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Patterning of SiO_2 nanoparticle–PMMA polymer composite microstructures based on soft lithographic techniques

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ABSTRACT

Soft lithography and self-assembly provide powerful means of organizing colloidal solution of synthesized nanoparticles (NPs) for a wide variety of application. Pattern transfer of silicon dioxide (SiO_2) nanoparticles–polymethylmethacylate (PMMA) nanocomposite was investigated using two such soft lithographic techniques, micro molding in capillaries (MIMIC) and micro transfer molding (μTM) using an elastomeric stamp in Polydimethyl siloxane (PDMS). Nanocomposite periodic arrays of 20 μm wide and 10 μm deep lines with 10 μm spacing were obtained over approximately 1 cm^2 area on silicon substrates by μTM and MIMIC using a 3 wt.% monodisperse silica nanoparticles (~338 ± 2 nm) in polymethyl methacrylate (PMMA) solution. In addition, free standing nanocomposite self-standing films of centimeter size were also manufactured by μTM. Single line of nanocomposite could also be obtained using MIMIC with a lower concentration of silica NPs (0.25 wt.%) in PMMA.

1. Introduction

Nanoparticles (NPs) have an enabling role in various branches of nanotechnology due to their capability of being a bridge between bulk materials and atomic or molecular structures [1,2]. It has become increasingly important to understand and manipulate nanomaterials to develop new functional materials for engineering and biomedical applications. Nanostructured and nanocomposite materials can show dramatic improvement of mechanical, tribological, electrical and chemical properties [3].

Recently, composite materials made of polymers and NPs, such as inorganic, metal, semiconductor, carbon black, and magnetic nanomaterials have attracted great attention because of the stabilizing effects of the polymer matrix on the NPs and relative easiness and flexibility of engineering this class of materials with advanced functionalities [4–7]. Such composites exhibit macroscopically novel properties for a wide variety of applications. This is due to the combined action of quantum size effects, inter-face between nanostructures and matrix, and morphologies of nanoparticle. For example, NPs used as filler in the polymer composites dispersed uniformly lead to high fracture toughness compared to microparticle reinforced polymer composites. The strong interfacial bonding between the nanoparticles and the polymer matrix due to high specific surface area of nanoparticles also enhances the wear resistance of the nanocomposite which results in better nanotribological performance compared to that of the microcomposite. Use of rigid nanoparticles to improve mechanical performance of thermoplastic polymers has received considerable attentions in recent years [8–10]. Strength, stiffness and toughness of nanocomposites can be simultaneously enhanced by improving dispersion of NPs in polymer matrix as well as interfacial interaction between NPs and matrix [11–13]. Besides, some researchers also showed that the glass transition temperature (Tg) of polymers, determined by loss modulus and loss tangent in dynamic mechanical analysis, could be increased by the incorporation of NPs owing to a good bonding at the inter-face that restricts motion of the polymer chains [14,15]. All of the above manifest that with the aid of inorganic NPs, performance of thermoplastic polymer is becoming more attractive.

Polymethyl methacrylate (PMMA) is one of the most commonly used thermoplastic polymers. PMMA has several desirable properties, including exceptional optical clarity, biocompatibility, good weatherability, high strength, and excellent dimensional stability. It can also be processed at the micro and nanoscale by lithography (deep UV and electron beam) and replication technologies (injection moulding, hot embossing) and has applications in micro-optical and microfluidic devices [14–19].

Micron-scale periodic structures are essential for the applications such as photonic or optoelectronic devices and biochemical sensors [20–22]. For instance, photons can be controlled through the band gap of photonic crystals, which requires photonic

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materials to be periodically structured on a length scale comparable to that of the wavelength of light i.e., the submicron range for the optical domain [23–29]. Therefore, there is a need for an efficient approach to pattern nanoparticle/polymer composites into periodically ordered structures. The pattern can be defined by a large number of techniques such as spot lithography technique based on the lift-off of spin coated particles solution, guided molecular self-assembly methods, interference lithography or holographic lithography, nanosphere lithography and soft lithography [30–36]. In particular, a soft lithography technique based on self-assembly and molding like micro molding in capillaries (MIMIC) and micro transfer molding (μTM) allows rapidly producing large-area of such microstructures [37]. Blümel et al. fabricated the silver source/drain electrodes in bottom-gate/bottom-contact organic field-effect transistors (OFETs) with poly(3-hexylthiophene) as active layer material using MIMIC and μTM techniques [38]. Paloczi et al. also used this soft lithography technique for the fabrication of polymer optical waveguide devices [39]. Polymeric light emitting diodes (LEDs) have been manufactured by Park et al. using MIMIC technique with electroluminescent (EL) polymers [40]. Yang et al. used acidic sol–gel block copolymer templating chemistry and soft lithography technique for the fabrication of mesostructured silica waveguide arrays [41].

In our previous work, MIMIC, was used for the 2D ordering of silica NPs (1–3% by weight) in colloidal suspension of ethanol medium [42] and the optimum results were obtained by using 2 wt.% of particle concentration. In the present work, we investigated the manufacture of line arrays composed of silica NPs in thermoplastic (PMMA) polymer matrix using MIMIC and μTM techniques.

2. Experimental

Monodisperse silica nanospheres of ~338 ± 2 nm were synthesized using selective precipitation method which involves a tight control of both nucleation and growth of the nucleus (Fig. 1) [43,44]. These silica NPs obtained in powder form were dispersed and mixed with poly methyl methacrylate (PMMA) crystals (0.001 g) to make a PMMA solution in liquid chloroform (5 ml). Solutions of 0.25–3 wt.% colloidal silica NPs in PMMA were formed.

The silicon substrates were cleaned by sequentially immersing them in hydrofluoric acid, detergent water, acetone and ethanol while sonicating.

The MIMIC and μTM techniques are illustrated in the schematic figure (Fig. 2). In both patterning techniques, an elastomeric mould of 1 cm^2 area and 500 μm thickness in poly (dimethylsiloxane) (PDMS) (Dow Corning; Sylgard 184, Midland, MI) with a network of rectangular-shaped micro ridges (each groove of ~20 μm width, ~10 μm height and spacing of ~10 μm) is used (Fig. 3) [45]. The microstructured channel can be fill completely using polymeric solution in less than 60 s.

In the MIMIC technique, the PDMS mould is placed on the surface of a chemically cleaned silicon substrate. The elastomer mold makes conformal contact with the silicon substrate, sealing the network of channels. The polymeric solution including the NPs is added to the open end of the elastomeric mould. After filling the channels, the solvents were evaporated by heating the sample at 80 °C while the PDMS stamp remained on the support for 5 min. This drives a flux of microspheres into the microchannels, inducing the self-organization of the nanospheres and ultimately leads to a close-packed, well-ordered structure. Once curing has taken place, the PDMS mould is removed carefully and the network of silica–PMMA composite remains on the surface of substrate. The low reactivity of PDMS mould allows easy separation from the patterned microstructures from the silicon wafer.

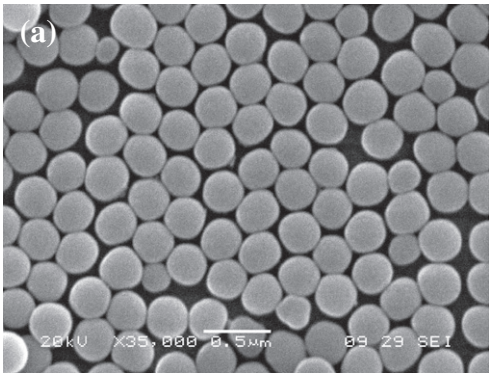
In the alternative μTM technique drops of colloidal solution is applied over the PDMS stamp. By removing the extra liquid using the plane surface of a glass slide, the PDMS mould is placed on the silicon substrate with the colloidal solution facing the substrate and contacted with it. The whole assembly is cured at 80 °C for 5 min and the stamp removed carefully. The adhesion of the thin silica–PMMA composite structure with the silicon substrate is good.

If a free-standing structure is needed, the patterned silicon substrate is dipped in a beaker with diluted nitric acid (33%) aqueous solution (1:10) at room temperature placed in an ultrasonic vibration bath for 5 min. The polymer nanocomposite pattern is then lifted-off and floats in the beaker, resulting in a free standing membrane.

The scanning electron microscopy (SEM) images were recorded using JEOL, JSM-6360, with an accelerating voltage of 20 kV. All the samples for SEM studies were coated with thin layers of platinum (~25 nm thick) before imaging to make the sample conducting.

3. Results and discussion

Soft lithographic techniques have emerged in recent years as alternative techniques to generate patterns in nanometer to micrometer scale on large area in relatively short time period without using any expensive equipment or stringent conditions. In par-



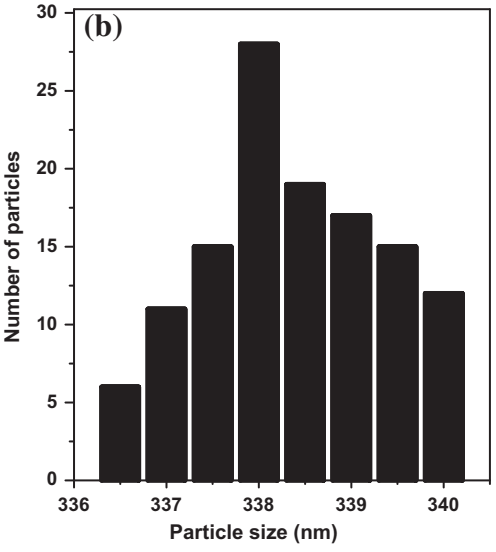


Fig. 1. (a) SEM image of monodisperse silica particles of ~338 nm diameter and (b) size distribution plot.