Honors College Thesis Proposal

Introduction

Patterning of surfaces with submicron pits or the negative, submicron bumps, is very important in several technologies. These pits can be used as nanovessels for micro/nano chemistry. Or, if the material is thin and the pit is able to extend through the surface a pathway for controlled transport would be made. Patterned arrays of these pits can be used as molds for submicron lens formation, which has applications in data transmission, copy machines, and laser printers.[1] These arrays, patterned or not, can affect the washing, printing, painting, and coating properties of surfaces as well.[2-5] For instance, the submicron raised bumps on the tree frog's toe pad provides the organism with its adhesion ability.[6]

We already know that pits can be formed on polymers through the use of volatile solvents.[7-10]. Using an ink-jet system to deposit drops of toluene on polystyrene, Bonaccurso et al.[7] produced patterns of pits as small as 20 µm in diameter, with aspect ratios (depth-to-diameter) as high as 0.1. This pit formation was decided to be due to the "coffee stain effect," where polymer dissolved near the center of the drop is transported to the perimeter and deposited as the solvent evaporates. (A similar process produces ring-like stains when coffee is spilled on a hard surface.[4])

I will attempt to characterize the formation of pits on poly-(methyl methacrylate) (PMMA) films by the condensation of small acid drops from formic acid vapor. Formic acid is a strong solvent for PMMA and has a high vapor pressure at room temperature. Under these conditions, pit formation is strongly affected by the kinetics of drop growth and coalescence, and should be able to be modified by exposing the polymer film to ammonia vapor immediately after exposure to formic acid.

With vapor condensation the pits will be randomly distributed but high pit densities will be easily achieved. These pits should be much smaller than the pits formed by Bonaccurso et al.7 and will hopefully have higher depth-to-diameter ratios due to the smaller radii of the droplets.

Research Question and Hypothesis

We will test the hypothesis that we can, utilizing the coffee stain effect and vapor deposition, improve upon previous methods of forming micron and sub-micron diameter pit features on the surface of a polymer, namely poly(methyl-methacrylate) (PMMA), with formic acid by a using new method of drop deposition. We hypothesize that our new method will decrease the diameters of the resultant pits, vastly increase the efficiency of nanometer-scale pit formation, and result in a much more economic method for fabricating polymers with similarly patterned surfaces.

Methodology

Materials. Glass microscope slides (Precleaned Gold Seal Micro Slides from Becton, Dickinson, and Company) will be used as received. A 15% by weight solution of poly(methyl methacrylate) (Aldrich, $M_w \approx 145{,}000$ amu) powder in a mixture of 67% propylene glycol methyl ether acetate and 33% γ-butyrolactone will be prepared. A few drops of polymer solution are placed on a glass slide, spun at 500-1000 rpm for 10–30 s, and baked at 95 °C for one hour. The resulting films should be 5-15 µm thick. Formic acid solutions will be prepared from purum grade (≥ 98%, Fluka), or reagent grade (88%, J.T. Baker) solutions, diluted with deionized water. Reagent grade ammonium hydroxide (28-30%, J.T. Baker) will be employed in some experiments.

Instruments. The resulting pits will be imaged with a Molecular Imaging PicoScan atomic force microscope (AFM) using square-pyramidal tips with tip angles of 70° ± 4°, and nominal radii of curvature of 20 nm (maximum 60 nm). The nominal cantilever forces constants are between 0.06 Nm^{-1} and 0.60 Nm^{-1}. Nanoindentation experiments will be performed with a Hysitron Triboscope and Nanoinstruments Nanoindenter II with a 3-sided pyramidal diamond Berkovich tip at loads from 25 to 400 µN and loading rates between 2.5 and 40 μNs^{-1}.

Methods. Formic acid drops will be condensed onto a PMMA-coated glass slide by holding the slide (PMMA side down) over a 400 mL beaker containing 20 mL warm formic acid. The solution temperature will be controlled with 300 mL water bath in a 14.5 cm diameter dish; unless otherwise noted, the reported temperature is that of the bath. In some cases, the slide will then be immediately exposed to ammonia vapor by holding the slide over a 400 mL beaker containing room temperature (RT) ammonium hydroxide. The slide will then be removed, allowed to dry 1-50 minutes, and imaged by AFM.

The dimensions and net volumes of the selected pits will be calculated from the AFM images with a Mathematica® program. The program identifies image pixels lying above and below the flat background surface and sums the volumes associated with each set of pixels. The difference between the volume of the elevated regions and the depressed regions corresponds to the net volume change. Pit diameters, depths, average heights, average depths, and average diameters were also determined.

The hardness and Young's modulus of PMMA material both inside and outside the pits will be determined from nanoindentation measurements.

Expected Results

Our new vapor condensation method should both decrease the diameters and increase the aspect ratios (ratios of pit depth to pit diameter) of our micron and sub-micron scale pits relative to previous ink-jet drop technologies. Although our method will sacrifice control over specific pit location, formic acid vapor condensation produces orders of magnitude more pits per experimental setup relative to the ink-jet drop deposition method.[7]

We expect the net volume change of the pits to be positive to coincide with previous work.[7] This change in volume should be due to a local decrease in density of the polymer exposed to the solvent. Increasing the length of exposure time to the warm solvent vapor should increase the diameters of the resultant pits somewhat linearly for particular conditions. The effect of formic acid concentration is expected to follow this linear pattern as more concentrated solutions produce deeper features. Since the shape of a drop is a function of its surface tension an increase in the surface tension should produce higher contact angles for the droplet on PMMA. This can be achieved by exposing the film to formic acid and then ammonia vapor. The ammonia should react with the formic acid to form an electrolyte, thereby increasing the surface tension greatly.[9]

Annotated Bibliography

1. M.C. Wu: Micromachining for optical and optoelectronic systems. *Proc. IEEE* **85,** 1833 (1997).
    a. This article discusses the formation and use of lenses in the optical systems outlined in the introductory paragraph.

2. N.D. Denkov, O.D. Velev, P.A. Kralchevsky, I.B. Ivanov, H. Yoshimura, and K. Nagayama: Mechanism of formation of two-dimensional crystals from latex particles on substrates. *Langmuir* **8,** 3183 (1992).
    a. References 2-5 detail the applications of surface patterning and the effects of these treatments on the surface properties.

3. A.B. El Bediwi, W.J. Kulnis, Y. Luo, D. Woodland, and W.N. Unertl: Distributions of latex particles deposited for water suspensions, in *Hollow and Solid Spheres and Microspheres: Science and Technology Associated With Their Fabrication and Application*, edited by D.L. Wilcox, Sr., M. Berg, T. Bernat, D. Kellerman, and J.K. Cochran, Jr. (Mater Res. Soc. Symp Proc. **372**, Pittsburgh, PA, 1995), p. 277.

4. R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S. Nagel, and T.A. Witten: Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **389,** 827 (1997).
    a. This paper is important because it lays out the method of formation for these craters and is cited as the method of formation for pits produced by ink-jet liquid deposition.

5. P. Laden, editor: *Chemistry and Technology of Water Based Ink* (Blackie Academic, London, 1997).

6. G. Hanna and W.J.P. Barnes: Adhesion and detachment of the toe pads of tree frogs. *J. Exp. Biol.* **155,** 103 (1991).
    a. This article is very important as it pertains to the actual method of attachment/detachment of the tree frog toe pad, which was debated for quite some time. Some thought the method was the use of a glue-like substance or a mucous membrane while others thought there was some sort of suction cup. The results of this paper indicate the method of attachment is based solely on the structural properties of the toe pad. This paper is so important because the negative of some of our formed structures are very similar to the tree frog toe pad topography.

7. E. Bonaccurso, H-J. Butt, B. Hankeln, B. Niesenhaus, and K. Graf: Fabrication of microvessels and microlenses from polymers by solvent droplets. *Appl. Phys. Lett.* **86,** 124101 (2005).
    a. This article details the formation of pits in a polymer through the use of solvent. The difference, however, is the application method as Bonaccurso et al. used liquid drop deposition as opposed to solvent vapor condensation. References 7 and 8 both outline the formation of pits on polymer surfaces through the use of solvents.

8. G. Li, H-J. Butt, and K. Graf: Microstructures by solvent drop evaporation on polymer surfaces: Dependence on molar mass. *Langmuir* **22,** 11395 (2006).

   a. This reference details the structure formation on polymers due to solvent drop evaporation. This paper is dissimilar to ours in that it tests the dependence on the molar mass of the polymer and the deposition method is the use of liquid solvent in a syringe.

9. A.W. Adamson and A.P. Gast: *Physical Chemistry of Surfaces*, 6th ed. (Wiley, New York, 1997).
   a. This book contains information about the effect of the formation of an electrolyte on the surface tension of liquids. From this we obtain the idea that the formation of an electrolyte in our vapor deposited drops should increase the contact angle of the drops and the results pit depth-to-diameter ratios.