreover, in regime III zone a similar activation energy $E_{act \, III}$ of about 135 kJ/mol was found for both HDPE and LDH-2. The highest mechanical properties (Figures 4 and 5) were obtained for HDPE and LDH-2 fibers drawn at 125°C, where HDPE crystallized according to regime II and I, so that both nucleation and growth rates are comparable. At 140°C, crystallization proceeds owing mainly to the intense nucleation because the nucleation rate is higher than surface spreading, and hence, lower mechanical properties were achieved. These results, even those of LDH-2, are in agreement with data of HDPE fibers reported by Ward, where the highest elastic modulus and the draw ratio were achieved for drawing temperature close to 120°C. 7

Characterization of Fibers Drawn at 125°C
Following our previous findings, 125°C was selected as drawing temperature for both HDPE and all other LDH nanocomposites, and an extensive study is reported in the next paragraphs, where XRD analysis and thermal and mechanical characterization are described.

XRD Analysis
The XRD analyses of the HDPE/LDH as-spun and selected drawn fibers are shown in Figure 6(a–c), in order to evaluate the extent of intercalation and exfoliation of the nanofiller. The

![Graph showing stress at break as a function of draw ratio for various drawing temperatures.](image-url)

**Figure 5.** Stress at break of the neat HDPE (empty symbols) and LDH-2 (full symbols) fibers for various drawing temperature (square-100°C, circle-125°C, and triangle-140°C) as function of the draw ratio.

![Graph showing XRD patterns for different draw ratios.](image-url)

**Figure 6.** XRD patterns of the HDPE-LDH nanocomposite fibers for selected draw ratio (DR) at 125°C and different nanofiller content (a) LDH-1, (b) LDH-2, and (c) LDH-3.
XRD pattern were interpreted with respect to the position of the basal peak (003) of the hydrotalcite phase (Mg₆Al₂(−CO₃)(OH)₁₆·4H₂O, PDF card n. 41–1428), which depends on the distance between two adjacent metal hydroxide sheet in the LDH crystal lattice. The higher order peak of the same hkl series (006, 009) was also reported and both peaks indicate the presence of repeating crystal planes and symmetry in a specific crystallographic direction. On the XRD spectra of LDH-1 nanocomposites, three characteristic Bragg reflections at about 6° (003), 8.1° (006), and 11.5° (009) of LDH presence can be observed [Figure 6(a)]. The first and the third can be univocally attributed to (003) and (006) reflexes of the reported reference phase, set at 5.48° and 11.27°, respectively. The second peak can be tentatively assigned to a minor Dypingite phase (ICPDS Powder Diffraction File card n. 23–1218), present in the starting mineral raw material. After the drawing process (DR = 10) the XRD patterns show change in the position of the basal reflection of the HDPE/LDH nanocomposites. For LDH-1 the peaks were shifted, respectively, from 6° up to 5.2° and 8.1° till 7.2° [Figure 6(a)]. As reported by other researchers, these results might suggest possible intercalation along with partial exfoliation.30,40,41 In the case of LDH-2 the first basal reflections become very broad and the maximum of the bands, from 8.2° and 11.5°, shifts to lower 2θ, 7.8°, and 11.0° respectively, as compared with as-spun fiber [Figure 6(b)]. Moreover, in order to check the change in the LDH intercalation/exfoliation process during drawing, XRD analyses for DR = 15 samples were also performed. In this case the first basal peak cannot be observed for both compositions LDH-1 and LDH-2, whereas the position of the other two peaks remains unchanged in comparison to DR10. This suggests that with further drawing the exfoliation process is more effective. In contrast, the results of LDH-3 were reported in Figure 6(c), and no change in the position of the three peaks was observed, even at high draw ratio. These findings suggested that nanoparticles in LDH-3 were not well dispersed and the formation of aggregates prevented the intercalation process.40 Moreover, it is worth noting the increase of intensity of the peaks related to the polyethylene (21.4° and 23.7°) after drawing for all LDH composition. High enhancement of crystallinity content was obtained up to DR = 10, whereas after higher drawing (DR = 15) only minor variations were observed, in agreement with DSC analysis (see next paragraph). The overall XRD results confirmed that LDH layers were partially/fully separated with the formation of an intercalated/exfoliated.42 It can be concluded that XRD analysis of HDPE nanocomposite fibers shows significant change in the position of the basal peak after drawing process. Moreover the disappearance of the (003) peak for LDH-1 and LDH-2 at DR = 15, suggested that LDH particles undergo more and more fragmentation during drawing process and lose their order structures to a great extent.40

**Differential Scanning Calorimetry**

DSC thermograms of the first heating scan for neat HDPE and LDH-2 nanocomposite fibers with different draw ratios are compared in Figure 7, while all results of the heating–cooling–heating cycle are summarized in Table V. Melting temperature of the as-spun HDPE and LDH nanocomposite fibers was found at 133°C, (Table V), whereas a higher crystallinity...
content was detected for LDH fiber (52–54% vs 50% of neat HDPE), in conformity to literature data of polyolefin/clay nanocomposites. The increase in fiber orientation upon solid-state drawing determined not only an increase in the melting temperature up to 140–146°C but also in the degree of crystalinity from about 50% up to 74–78%. The highest crystallinity content was found for LDH-1 (78% at DR15). The multiple melting peaks observed for fibers with DR = 5 (Figure 7), are related to the difference of crystal forms or the degree of their perfection obtained during drawing. The substantial increase of crystallinity of LDH composite fibers in comparison to neat HDPE was obtained for draw ratio between 5 and 10, reaching an almost plateau value for drawing 15–20. The degree of crystallinity of oriented samples follows a trend similar to that of the melting temperature, that is, both quantities increase with orientation and level off at higher degrees of molecular chain alignment. In particular the orientation-induced crystallization, and typical folded-chain lamellar structure of flexible polymers convert into the extended–chain structure. In the cooling step, the crystallization temperature of the as-spun LDH composite was found 1–4°C higher than that of the neat HDPE, confirming the role of hydrotalcite as nucleating agent, in conformity to other literature data. It can be concluded that during drawing at 125°C, the higher the draw ratio, the higher polymer chains orientation, and the higher crystallinity, particularly effective in the case of LDH-1 fiber.

Table V. Results of the DSC Analysis (1st heating–cooling–2nd heating): Crystallinity Content ($\chi$) Melting Temperature ($T_m$), and Crystallization Temperatures ($T_c$) for Neat HDPE and HDPE Nanocomposite Fibers at Selected Draw Ratio (DR)

<table>
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<tr>
<th>Material</th>
<th>DR</th>
<th>$\chi_{1}$ [%]</th>
<th>$T_m_{1}$ [°C]</th>
<th>$\chi_{c}$ [%]</th>
<th>$T_c$ [°C]</th>
<th>$\chi_{2}$ [%]</th>
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Table VI. Mechanical Properties of Neat HDPE and Nanofilled HDPE Fibers at Selected Draw Ratio (DR)

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<tr>
<th>Material</th>
<th>DR</th>
<th>Linear density[^a]</th>
<th>Elastic modulus [GPa]</th>
<th>Stress at break [MPa]</th>
<th>Strain at break [%]</th>
<th>Tenacity[^a] [cN/tex]</th>
<th>True strength[^b] [MPa]</th>
<th>Mechanical draw ratio ( \lambda_{MEC} )</th>
<th>Total draw ratio ( \lambda_{TOT} )</th>
<th>Draw stiffening factor[^c]</th>
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[^a]: For definition of Linear density and Tenacity see ASTM.[48]
[^b]: Calculated according to eq. (6).
[^c]: Calculated as the ratio between the modulus of drawn fiber and the modulus of as-span fiber.
Mechanical Properties

Representative stress–strain curves of the neat HDPE and nanofilled polyethylene fibers at different draw ratio are reported in Figure 8, while the most relevant mechanical parameters are summarized in Table VI. It can be seen that fibers do not manifest a clear yield point at lower strains as usually observed for as-spun products. In fact, the drawing process produces a strong orientation of the macromolecules along the draw direction and the strain-induced crystallization of the amorphous regions, with a consequent increase in the fiber stiffness and the disappearance of yielding phenomena. These results are in conformity to previous researches, where a good dispersion enhanced the elastic modulus and the strength, and reduced the tensile ductility in comparison to neat matrix.28,49

Tensile modulus values at different draw ratios are summarized in Figure 9. It is worth noting that the stiffness of the nanofilled fibers notably increased with only a few weight percent of hydrotalcite. The highest improvement was obtained for LDH-1 and LDH-2 samples, whose tensile modulus at DR = 15 reached 9.0 GPa and 9.3 GPa, respectively, in comparison to 8.0 GPa of the neat HDPE.

The positive effect of the nanofiller on the tensile modulus can be explained by the percolation theory described by He and Jiang.30 According to these authors, the matrix zone around each particle is affected by the stress concentration. If the distance between particles is small enough, these zones join together and form a percolation network which increases the modulus. For constant filler loadings, if the particles are fine and well dispersed, the total volume will be high, and the distance between the particles will be small. Therefore, the percolation network develops more easily and the modulus increases. The uniform nanofiller dispersion in case of compositions with 1 and 2 wt % of LDH was observed by SEM analysis (see Figure 2(a–d)).

The stiffening effect provided by LDH nanoparticles at various draw ratio is well documented by the relative tensile modulus \( E_R \) (Figure 10) according to the following equation:

\[
E_R = \frac{E_{LDH}}{E_{HDPE}}
\]

where \( E_{LDH} \) is the modulus of the nanocomposite fibers and \( E_{HDPE} \) is the modulus of HDPE fibers at the same draw ratio (data from Table VI). Relative modulus was found to increase with the nanofiller content reaching a relative maximum for LDH-1 and LDH-2, particularly significant at DR5 and DR10. Moreover, at the highest concentration of hydrotalcite (3 wt %), a lower stiffening effect (Figure 10) and modest increase of stress at break (Table VI) are especially visible for higher draw ratio (DR > 10). These effects can be explained in terms of filler dispersion, as reported by Costa et al. in the case of polyethylene/Mg-Al LDH nanocomposites, describing a critical concentration range of 2.5–5 wt % above which the LDH particles do not show strong interfacial adhesion with the matrix.30

The existence of an optimal amount of the nanofiller was already observed by several authors.15,17,19 In this article, the critical concentration of LDH in HDPE for fiber spinning was limited by the presence of molecular entanglements.52

Stress at break values of the neat and nanofilled HDPE fibers were plotted versus draw ratio in Figure 12. Scientific literature showed various dependency of stress at break on nanofiller content, either increasing values after addition of 0.5–5 wt % of nanofiller, or unchanged, or even decreasing results, as in the case of nanofilled polypropylene fibers.18,21,23,51 In this case, stress at break for LDH-1 and LDH-2 remained practically unchanged in comparison with that of neat HDPE fibers (Figure 12) up to DR15. Slightly lower values were found for the fibers with 0.5 wt % and 3 wt % of LDH.

Figure 13 shows the decreasing of strain at break values at the increase of draw ratio. All the compositions of as-spun HDPE-LDH fibers evidence higher strain at break than that of the neat HDPE fiber. With the higher draw ratio, strain at break decreases from about 1200% for as-spun HDPE and 1860% for LDH-0.5 up to 16% and 17%, respectively, for the fibers with DR = 20. As interpreted by Bilotti et al., the drawability of melt-crystallized flexible chain polymers achieved by drawing is limited by the presence of molecular entanglements.32

Some more information about spinnability and drawability could be obtained considering the mechanical draw ratio (\( \lambda_{MEC} \)), the true strength (\( \sigma_{MAX} \)), the processing draw ratio (\( \lambda_{PRD} \)), and the total draw ratio (\( \lambda_{TOT} \)) of selected fibers, as described in the followings and compared in Table VI.
The mechanical draw ratio ($\lambda_{\text{MEC}}$) is defined by eq. (5):

$$\lambda_{\text{MEC}} = (1 + \varepsilon_b),$$

(5)

where $\varepsilon_b$ is the strain at break. The true strength ($\sigma_{\text{MAX}}$) is calculated as the stress at break ($\sigma_b$) multiplied by the mechanical draw ratio [eq. (6)]:

$$\sigma_{\text{MAX}} = \sigma_b \cdot \lambda_{\text{MEC}} = \sigma_b (1 + \varepsilon_b).$$

(6)

Moreover, the processing draw ratio ($\lambda_{\text{PRO}}$) is defined as the ratio between the section of the die $S_d$ and the section of the fiber $S_f$ according to eq. (7):

$$\lambda_{\text{PRO}} = \frac{S_d}{S_f}.$$  

(7)

And the total draw ratio ($\lambda_{\text{TOT}}$) has been calculated from eq. (8):

$$\lambda_{\text{TOT}} = \lambda_{\text{PRO}} \cdot \lambda_{\text{MEC}}$$

(8)

which depends on both processing and mechanical drawing. For the as-spun fibers, higher true strength values were obtained for all the composites with hydrotalcite. For example, the true strength of LDH as-spun fibers is between $\sigma_{\text{MAX}} = 675–1098$ MPa and their total draw ratio from $\lambda_{\text{TOT}} = 159–213$, whereas the correspondent values of the neat HDPE as-spun fibers are 549 MPa and 142, respectively. In the case of drawn fibers, true strength and mechanical draw ratio are very similar for both neat and nanofilled HDPE fibers. Also, the total draw ratio indicates that LDH fiber could be spun and drawn at the same levels of HDPE fiber, confirming the good processability of hydrotalcite composites.

Moreover, a quantitative evaluation of the fiber properties and drawability of each composition could be remarked considering the draw-stiffening factor, calculated as the ratio between modulus of drawn fiber and modulus of as spun fiber, also reported in Table VI. These values are directly dependent on the draw ratio, and it is well evident the higher draw-stiffening factor of the LDH fiber containing 0.5–2% of hydrotalcite, with respect to the neat HDPE fiber up to DR15. Once again similar or lower values for LDH-3.

For the as-spun fibers, a complementary evaluation of the maximum attainable property $P_\infty$ (either modulus or stress at break) could be calculated.
Table VII. Maximum Attainable Values of Elastic Modulus ($E_\infty$) and Stress at Break ($\sigma_\infty$) of Neat HDPE and LDH Nanocomposite Fibers, as Predicted from eq. (9).

<table>
<thead>
<tr>
<th>Drawn fiber</th>
<th>$E_\infty$ [GPa]</th>
<th>$\sigma_\infty$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>11.8 ± 0.9</td>
<td>1180 ± 50</td>
</tr>
<tr>
<td>LDH-0.5</td>
<td>11.1 ± 0.8</td>
<td>1117 ± 26</td>
</tr>
<tr>
<td>LDH-1</td>
<td>11.8 ± 0.4</td>
<td>1029 ± 18</td>
</tr>
<tr>
<td>LDH-2</td>
<td>12.9 ± 0.2</td>
<td>1218 ± 56</td>
</tr>
<tr>
<td>LDH-3</td>
<td>13.2 ± 0.4</td>
<td>1205 ± 31</td>
</tr>
</tbody>
</table>

by the linear fitting of all experimental data $P$ versus $1/DR$ according to the equation:

$$P = P_\infty - k_p 1/DR$$  \hspace{1cm} (9)

where $k_p$ is a proportionality constant taken into account the sensitivity of the property to the drawing. Following this approach, predicted attainable strength of the compositions with 2 and 3 wt % of the filler ($1218 \pm 56$ MPa for LDH-2, and $1205 \pm 31$ MPa for LDH-3) was slightly higher than $1180 \pm 50$ MPa of neat HDPE fiber, as presented in Table VII. Similar tendency was also observed in the case of the maximum attainable tensile modulus, that is, 12.9 GPa for LDH-2 and 13.2 GPa for LDH-3, with respect to 11.8 GPa of neat HDPE.

CONCLUSIONS

High density polyethylene (HDPE) and its composites with 0.5–3 wt % of organically modified hydrotalcite (LDH) were compounded and spun by combining melt-extrusion and hot-drawing at temperature between 100°C and 140°C. The most suitable drawing temperature was found to be 125°C for both the neat HDPE and nanocomposites. Fibers could be easily drawn at high draw ratios (up to 20) reaching linear density up of 9 tex and tensile modulus of about 10 GPa. In general, spinnability and drawability of the nanofilied polyethylene were found analogous to those of the neat HDPE.

The incorporation of LDH increased the thermal stability of composite fibers in comparison with HDPE. Moreover, crystallization kinetics indicates a nucleation effect of LDH on the HDPE matrix and evidences slightly enhanced temperature of the transition between Regimes II/III at 119°C for the composites containing 1–2% by wt % of LDH. Morphology and XRD analysis revealed a high degree of exfoliation of LDH in fibers containing 1–2% by weight of nanoclay, which was particularly evident after drawing. Consequently, tensile modulus of nanofilied fibers rose with the LDH content and drawing ratio. Tensile stress at break and strain at break of composite fibers approximately corresponded to those of the neat HDPE. Using the experimental data, a maximum value of elastic modulus of about $12.9–13.2$ GPa was obtained through stiffness extrapolation of the nanofilied fibers containing 2–3% of LDH (with respect to 11.8 GPa found for the neat HDPE).

Practically, the addition of nanoparticles has been found advantageous in terms of improvement of the thermal stability, and favorable for developing at least the same mechanical performances of polyethylene matrix. These beneficial effects can be attributed to a good dispersion of hydrotalcite particles, which promote molecular orientation and crystallization in the HDPE matrix and also act as thermal barriers.

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