



Original research article

# Enhancement of haze reflectance through thin-film buckling using a shape memory polymer foundation



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## ABSTRACT

The optical haze characteristics of buckled thin-films on a thermoresponsive shape-memory polymer(SMP) foundation have been investigated in the present study. The SMP was pre-stretched to exhibit negatively anisotropic thermal expansion, and coated with a layer of aluminum thin-film. Self-regularized grating patterns of which wavelengths range from 883 nm to 5.0  $\mu\text{m}$  were obtained on the surface upon annealing due to the shape recovery of SMP. The optical haze spectra from the sample were measured using a spectrophotometer, and results show improvement of reflection haze up to 93%. The present study proposes a novel technique for facile and inexpensive fabrication of grating patterns for thin-film based organic devices.

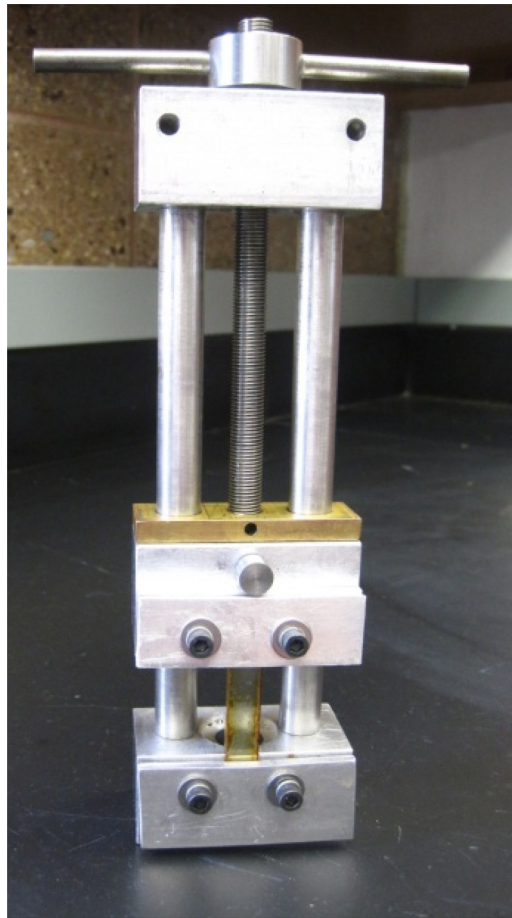
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## 1. Introduction

Shape-memory polymers(SMPs) are a class of materials that can restore their original shape from a programmed temporary shape upon external stimuli such as temperature, light, chemical reactions, or applied electrical/magnetic fields. Since their unique ability to “remember” their shape enables them to return to an original state, they are being widely considered for novel applications such as a deployable hinge in aerospace structures, wrinkle-free fabrics in the textile industry, air-flow systems in automobiles, and biomedical devices for minimally-invasive surgery [1]. Specific investigations show the fabrication of nanowrinkles on gold-coated polystyrene SMPs for metal-enhanced fluorescence [2], micropatterns on the sidewalls of SMP blocks for 3D microelectronic circuits [3], pyridine containing polyurethanes for moisture-sensors [4], and so on.

Buckling of thin-films, or ‘wrinkling’, on elastomeric foundations has been vigorously studied since it can lead to various complex surface structures that can be useful for many micro/nanodevices. Earlier works [5–7] focused on the clarification of the wrinkling mechanism based on Euler buckling theory or considerations of dispersion force in the material system, and recent studies have been developing practical applications for stress/strain sensors, modulus measurements, polymer dynamics, and wettability control [8–10]. Attention has not been fully paid yet, however, to the aspect of optical characteristics of the wrinkled surfaces. Especially with increasing interest in energy research, surface texturing is becoming more important in order to enhance light-trapping in thin-film solar-cells, which in turn increases the power conversion efficiency. Attempts have been made to use randomly-textured surfaces obtained from etching processes [11], diffraction gratings using photolithography, Bragg stacks, and photonic crystals as a reflector in silicon-based photovoltaic cells [12], but these are significantly more expensive approaches than utilizing self-assembled surface structures in organic-inorganic hybrid structures, which would be useful for organic photovoltaics (OPVs).

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**Fig. 1.** The elongation frame to strain polymer foundation.

Therefore, the optical haze characteristics of self-regularized gratings patterns on a thermoresponsive SMP are discovered in this work. Taking advantage of the spontaneous structure formation through the buckling of metallic thin-film on an SMP substrate during its recovery process, well-aligned unidirectional ridge patterns were generated, and their light-scattering characteristics were studied. The optical haze spectra in the ultraviolet (UV)-visible (Vis)-infrared (IR) have been quantified in detail using a spectrophotometer, and results show significant enhancement of the haze factor on the surface, suggesting that the proposed approach is potentially a viable one for facile fabrication of surface grating patterns in organic thin-film devices that requires promotion of light scattering.

## 2. Experimental

### 2.1. Sample preparation

A thermoresponsive SMP was prepared using a two-part epoxy resin composed of the diglycidyl ether of bisphenol A epoxy monomer (EPON 826, Hexion) and the poly(propylene glycol)bis(2-aminopropyl)ether (D230, Huntsman) as a curing agent [13]. Epon 826 and D230 were mixed with the molar ratio of 2:1, and cured at 100 °C for 1.5 h. After a post-curing process for 1 h at 130 °C, samples were taken out of the mold and divided into  $50 \times 20 \times 1 \text{ mm}^3$  slabs.

Upon completion of the substrate preparation, the sample is stretched to a temporary shape using a custom-made SMP-programming apparatus, as shown in Fig. 1. First, the SMP slab is fixed on the frame at room temperature and heated in an oven up to 100 °C for 20 min. Next, 3% strain was applied to the sample at the elevated temperature. Finally, the substrate is cooled down while it is still fixed in the apparatus. After the programming procedure, a 10–70-nm thick aluminum (Al) layer was deposited on the substrate surface in an e-beam evaporator (Edwards Auto 500). The chamber pressure was maintained at  $4 \times 10^{-6}$  Torr, and a deposition rate of 0.15 nm/s was obtained during the evaporation.

The shape recovery takes place in the oven at 100 °C to form microgratings. Normally it takes less than 2 h. The initially planar Al film corrugates once the process is thermally activated due to the anisotropic compressive stress. Then the pattern

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