Microcrystal alignment in drawn fiber over sub-meter to kilometer length scales

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Abstract

This paper describes a method for aligning stiff, high-aspect-ratio microcrystals over macro-length scales using a polymer fiber drawing process. A composite preform was constructed with an interfacial, liquid shell layer of grapeseed oil suspending ytterbium-doped potassium lutetium fluoride microcrystals (30% Yb:K₂LuF₅, KLF) between adjacent cylindrical surfaces of acrylic (polymethyl methacrylate, PMMA). The mean length of synthesized KLF microcrystals was 67 microns, and the mean aspect ratio, equivalent to crystal length divided by diameter, was eight. The acrylic-host preform was drawn into fiber, resulting in uniform reduction of all cross-sectional dimensions by a factor of approximately 20 in the final fiber. A corresponding width reduction of the interstitial liquid-filled gap, containing microcrystals between the polymer surfaces, constrains the microcrystals and causes alignment of the crystal long axes parallel to the axis of the drawn composite fiber. Alignment was best for clearly separated microcrystals and improved even further with the longest lengths, or highest aspect-ratio microcrystals.

Keywords Microcrystal alignment · Composite fiber · Macro-scale ordering · Fiber draw process

1 Introduction

Since the 1980's when carbon nanotubes were first reported, persistent attempts have been made to organize nanostructures and microcrystals [1–15], over macro-scale dimensions, in order to fully exploit their excellent crystalline properties, including mechanical, electrical, thermal, and optical properties [16–19]. Here we report on a method to align stiff microcrystals of aspect ratio on the order of 10, using geometric confinement within an interior liquid shell layer of a polymer-host, composite fiber.

The majority of previous reports on alignment processes are with carbon nanotubes. Jin et al. applied one-dimensional stretching to achieve alignment of carbon nanotubes in a polymer matrix [1]. They found that sample elongation of 330% led to 23% alignment in the normal stress/strain direction for most (58%) of the carbon

nanotubes. They also learned that stretching ratios positively correlate with degree of alignment, and that concentration of nanotubes correlates negatively with alignment. They further concluded that the nanotube's aspect ratio and stiffness both play key roles in the ease and degrees of alignment that can be achieved using one-dimensional stretching. Badaire et al. improved the alignment degree of single-walled carbon nanotubes (SWNT) via the application of a tensile load [2]. Similarly, Haggemuller et al. achieved SWNT alignment through melt-spinning of composite polymer fibers [3].

Baik et al. explored the alignment of carbon nanofibers embedded in copper preforms [4]. Multiple extrusions through dies and several rounds of mechanical drawing were performed to achieve high degrees of alignment, although their carbon nanofibers were entangled and less rigid than carbon nanotubes. The final degrees

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of nanofiber alignment were unmeasured, but tensile strengths of their most highly aligned carbon-nanofiber/copper (CNF/Cu) composites were approximately double that of unaligned CNF/Cu composites.

High-density arrays of aligned nanostructures were achieved in ordered matrices, including electrodeposition into a porous anodic alumina template [5, 6] as well as electrodeposition into the pores of a polymer membrane [7]. Further attempts at aligning nanotubes, nanofibers, and nanowires have included electrospinning [8], micro-combing [9] and evaporation processes [10]. Zhang et al. applied mechanical shear forces between two glass planes to align nanowires [11], and magnetic nanostructures have been aligned with the aid of magnetic fields [11, 12]. Aluminum nanowires were deposited in thin lines on silicon wafers using an evaporative dip coating process, utilizing surface tension and fluid capillary forces to partially align the nanowires [13].

Kinowski et al. first aligned nano-cylinders using an optical fiber drawing process [14]. Their focus was on the synthesis of YbPO_4 nano-cylinders within a preform as it was being drawn into optical fiber. They reported very good alignment of their nano-cylinders synthesized within the preform/drawn fiber, but did not quantify the degree of alignment in any way, mentioning only in conclusion that alignment is favorable to reducing light scattering in an optical fiber. Vermillac et al. utilized a fiber drawing process [15] and attempted to “elongate and break” nanoparticles within the core of silica optical fibers; the goal was to fine tune the resulting sizes and shapes of the formed nanostructures. Though they reported on nanostructure alignment within the drawn fiber, this did not appear to be a primary focus of their work.

Herein we describe a fiber drawing process to achieve nearly complete alignment of small-scale (micro) tubes, wires or crystals over macro-length scales, from sub-meter

to kilometer distances. The preform-to-fiber drawing process is a batch process ideally suited to strategic placement of micro (or nano) structures within an interior fluid layer of a polymer-host preform. Upon drawing a preform that contains a thin interior (non-volatile) fluid layer, the polymer's inner and outer dimensions transverse to the drawing direction are uniformly reduced by as much as a factor of 10^2 typically, while the drawn fiber length increases up to an order of 10^4 , relative to the original preform length. Since the fiber drawing process is volume-conserving and behaves as nearly one-dimensional “permanent stretching,” it is feasible in either single or multi-stage drawing operations to geometrically constrain stiff, small-scale (micro or nano) structures of sufficiently high aspect ratio (from three up to about 13 in this work) such that the long axes can only align parallel to the composite fiber axis.

2 Polymer preform assembly

A polymethyl methacrylate (PMMA) preform was assembled by placing a smaller (nominal 3/8") diameter rod inside a larger (1/2" outer) diameter thick-walled tube, with a thin gap between the polymer rod and tube; the gap within the preform was filled to contain a liquid suspension of microcrystals. Scaled cross-sectional diagrams of the composite preform with *exaggerated* gap widths, all in metric units, are shown in Fig. 1. While both the rod diameter and inner diameter of the surrounding tube were nominally 3/8th inch, caliper measurements indicated the actual rod diameter closer to 9.30 mm and inner diameter of the tube $\approx$ 9.65 mm. Ytterbium-doped potassium lutetium fluoride (30% $\text{Yb:K}_2\text{LuF}_5$, KLF) microcrystals [20] were suspended in grapeseed oil, and this mixture was filled into the thin gap between the polymer rod and surrounding tube of the preform.

Fig. 1 **a** Cross-section of concentric preform with caliper measured diameters. Oil-filled (crystal-laden) gap widths are *exaggerated* for clarity in **a** concentric and **b** acentric cases

For the idealized case of a preform rod positioned concentrically within the surrounding tube, the liquid suspension of microcrystals in the gap is approximately 180 microns wide as shown in Fig. 1a. In the actual assembled preform, the rod and surrounding tube's center axes are approximately parallel but rarely coincident; thus, the gap width in the preform, containing the suspension of microcrystals, is as wide as 360 microns as shown in Fig. 1b.

A short five-centimeter-length preform section containing the liquid suspension of KLF microcrystals was grafted into the mid-length of a ~60 cm full-length acrylic preform. Common grapeseed oil was chosen for its refractive index contrast with KLF microcrystals (easing visualization of microcrystals/oil via optical microscopy), and its smoke point of 216 °C, which is comparatively higher than peak temperatures (~170 °C) during the acrylic fiber drawing process. To drive off moisture absorbed by the acrylic (on the shelf), the full-length rod and tube assembly (nominal $1/2'' = 12.7$ mm outer diameter preform) was heated inside a drying furnace at 80 °C for one week prior to drawing it into smaller (< 1 mm outer) diameter composite fiber.

3 Polymer fiber drawing process

As illustrated in Fig. 2, the polymer fiber drawing process reduces the outside diameter D of a preform to a final fiber outer diameter d , via applied tension with axisymmetric radiative and convective heating in an enclosed furnace; the process is described in detail elsewhere [21], and in these experiments, a draw-down ratio D/d of approximately 20 was used, yielding a final fiber outer diameter between 0.6 and 0.8 mm. Fiber samples from this batch drawing process were collected within the initial two-hour transient period of the draw. "Steady-state" drawing would have yielded a narrower range of fiber diameters, with $d \approx 12.7 \text{ mm} \div 20 \approx 0.64 \pm 0.01 \text{ mm}$, but the crystal-laden preform section was drawn before steady-state conditions were obtained.

In the idealized case of a concentrically assembled preform and concentric fiber (cross-section similar to Fig. 1a), the crystal-laden liquid layer is reduced from an original width of 180 microns in the preform to about $(180 \div 20 =)$ nine microns in the final fiber. In the most extreme case however, where the fiber's core rod is immediately adjacent to an inner wall of the surrounding tube (similar to Fig. 1b), the widest liquid gap in the drawn composite fiber is estimated to be approximately $360 \div 20 \approx 18$ microns.

Fig. 2 Polymer fiber drawing process, illustrating a reduction of preform diameter D to fiber outer diameter d , via applied tension and axisymmetric heating; the draw down ratio $D/d \approx 20$

4 Microcrystal morphology and geometric constraints

The KLF microcrystals used in these experiments have a mean diameter of 8.4 microns (distributed from two to 18 microns), with lengths (mean of 67 microns) ranging from 20 to 120 microns as shown in Fig. 3. Microcrystal dimensions were obtained from a sample set of about 30 microcrystals, representing ~7.5% of an estimated total ~400 microcrystals incorporated within (a five-centimeter-length section grafted at the mid-length of) the acrylic preform. The aspect ratio (length/diameter) of most microcrystals in the sample set was about eight.

With a nominal concentric liquid gap width of ~180 microns in the preform's cross-section (Fig. 1a), the microcrystals are relatively free to orient in any direction within this fluid layer. However, as the preform is drawn into fiber, the liquid gap width is reduced by a factor of ~20, such that

Fig. 3 Microscope image of KLF microcrystals with length and diameter characterizations. Aspect ratio (length/diameter ratio) of most microcrystals is about 8, ranging from three to 13

the microcrystal mean diameter (8.4 microns) and the concentric liquid gap width (~ nine microns) are relatively close in scale; thus, the stiff KLF microcrystals are geometrically constrained to “funnel down” in the fluid cylindrical shell and orient with long axes parallel to the drawn fiber axis. Note that the acrylic polymer material goes through “glass transition” and never becomes liquidous, even as it is drawn; hence, the moving acrylic surfaces function as barrier walls, impenetrable by the stiffer KLF microcrystals suspended in liquid oil.

Figure 4 illustrates a vertical plane through the acrylic “solid” sections and (an exaggerated width-scale) liquidous layer, laden with microcrystals, as the preform necks down ($D/d \approx 20$) from an outer diameter $D \approx 12.7$ mm to a final fiber outer diameter $d \approx 0.64$ mm. The corresponding liquid gap in the composite fiber typically ranges from nine microns (idealized concentric case) to a maximum of ~ 18 microns in width, depending on the acentricity of the outer polymer tube and enclosed rod. In sufficiently high concentrations, microcrystals may be present within the liquid oil layer at any azimuthal coordinate; the rod and tube of the fiber are thereby constrained by geometry to be concentric on average over sub-meter and greater lengths.

5 Alignment results

The aforementioned drawing process resulted in relatively high degrees of microcrystal alignment as shown in Fig. 5. Alignment was poor in areas where KLF crystals were clumped or linked together (as in the linked V-shaped microcrystal in Fig. 5). Excellent alignment appears to occur along significant fiber lengths wherever microcrystals are clearly separated.

Using open-source ImageJ software, the degree of microcrystal alignment is characterized in Fig. 6 as a function of crystal length; this plot is for a small sample set of 16 crystals, excluding several crystals that were linked together. For all isolated crystals, the measured off-angles in the image plane were less than three degrees from the fiber axis. Longer crystals approaching a length of 100 microns, with higher aspect ratio, show better alignment compared to shorter crystals. This finding is consistent with known geometric constraints for longer crystals: because the KLF microcrystals are stiff, suspended in liquid oil, and geometrically constrained

Fig. 4 Crystal-laden liquid layer in the preform **a** is reduced in width by the same factor as the outer diameter; expanded view **b** illustrates resulting geometric constraint of microcrystals

Fig. 5 Microscope image of drawn composite fiber with incorporated KLF microcrystals

by two interior curved polymer surfaces, the longest cannot orient to any significant extent off-axis.

6 Conclusions

A method of drawing fiber from a polymer preform with an internal liquid interface layer containing stiff, high-aspect-ratio microcrystals has been developed to align the crystal long axes parallel to the fiber axis within several degrees, over macro-length scales. In regions of the drawn

fiber where individual crystals occur over the full range of azimuthal coordinates, the crystal-laden oil interface remains nearly concentric in the composite fiber, since the center rod of the fiber is geometrically constrained by surrounding crystals and the outer tube material. Where crystal “clumps” occur, the fiber’s core rod is not concentric with the outer surface of the fiber, and in such cases, those clumped crystals cannot align parallel to the fiber axis.

This method of geometric confinement resulting in axial alignment of stiff, long microcrystals may be extended from the current work to (stiff, long) nanocrystals. The

Fig. 6 KLF microcrystal alignment as a function of crystal length

criterion for obtaining a high degree of alignment with much smaller nanoscale crystals, (nanotubes or nanowires,) is to produce cylindrical shell gap widths slightly larger but very close to the nanocrystal diameters, using the aforementioned drawing process or a process similar to it. In a dual-stage polymer drawing process for example, an original micro-gap of ~ 200 microns within a preform can be reduced by a factor of 100 in the first draw and by a factor of 100 again in a second-stage draw, resulting in a final liquid shell gap width of ~ 0.02 micron or 20 nm. Multistage polymer drawing processes are feasible for even greater reductions in cylindrical shell gap widths to achieve alignment of stiff, long nanocrystals, nanotubes or nanowires of practically any diameter, provided the diameter distribution is sufficiently narrow.

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Availability of data The data that support the findings of this study are available from the corresponding author upon request.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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