HIGH-THROUGHPUT MILLI-FLUIDIC PLATFORM FOR POLYMER FORMULATIONS

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Introduction

Scientific insight into complex polymer formulations in the coatings and surfactant industries requires the exploration of a multi-parameter space that includes varying amounts of key components and appropriate processing conditions (e.g., temperature, time, hv dose and duration), and correlating these to final product properties.^{1,2} Quantitative, insightful materials studies have been previously demonstrated at the NIST Combinatorial Methods Center (NCMC) in the areas of thin films and bulk materials properties.³⁻⁷ Milli-fluidic handling will complement existing high-throughput and combinatorial capabilities to increase the dimensions of parameter space that are available to accurate and systematic study of polymer solutions. These new capabilities in fluid handling and measurements will also enable generation of new knowledge in the field of polymer formulations, which is presently dominated by empirical knowledge.

Rapid prototyping of microfluidic handling devices has gained in popularity due to the ability to quickly test and modify new design features several times in one day.⁸⁻¹³ While elastomer-based methods have dominated the literature and are remarkably well-suited to life sciences research, there are certain limitations that make the structures prepared by these methods inappropriate for broader application in polymer science. Most notably, the limitations of small vertical dimensions accessible by soft photolithography and the limited solvent resistance of elastomeric networks restricts the development of a robust platform for testing multi-component complex fluids.

Experimental

Common microfluidic fabrication techniques were modified to extend their use to organic fluids. This has allowed the preparation of new types of combinatorial libraries and development of new measurement methods to complement the small sample sizes of these libraries. Most importantly, it can be used to tie together multiple stages of the formulation process, from the synthesis of raw materials to the measurement of complex-fluid properties, into small, inexpensive and simple platforms. The NCMC's first demonstrations of this technology are in the areas of emulsions and polymer blends.

UV curable adhesives were used to create molded resins with increased solvent resistance (Figure 1).¹³ The range of depth (100 μ m to several millimeters) is much higher than available in most other rapid processes. The lateral dimensions range from 10's μ m up to millimeters and are determined by the mask, which is printed on a transparency using a standard laserjet printer (resolution ≥ 600 dpi). These features are particularly important in developing tools for handling the flow of polymer solutions because their viscosities often generate back-pressures that become tenable in channels with these larger length scales, typically on the order of hundreds of microns.



Figure 1. Examples of active (a) and passive (b) mixing devices integrated into measurement schemes.

Results

This fabrication method has been used to prepare sample well arrays for measuring properties of polymer blends such as phase separation. Channels for carrying out polymer chemistry, measuring interfacial behavior and controlling flow type are under development.¹⁴

As an example, a simple multi-capillary viscometer has also been fabricated. The principle of operation is simple and works well with Newtonian fluids. The fluid velocity through a channel of known dimensions is measured for a given pressure drop and the viscosity is then calculated. For a cylindrical channel, the well-known equation for a capillary viscometer is used:

$$\eta = \frac{\pi R^4 \Delta P}{8QL}$$

where R is the radius of the capillary, ΔP is the pressure drop, Q is the volumetric flow rate, and L is the length of the capillary. Although this device works best with Newtonian fluids, shear rate dependence may be explored along with potential wall slip effects by varying the channel dimensions and pressure drop. The advantage of the capillary viscometer is its ease of use and the straightforward calculation of the apparent viscosity. Figure 2 displays one such device constructed in our laboratory where an array of channels are used to access different shear rates.



Figure 2. Milli-fluidics chip viscometer.

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References:

- (1) R. Dagani, Chem. & Eng. News, 2003, 80, 58.
- R. Hoogenboom, M. A. R. Meier, U. S. Schubert, *Macromol. Rapid Commun.*, 2003, 24, 16.
- J. C. Meredith, A. Karim, E. J. Amis, *Macromolecules*, 2000, 33, 5760;
 J. C. Meredith, A. P. Smith, A. Karim, E. J. Amis, *Macromolecules*, 2000, 33, 9747.
- (4) A. P. Smith, J. F. Douglas, J. C. Meredith, E. J. Amis, A. Karim, *Phys. Rev. Lett.*, 2001, 87, 015503.
- (5) C. M. Stafford, C. Harrison, A. Karim, E. J. Amis, Am. Chem. Soc., Polym. Preprints, 2002, 43, 1335.
- (6) K. L. Beers, J. F. Douglas, E. Amis and A. Karim, *Langmuir*, 2003, 19, 3935.
- (7) A. J. Crosby, A. Karim, E. J. Amis, Adv. Mat., 2003, 41, 883.
- (8) G. M. Whitesides, A. Stroock, Phys. Today, 2001, 54, 42.
- (9) S. R. Quake and A. Scherer, *Science*, 2000, 290, 1536.
- (10) D. J. Beebe, J. S. Moore, Q. Yu, R. H. Liu, M. L. Kraft, B.H. Jo, C. Devadoss, P.N.A.S., 2000, 97, 13488.
- (11) D. J. Beebe, J. S. Moore, J. M. Bauer, Q. Yu, R. H. Liu, C. Devadoss, B. H. Jo, *Nature*, **2000**, 404, 588.
- (12) T. Thorsen, S. J. Maerkl, S.R. Quake, Science, 2002, 298, 580.
- (13) C. Harrison, J. T. Cabral, C. M. Stafford, E. J. Amis, A. Karim, in preparation.
- (14) S. D. Hudson, R. R. Phelan, Jr., J. T. Cabral, in preparation.