

Metastable structures, interplay of sequential deformations, and interactions between tungsten disulfide nanotubes and poly(L-lactide) studied by *in situ* X-ray scattering

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Polymer crystallization, particularly near the glass transition, exhibits strong nonlinearities and prolonged metastability that enable fabrication of devices with complex hierarchical structure from nm to mm. A fascinating example arises in the production of bioresorbable scaffolds (BRS) from poly(L-lactide) (PLLA), in which a sequence of processes (extrusion, stretch-blow molding and crimping) create diverse semicrystalline morphologies, side-by-side within a span of a hundred microns (**Figure 1**). To discover how these structures form, we need to examine transient structure under conditions that mimic manufacturing processes. An apparatus that enables scattering measurements during the stretch-blow molding step, called “tube expansion” imposes a nearly constant-width elongation as it converts an extruded “preform” into an “expanded tube”. To increase the range of accessible properties of PLLA-based BRS, we use this apparatus to examine inorganic nanotubes as potential reinforcing agents that also enhance radiopacity, relevant to clinical applications. Understanding how their microstructure develops during processing is relevant to increasing strength to enable thinner devices and improving radiopacity to enable imaging during implantation. Consistent with the premise of this MS, *in-situ* X-ray scattering reveals unanticipated phenomena in the transient microstructure of PLLA/WS₂NTs nanocomposites during “tube expansion” (**Figure 2**).

Surprisingly, the WS₂NT orientation hardly changes from that produced during extrusion of the preform (z-dir., defined Fig. 1A),

despite significant strain in the transverse direction (at inner diameter, 500% strain in θ -dir.). Although WS₂NTs promote PLLA nucleation, the NTs do *not* modify the orientation of crystallization (c-axis along θ , just as observed in tube expansion of neat PLLA). The striking independence of the orientations of the NT and polymer crystals stems may arise from the favorable interaction between PLLA and WS₂NTs: facile and stable dispersion of WS₂NTs in PLLA enables strong NT orientation in shear (extrusion); NT that are orthogonal to the stretching direction do not reorient; remaining orthogonal to decouples WS₂NT orientation from that of PLLA crystals. Future directions include evaluating cross-reinforcement of the mutually orthogonal NT and PLLA crystals. Based on the surprising effects we have found, further discoveries likely lie ahead in the effects of WS₂NT on morphology development during crimping.

Keywords: stretch-blow molding; WS₂NT; flow-induced crystallization; microdiffraction; SAXS/WAXS

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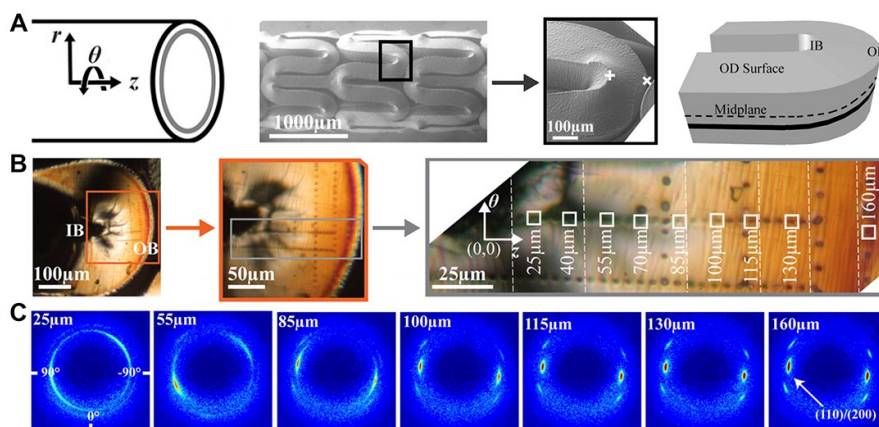


Figure 1. Diverse morphologies form during manufacture of PLLA bioresorbable scaffolds: **A.** a thin-walled (150 μm) tube, created by “tube expansion”, is laser cut and crimped. **B.** Polarized light micrographs guide microdiffraction. **C.** Morphology changes from weakly-oriented to highly-oriented over 150 μm .

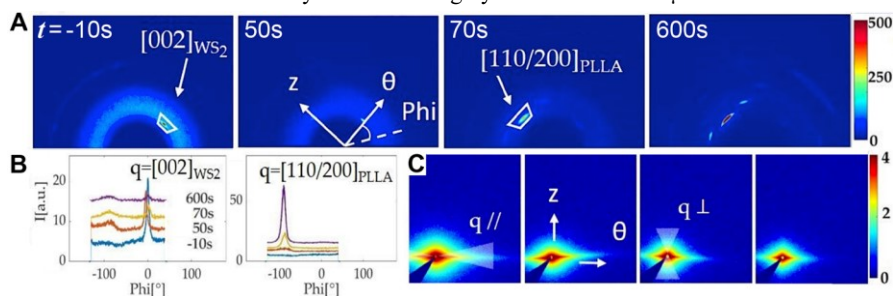


Figure 2. During “tube expansion”, WS₂NT orientation and PLLA crystallization are probed by **A,B.** WAXS and **C.** SAXS. Initially, PLLA is amorphous and WS₂NT are aligned along z. Heating begins at $t=0$ from 25°C to 80°C at 0.5°C/s; internal pressure of 7 bar is imposed at $t=30\text{s}$ ($T=40^\circ\text{C}$); elongation in the θ -direction stops at $t \cong 90\text{s}$ ($T \cong 70^\circ\text{C}$) when the sample meets the mold walls. After $t \cong 110\text{s}$, the sample is isothermal at 80°C.