Abstract

Efficient molecular orientation of polymers in the melt- or solution state requires concentric contraction flows, which result in single or multi-filament fiber shaped products. Directed molecular orientation in pipes, sheets, foils and films, like strip bi-axially, planar or tri-axial, are difficult to achieve and require complex multi-stage processing often supported by the addition of extra external magnetic, electric, or temperature gradient fields that put constraints to the materials to be processed. Here we aim at a simple continuous process to produce uni-axially oriented foils, by designing a special die in a standard miniaturized laboratory scale film casting process. The internal of the die consist of a fiber forming, and a fiber fusing part. The specific design of the fiber forming part allows the combination of the fibers formed, without them crossing, into a line that forms a sheet. Flow in the total volume around the slit ends up in molecularly oriented flow inside the slit. To preserve orientation, an air gap extrusion process follows the exiting slit flow, to allow for a strong draw down under high melt stress. Small air-gaps and a cold cooling nose, combined with a supporting carrying film, make the total process easy, clean and cheap, and the products unique. We will demonstrate that, mounted on the miniature Xplore MC 15 lab compounder, the device is able to produce not only high performance fully oriented foils based on a thermotropic liquid crystalline polyester (Vectra), but also extremely thin foils of polyamides and polyesters. In the last application, the melt orientation is used only to temporary obtain a high melt strength that allows a high draw-ability in the air gap.

Introduction

During the last years, we developed with and in Paul Smith’s Polymer Technology group at the ETH in Zurich, a new processing route to obtain, in one processing step, high-performance ultra-oriented foils and tapes. As a first test material we used the thermotropic liquid crystalline copolyester (based on p-hydroxybenzoic acid, HBA, and 2-hydroxy-6-naphthoic acid, HNA, as sold by Ticona under the trade name) Vectra, see Figure 1.

![Figure 1. The Vectra LCP used, with copolyester ratio HBA\textsubscript{0.73}/HNA\textsubscript{0.27}.](image1)

Optically clear foils, basically one huge single crystal of 10 micron thickness, 120 mm width and infinite length were produced, see Figure 2, with interesting properties, see Figure 3.

![Figure 2. The high performance foil produced.](image2)
Figure 3. Mechanical properties of the foils produced.

Finally, Table 1 summarizes some exceptional properties of the foils produced that could make them unique in producing objects.

Table 1. Properties advantage for making products.

<table>
<thead>
<tr>
<th>Property</th>
<th>Advantage</th>
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<tbody>
<tr>
<td>Processing MHA/HMA foils into monoliths</td>
<td>no matrix, infinite shelf life, non-toxic, ...</td>
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<tr>
<td>Good damping properties</td>
<td>of MHA/HMA retained in foils</td>
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<tr>
<td>Applicable also in classical composite lay-ups</td>
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<tr>
<td>Excellent barrier properties</td>
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<tr>
<td>High mechanical properties</td>
<td></td>
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<tr>
<td>Additional design freedom due to thin plies</td>
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<td>Translucent and novel appearance</td>
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</table>

**Principle of the die design**

The new processing route is on one hand based on a new die design and on the other on introducing, in the processing, air-gap extrusion (in analogy to air-gap spinning). The die, see Figure 4a, combines a fiber forming part with a fiber fusing part. The traditional coat hanger section, see Figure 4(b), is combined with an extra unit made to orient the melt or solution, see Figures 4c and 5, placed underneath.

Figure 4. The die used (a) (here bottom view) consist of a standard coat hanger section (b) combined with a orientation section (c) underneath, with details shown in Figure 5.

Figure 5. Details of the orientation section, *top:* side-view of the total fiber forming and fiber fusion section; *bottom:* top-view of the fiber forming section showing staggering of the fiber forming die-holes.

The details of the orientation section, see Figure 5, reveal that the hierarchical positioning of the fiber forming, 100 micron diameter, holes allows to combine all fibers in one single line in the mid plane, to be fused to form the foil, without them crossing, see Refs [1, 2] for further details.

**Principle of the process design**

Molecular orientation is introduced to the solution, or melt, in the upstream region of the fiber forming holes. It is beneficial for both: (i) a high melt strength during processing, and (ii) unique mechanical, optical and barrier properties of the product. Orientation must be preserved during fiber fusion in the part of the die below the fiber forming part, see Figure 5-top. And moreover during foil extrusion and draw down prior to by cooling. Maintaining orientation is preventing molecular distortion and randomization, and thus requires high axial stresses in the solution, or melt. High stress is most easily obtained by applying elongational flow. This is induced by stretching during draw down. Elongational stress in stretching is proportional to the processing speed and the draw down ratio, and inversely proportional to the stretch length. The last explains why air-gap extrusion is advantageously introduced in the process. This is clearly illustrated in Figure 6 where airgap drawing (coloured symbols) proves to be much more effective that standard draw down (grey symbols).
Figure 6. Experimental results of (top) modulus and (bottom) width development during draw down without (grey symbols) and with air gap extrusion (colored symbols). Different colors represent different stages of the optimization process, for details see Ref [1].

Top: Modulus development as a function of draw-down $\lambda = v_1/v_0$, with $v_0$ the extrusion velocity and $v_1$ the winding velocity.

Bottom: Decrease in width during draw-down, expressed in the $W_{\text{ratio}} = W_1/W_0$, with $W_0$ the extrusion width and $W_1$ the winding width. Colors show improved processing from batch to continuous, at higher speeds and introducing air gaps, see ref [1].

Figure 6 reveals the modulus development during draw down and indicates that only little of the upstream orientation is lost in the down stream process. Width retention is shown Figure 6 bottom showing that airgap extrusion also prevents width reduction during draw down. A real high performance tape is produced in the end.

A lab-micro-scale design

Xplore Instruments BV produces micro-scale polymer processing equipment, based on the unique performance and flexibility of the co-rotating MC 15 twin screw compounder. Where originally the focus was on speeding up product development, especially in the area of new materials, with typically small scale batch compounding, and one-shot molding, over the years an extension has been realized to also be able to study lab-micro-scale continuous processes. Mono- and multi-filament fiber spinning and simple tape making are examples. Pipe and tube making is under development. Here we focus on introducing the principles of high-performance tape and foil making technologies, to lab-micro-scale equipment. The result of the design of the small die is –in overview- shown in Figures (7) and (10), while Figures (8,9) reveal the details of coat-hanger part and the fiber forming and fusing part.

Figure 7. The high-tech foil die designed for the lab-micro-scale compounder.
It combines again a standard coat hanger die section, see Figure 8, with a fiber forming and fiber fusing part, see Figure 9. Since for flexible lab-micro-scale applications not only high performance foils are of interest, but also extremely uniform and thin films, the die gap is made adjustable.

The final result is shown in Figure 10.

**Discussion**

During the lecture, we will present the first results obtained combining this unique die with the continuous lab-micro-scale equipment that allows producing small amounts of products at high development speeds. The focus will be not only on high performance Vectra tapes, but also on ultra thin foils of, as is the case for the liquid crystalline polymers like Vectra, relatively low viscous polymers like polyesters (PET) and nylon (PA). In the future we will also use guided supported contraction flows, to stabilize up stream flows of higher viscous
Figure 11. Fiber forming and fiber fusing die made to process very high viscosity polymers like (solutions of) UHMWPE. (a) All individual die parts. (b) Fiber forming and fiber fusing section. (c) Fiber forming plate bottom. (d) Fiber forming plate top with conical contractions flows with 500 microns final hole size.

The die shows individual conical contractions and is made by a mold-less fabrication technology, using laser sintering of metal powder. The process limits the final diameter of the holes to 500 microns. But the exiting fiber pattern is very similar to the one in the low viscous die, compare Figure 5.

References
