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Adaptive polymer particles

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Adaptable polymer particles that can change geometry, flow characteristics, and adsorption properties upon the stimulation of an environmental change, such as temperature, are fabricated by utilizing the residual stress developed at the interface of a bilayer. We propose a phase diagram that can be used to predict the shape and size of the adaptive polymer particles as a function of the material modulus, thickness ratio, and the bilayer's lateral dimensions. The materials used are gold/titanium and polydimethylsiloxane, but the method is applicable to a wide range of material combinations. Initial demonstrations of this responsive control and its impact on properties of the adaptive polymer particles are also presented. © 2008 American Institute of Physics.

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The bending of a bilayer structure due to the development of residual stress at an interface has been classically studied and used for a wide range of applications, e.g., bi-metallic strips in thermostats,^{1,2} and more recently in the fabrication of three-dimensional (3D) micro- and nano-objects.^{3–6} In these examples, strained planar heterostructures are grown or deposited layer by layer on a sacrificial substrate and, due to the presence of lattice-misfit strain, roll up to form freestanding scrolls or tubes upon debonding from the substrate. These structures have been used as capacitors for transistors and sensors.^{7–10} This process has also been used to fabricate multilayer microscale polymeric vesicles for drug delivery.^{11,12} Here, we employ scrolling in the fabrication of adaptable polymer particles that can alter their geometry when triggered by given stimuli, such as temperature, thus altering flow characteristics and adsorption properties, provide understanding of how the materials and processing conditions alter the particle geometry, and quantify the responsive kinetics for these particles.

A cylindrical geometry offers several advantages (Fig. 1) compared to other shapes for the design of adaptive particles. A multiwall tubular geometry allows for high density packing (high surface to volume ratio) and thus for potential formation of a percolated network upon unfolding, altering properties such as permeability and conductivity of the dispersing medium. Furthermore, due to their cylindrical shape and high aspect ratio, the multiwall scrolls can align in a flow field and be easily transported.

The particles were fabricated using polydimethylsiloxane (PDMS) elastomer (Sylgard 184™) coated with a gold layer. The processing begins by spin coating of polyacrylic acid (PAA 20 wt % aqueous solution, Sigma-Aldrich) on a clean glass slide followed by heating at 70 °C for 30 min. PDMS (10:1 ratio of prepolymer to cross linker) is spun on the PAA-glass surface and cured at temperatures ranging from T_{ambient} to $T = 150$ °C. Gold, with a film thickness of 30 or 60 nm (current ~ 115 mA, rate ~ 0.7 Å/s) and a 5–6 nm adhesion interlayer of titanium (current ~ 100 mA, rate

~ 0.2 Å/s), were deposited by e-beam evaporation. The Au-PDMS film on the PAA-coated glass slide was cut into rectangular pieces with the width (W) and the length (L) ranging from 0.5 to 4 mm using a custom made cutting device. The Au-PDMS-PAA-glass assembly was then transferred to a water bath, where upon the dissolution of the PAA, microscale, equilibrated structures of tubes and coils were formed as a result of the relaxation of residual thermal stress developed at the Au-PDMS interface during fabrication.

The radius of curvature of the bilayer structures is defined as¹³

$$\rho = (h_s/6\epsilon)[1 + hm(4 + 6h + 4h^2) + h^4m^2]/(hm + h^2m), \quad (1)$$

where β and $m = (E_f/E_s)[(1 - \nu_s)/(1 - \nu_f)]$. The quantities h_i , E_i , and ν_i are the thickness, elastic modulus, and Poisson's ratio, respectively, of the i layer (f for the Au film and s for the PDMS layer). The strain (ϵ) is the uniform mismatch strain in the film, defined by the processing history and the different coefficients of thermal expansion. This relationship

FIG. 1. (a) Unfolding of polymer scrolls upon temperature change. (b) Alignment of particles in presence of a flow field—forced flow along the glass tube (top) and random flow of particles in the absence of a flow field—flow outside the glass tube (bottom).

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FIG. 2. (a) Theoretical phase diagram predicting the size/shape of the particles with the y - and x -axes being the normalized radius of curvature and the layers' thickness ratio. Each line corresponds to a different ratio of biaxial modulus m with tubes/rings forming above the line and arcs/coils below. (b) Experimentally observed structures, cylinders or rings above the black solid line, that correspond to the experimental m value or coils and arcs below the line.

is valid for any material combination given strong interfacial adhesion and can be used to design adaptive particles.

When the lateral dimensions of the bilayer are much larger than its thickness and characteristic bending scale ($2\pi\rho$), i.e., $L \sim W \gg h_s + h_f$ and $L \sim W \geq 2\pi\rho$, then both folding directions are preferred equally and tubes (rolling along L) or rings (rolling along W) form. In the case that $L \geq W$ and $W \leq 2\pi\rho$, open structures such as coils or arcs form. Combining Eq. (1) with this criterion, a “phase diagram” is derived. Each line (different modulus ratio m) defines the boundary between the formation of tubes/rings and coils/arcs. The conditions used in this study correspond to the area enclosed by the rectangular shown in Fig. 2(a) and representative images of the cylindrical structures observed experimentally are presented in Fig. 2(b).

In addition to controlling the particles' shape and size with this simple process, the direction of bending, defined by the strain distribution across the bilayer's thickness, controls the relative position of the two layers with respect to the inner or outer cylindrical surface. The strain distribution in the PDMS substrate before the metal deposition depends upon the PDMS thickness and curing temperature, which can alter the surface energy¹⁴ and modulus.^{15,16} Specifically, two factors lead to volume contraction in the PDMS: (1) thermal contraction due to temperature decrease upon cooling from curing temperature to ambient conditions and (2) volume decrease associated with chemical crosslinking. Both of these factors lead to a decrease in the lateral in-plane dimensions of the PDMS film and an associated in-plane negative strain at the free surface, defined as

$$\varepsilon_{h_s} = (W_{h_s} - W_o)/W_o \approx -\alpha\Delta T - \beta. \quad (2)$$

W_i is the width of the PDMS layer at location i (along the h axis, thickness direction), α is the coefficient of thermal expansion, and β is the strain associated with chemical crosslinking. The Au/Ti deposition process expands the free surface of the PDMS substrate introducing a positive strain at the free top surface of the bilayer γ .

By definition, the strain ε_{y_n} at the neutral axis of the bilayer y_n is zero, and through strain continuity at the interface, the slope should be the same above and below the interface. Therefore,

FIG. 3. Schematic explanation of the change in the bending direction of the Au/Ti-PDMS bilayer.

$$\varepsilon_o \approx \alpha\Delta T + \beta - \gamma. \quad (3)$$

For curing temperatures up to $T_{\text{cur}} = 120^\circ\text{C}$, $\alpha\Delta T + \beta < \gamma$, ε_o is negative and the bilayer bends forming scrolls with the Au/Ti on the outside, whereas at higher curing temperatures ($\sim T_{\text{cur}} = 150^\circ\text{C}$), ε_o becomes positive resulting to scrolls with the Au/Ti on the inside (Fig. 3).

A unique property of these particles is that they can reversibly change between 3D and two-dimensional geometries with stress-inducing stimuli. To demonstrate the shape-altering transition, series of experiments were conducted to quantify shape changes for Au-Ti/PDMS scrolls dispersed in glycerol solutions. Glycerol has low viscosity and transparency allowing for convenient *in situ* observation of the particles' responsive behavior. Experiments with constant heating/cooling rates were performed to access the reversibility of the unfolding process. Representative results of two heating-cooling cycles for a sealed sample vial are shown in Fig. 4. The average unfolding rate of the particles at a constant bath temperature (isothermal observations) was also determined. The unfolding rate increases significantly with temperatures ranging from 0 to 0.42 and finally to 40.6 (percentage of opened scrolls per minute) at T_{ambient} , $T = 85^\circ\text{C}$, and $T = 124^\circ\text{C}$, respectively. Thermal transfer kinetics and changes in the supporting matrix (the viscosity and density

FIG. 4. Reversible response of polymer scrolls triggered by temperature changes.

of glycerol decrease with temperature) decrease the resistance to opening upon heating.

In conclusion, it was demonstrated that adaptable polymer particles capable of altering their geometry can be fabricated by a simple versatile method that utilizes the residual stress that develops at the interface of a bilayer. Understanding of the underlying mechanism was provided, a phase diagram that relates the shape and size of the adaptive particles to the material properties and thickness of the two layers was proposed, and the reversible response of the particles was demonstrated.

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