

A CONTINUOUS METHOD FOR MANUFACTURING POLYMER STRINGS AND TUBES

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ABSTRACT

We present a method for the continuous manufacture of micro scale polymer strings and tubes. The method utilizes hydrodynamic focusing and liquid phase photopolymerization. A number of different strings and tubes are demonstrated including the ability to control local properties. Strings and tubes are used in many applications. By including active biomolecules within the micro strings, biosensing strings are demonstrated.

INTRODUCTION

In nature, spiders produce a liquid that solidifies when exposed to air. Here we present an analogous process replacing spontaneous solidification via exposure to air with light initiated solidification. By utilizing 3D multiple stream laminar flow [1] and *in situ* photopolymerization [2], we create a continuous process for the creation of micro scale cylindrical structures.

Strings and tubes are perhaps the most common curved object in both the natural and man-made world enabling a plethora of functions across fields (e.g. medicine, biotechnology). Recent advances in man-made micro scale systems have largely relied on planar two and three dimensional (3D) geometries inherent to integrated circuit derived processes. Recent soft material-based micro systems have provided alternatives in functionality via elastomeric [3] and stimuli responsive materials [2], but their origins are still rooted in pseudo 3D constructs. Extrusion/casting [4], layering [5], or fugitive [6] processes have been used to create small-scale strings and tubes. While these approaches have merit, all have limitations associated with solid-solid and extraction effects for the production of micron-scale tubes or fibers in continuous lengths. The process presented here is conceptually simple using microscale phenomena (e.g. laminar flow, diffusion) and readily scalable to large volume manufacturing. Importantly, the process also allows flexibility in materials choice while providing control over local material properties.

RESULTS AND DISCUSSION

To make micro fibers, the polymerizable sample fluid (4-Hydroxybutyl acrylate (4-HBA)) and non-polymerizable sheath fluid (50 Vol% Polyvinylalcohol (PVA) + 50 Vol% DI water) are combined in stage X of the apparatus illustrated in Fig. 1 to produce a stable sheath flow around a sample stream. Next, the concepts of *in situ* and liquid phase photopolymerization are extended to “on the fly” photopolymerization (i.e. continuous radiation of a moving liquid) to polymerize the sample stream as it flows towards the outlet of the channel. There is no moving solid-solid interface, but rather the moving sample stream is transformed to a solid in a continuous process. By changing the sample and sheath flow rates, the size of the polymerized microstructure can be easily and precisely controlled (Fig 3). By adding a second stage to the apparatus (Fig. 1, left dotted square), micro tubes are fabricated (Fig. 2 bottom; Fig. 5 left). Into stage Y, the core fluid

(25 Vol% PVA + 75 Vol% DI water) and sample fluid (4-HBA) are introduced and a core surrounded by sample flow is produced. The core/sample flow then enters stage X where a second sheath fluid (50 Vol% (PVA) + 50 Vol% DI water) is introduced producing a core/sample/sheath flow construct. Upon subsequent and continuous UV exposure, micro tubes are continuously formed.

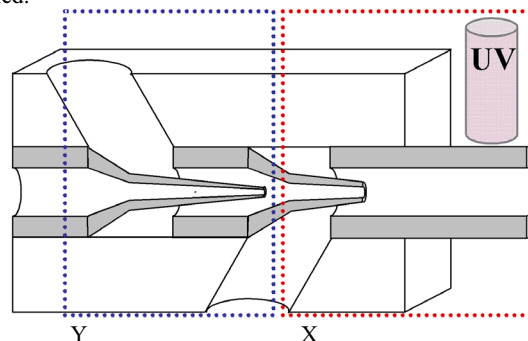


Figure 1. A schematic diagram of the first (right dotted box) and second stage (left dotted box) channel apparatus. A micropipette puller (P-87, Sutter Instrument Co.) was used to produce the pulled micropipettes with inner diameter of approximately 20 μ m.

Examples of the types of strings and tubes produced are shown in Fig 2. Importantly, the use of laminar flow and diffusion enables the local control of the physical and chemical properties of the resultant fibers and tubes. This concept is demonstrated by using two different fluids (one containing a dye and one without the dye) to form the sample stream; the resultant fiber contains a gradient of this dye (Fig. 4). The continuous nature of the process will allow one to scale a simple responsive swatch (Fig. 6) into cloth while simultaneously incorporating local functionality via parametric control combined with upstream microfluidic processing. For example, a “t” channel junction upstream of stage Y enables the creation of local packets within the sample fluid streams providing chemical and physical control of the fibers/tubes along their length while diffusion/gradients allow control along their width. By entrapping enzymes into the sample stream, sensing strings can be mass-produced [7] (Fig. 5 right demonstrates a glucose sensing string).

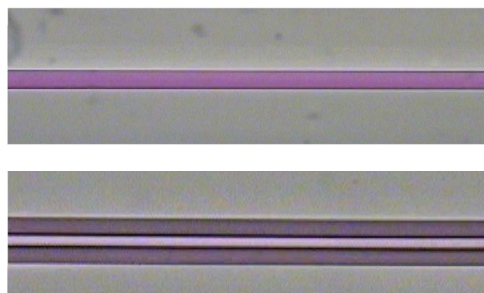


Figure 2. Top – String output from the first stage (sheath and sample flow). Bottom – Tube output from both stages (sheath, sample and flow flow).

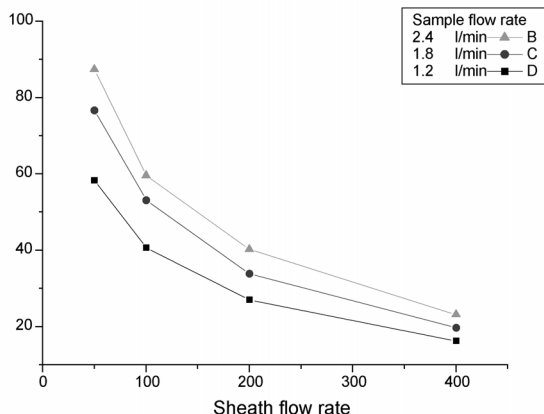


Figure 3. String diameter (x axis, um) is a function of sample and sheath flow rate. Note strings with outer diameters under 20 microns have been made in our first attempts. Much smaller strings should be possible with optimization of the process.

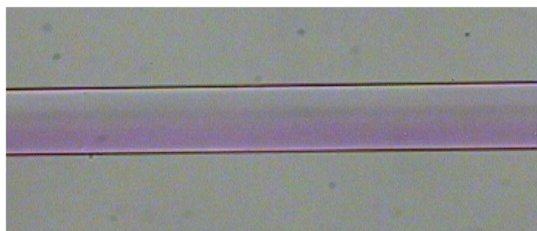


Figure 4. A gradient is produced from top (low) to bottom (high) across the string.

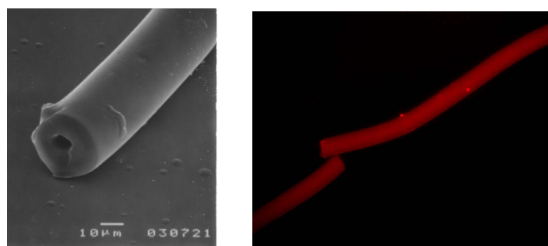


Figure 5. Left - A scanning electron micrograph of a micro tube. Right - Fluorescent image of a glucose sensing string.

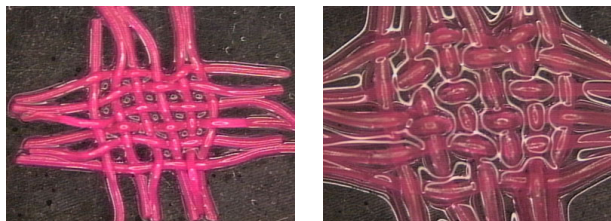


Figure 6. A patch of woven strings made of pH responsive polymer. Left - unswollen, right - swollen.

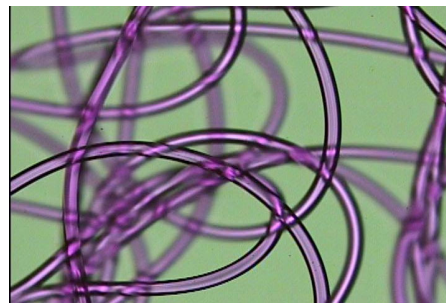


Figure 7. A jumble of micro polymer string produced using the continuously flowing liquid phase photopolymerization process.

CONCLUSION

The ability to continuously manufacture micro scale fibers and tubes cost effectively will facilitate their use in many applications. The flexibility of the method across different materials, geometries, and scales is a key advantage over many existing methods that require some form of re-tooling to realize different outcomes. By controlling the flow parameters (steady and time varying hydrodynamic focusing), polymerization parameters (time, distance, intensity), and material parameters (stimuli responsive, viscosity) a wide variety of physical and chemical properties (chemical composition, geometry, scale) can be achieved using a single manufacturing system. Natural shapes can now be readily produced enabling biomimetic designs for medicine (e.g. smart stents, tubular scaffolds) and biotechnology (e.g. embedded functionality, artificial xylem, sensors).

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