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Gradient nanocomposite printing by dip pen nanolithography

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ABSTRACT

Many biological systems consisting of mechanically graded composites can be used to join mechanically different materials like bone, cartilage and mussel. Synthetic routes have so far been unable to achieve both the 3-D nature and the property tuning at micrometer length scales to replicate such systems. Deliberate strengthening of the mismatched surfaces and weak regions could be beneficial for a wide range of applications such as flexible electronics with locally stiff constituents, NEMS and MEMS systems, dental prosthesis having heterogeneous particle distributions resembling to natural tooth and joining mechanically different biological materials such as bone, cartilage and mussel. Dip Pen Nanolithography (DPN) can be a strategy to achieve this goal. In this study, DPN is utilized to locally deposit graded polymer-based composite materials at the micron scale. Spatial resolutions of 3–20 μm are obtained on entire pattern profiles with 6–70 μm width and up to 2 μm height. Colloidal probe microscopy and nanoindentation are used for mechanical characterization. Results show that the hardness and modulus of the gradient nanocomposite patterns can be tuned locally by changing the concentration of the ceramic nanoparticles.

1. Introduction

Graded composites show locally adjustable behavior due to their spatially tuned compositions leading to varied mechanical, optical and electrical properties [1–9]. In Nature, biological systems deal with mechanically mismatched surfaces exhibiting extremely discrete elastic moduli by locally tuning mechanical properties in three dimensions which is achieved by spatially changing the concentration of the constituents [1,6].

As an example for artificial production, Libanori et al. [4] fabricated stretchable composites with extreme mechanical gradients (of five orders of magnitude) which was achieved by tuning both the polymer hard domains and the concentration of additives. The gradient composite layers were adhered by a solvent welding method with a spatial resolution of 0.1–0.2 mm.

In the case of scanning probe lithography, Carrol et al. [3] changed the surface chemistry by utilizing gradients. The amine concentration was tuned at the nanometer scale by using thermally activated cantilevers, which is the driving force for adhesion between the amine and the substrate. However, according to our knowledge, there are no studies on gradient nanocomposite patterning to tune the mechanical properties by probe-based lithography. With regards to mechanically graded composites, synthetic routes could not achieve 3-D nature and small scale tuning of concentrations observed in biological composites. Deliberate strengthening of the problematic areas such as mismatched surfaces and weak regions could be beneficial for a large number of applications such as flexible electronics with locally stiff constituents, NEMS and MEMS systems, dental prosthesis having heterogeneous particle distributions resembling to natural tooth and joining mechanically different biological materials such as bone, cartilage and mussel.

In this study, Dip Pen Nanolithography (DPN) was utilized to deposit a functionally graded material and produce polymer

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nanocomposite patterns. The spatial resolution, as well as the size and height values of the written patters were characterized. Mechanical tests by means of colloidal probe microscopy and nanoindentation were performed on the nanocomposites in order to confirm the hardness and especially the achieved elastic modulus gradients.

2. Experimental

2.1. Materials

NOA 68T is a UV-curable photopolymer from Norland Optics. NOA 68T is chosen for its suitable hydrophilicity and viscosity for DPN writing. Contact angle of water on cured NOA 68T surface was revealed as 35° and the viscosity of NOA 68T is 20000 cps. In addition, NOA 68T has a relatively low glass transition temperature (−60 °C) and is not composed of volatile components which makes it possible to preserve its liquid properties for longer times. NOA 68T is composed of Mercapto-ester Tetrahydrofurfuryl (45–65%) and Tetrahydrofurfuryl Methacrylate (5–20%) [10]. The benefit of mercaptan dopants, which are used for many adhesives, is the ability to cure resins rapidly at ambient temperature.

For nanocomposite production, barium titanate ($BaTiO_3$) particles with 10 nm average diameter were used [11]. Nanoparticles were prepared via a microwave-assisted sol-gel process and stabilized with metoxy-etoxy-etoxy acetic acid [12].

2.2. Ink and sample preparation

Polymer inks were used as-received whereas the nanocomposite inks were produced by mixing nanoparticles with polymer by ultrasonication and magnetic stirring. Nanoparticles were dispersed in the tetrahydrofuran medium prior to ink preparation. Most of the nanocomposite inks were subsequently either placed in a desiccator or exposed to ambient conditions to allow the solvent to evaporate. It is observed that the homogeneous distribution of particles depends on the freshness of the nanoparticle dispersions and the mixing time with the polymer.

Two batches of nanocomposite inks were prepared for writing different concentrations and gradients, respectively. The first batch – produced for writing different concentrations of nanocomposite inks – consisted of five distinct compositions having nanoparticle concentrations of 0.5 wt%, 1 wt%, 2 wt%, 4 wt% and 5 wt%, respectively. Nanocomposite inks with particle concentrations of 4 wt% and 5 wt% were prepared as having either homogeneous or inhomogeneous distribution of particles. It is observed that depending on the nanocomposite production parameters such as mixing route and mixing time with polymer, the distribution of nanoparticles could be controlled. Up to 5 h mixing time resulted in a more homogeneous particle distribution while around 30 min mixing time led to high level of agglomeration. Details of ink preparation for writing nanocomposite patterns were described in our previous work [13]. The second batch prepared for writing gradient nanocomposites consisted of four distinct inks having particle concentrations of 0 wt%, 0.5 wt%, 1 wt% and 2 wt%, respectively. The ink having 0.5 wt% particle concentration is the same as one utilized in the first batch. Yet, inks having particle concentration of 1 wt% and especially 2 wt% were prepared to achieve higher agglomeration levels which are beneficial in order to observe surface roughness differences between each part of the gradient and could result in higher modulus and hardness values in the region with the highest particle concentration. Silicon samples with native oxide layers were exposed to piranha treatment (H_2SO_4/H_2O_2: 3/7) for 5 min in order to increase surface hydrophilicity.

2.3. DPN writing

DPN cantilevers for writing and imaging were obtained from NanoInk's NSCRIPTOR™ which are Silicon nitride Type A single and Type M multiple pens (12 cantilever array). Type A and type M pens consist of two different cantilever configuration in each side. One side consists of a “diving board” shape cantilever which is suitable for contact mode imaging and delivery of thiolated inks while the other side contains an “A-frame” cantilever with a higher spring constant and is useful for patterning higher viscosity inks. In this study, A-frame cantilevers were thus used for writing polymer inks. Different concentrations of nanocomposites were patterned by either type A or type M pens, while the gradient nanocomposites were solely written by type M pens.

The DPN patterning was accomplished by DPN 5000 system in ambient conditions. Inkwells (Nanoink- Universal DPN Inkwell Array) were utilized to coat the tips with ink material. The inkwells consisted of reservoirs which were filled with ink material by micropipettes and micro channels running from individual reservoirs to the microwells. The inking for polymer patterning was accomplished by bringing the tips into contact with the microwells for 1 min. During nanocomposite patterning, the contact time is increased to 5 min in order to have a sufficient driving force for the ink delivery by increasing the ink amount. Patterned substrates were cured with UV light for 1–5 min. It is observed that as the nanoparticle concentration increases, the polymer chains become less mobile which deteriorates the ink delivery. Therefore, relative humidity percentage along writing was increased from 20 to 65% with increasing particle concentration in order to enhance water meniscus. The details for the DPN writing procedure of nanocomposites were described in our previous study [13].

Most of the gradient nanocomposite patterning was accomplished by *in situ* UV-curing after writing each constituent in order to be able to distinguish between the distinct parts having various particle concentrations. In addition to that, depending on the viscosity and wetting behavior of the inks, similar size and height values for each constituent were achieved by several ways. For instance, repeating the writing operation several times on the spot of the more wetting constituent increased the height value, and tuning the humidity level through the writing of each constituent changed the mobility of the ink as it enhances water meniscus.

Intermittent contact mode AFM imaging was conducted to visualize patterns in the same system (Nanoink DPN 5000) following writing operations.

2.4. Colloidal probe microscopy

Colloidal Probe Microscopy experiments were conducted on an Asylum MFP-3D system in ambient conditions. A silica colloid of 25 μm diameter was glued on top of a tipless cantilever (Budget sensors, all-in-one) using a home built micro-manipulator. The colloidal probe was prepared using the approach proposed by Kuznetsov et al. [14] by sintering the silica colloid onto the tipless silica cantilever at 1100 °C. This approach increased the stability of the probe on the adhesive polymer surface and partly eliminated