



Opto-mechanical programming of micro-scale information on transparent multilayer shape memory film

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ABSTRACT

Micro-scale surface shape memory effects were investigated on multilayer films that were produced with alternating layers of PVAc and PU. Two different types of micro-scale patterns, including a sharp microprismatic pattern and a smooth microlens pattern, were embossed on the surface of the PVAc/PU multilayer films by a PDMS replica mold using the soft lithography method. The microprismatic pattern as a permanent surface structure on the intrinsically transparent multilayer films renders the films opaque and the microlens surface pattern endows the clear films with focusing properties. The micro-structured surface is programmed by compression and recovery to switch the corresponding optical property of the film. Based on this switchable optical property, the patterned PVAc/PU multilayer film can be employed as an anti-counterfeiting feature in packaging. In this paper, the shape memory effect of the multilayered film was found to be dependent on the composition of the PVAc relative to the PU layers. In addition, the shape memory effect of the layered PVAc/PU films was enhanced compared to the PVAc control film. The recovery mechanism of the shape memory films was interpreted using Burgers viscoelastic model. The effects of the compression pressure, recovery temperature and the geometry of the patterns on the micro-scale shape memory behavior of the PVAc/PU multilayer films were also investigated.

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1. Introduction

The time and temperature dependency of visco-elastic behavior of polymer melt along with their lightweight and mechanical tunability facilitated the formation of thin films and thus information can be imprinted and stored on them. There has been numerous scientific and engineering efforts to tune the micro-structure of polymers to achieve optical and mechanical tunability and most often, it is hard to combine desired optical and mechanical properties in the polymer films. Force assembly co-extrusion method is a unique technology, which ideally can generate polymer thin film with unique optical, mechanical, barrier, and charge storage properties by manipulating the interface or inter-phase between layers of different polymers. This research paper presents a unique effort in combining the optical transparency, melt-memory and functional surface patterns to develop opto-mechanically tunable multilayer polymer film to store functional

surface pattern as information.

One of the key features of this work is to achieve shape memory property of the multilayer polymer films, which ultimately contributes to the optical and mechanical programmability of the film and surface patterns as a whole. Important to mention here that shape memory polymers (SMPs) are capable of deforming into temporary shapes and recovering to the original shape by the application of an environmental stimulus; typically, thermal. The conventional thermoplastic SMPs have been intensively studied for years and include polymer blends and block copolymer systems in which a glassy or semi-crystalline polymer (hard segment) serves as switching phase and an elastomer (soft segment) serves as a recovery phase [1–5]. The switching temperature window is determined as between the transition temperature (T_g or T_m) of the switching phase and recovery phase. Recently, Du and Armstrong et al., developed a new type of thermoplastic shape memory system created by a forced assembly multilayer co-extrusion [6,7]. This technique is capable of producing multilayer shape memory films with alternating layers of a normal glassy or semi-crystalline polymer and an elastomer that intrinsically have no shape

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memory effect. The layers of the glassy or semi-crystalline polymer with a transition temperature (T_g or T_m) serves as the switching phase. The layers of the elastomer serves as the recovery phase (physical network). Based on this, dual shape memory polymeric films were produced. In addition, the relative composition and scale of the switching layers and recovery layers can easily be tailored by changing the relative flow rates of the components and the number of layers to tune the shape memory effects. Du et al. produced 200 μm multilayer films consisting of polycaprolactone (PCL) and polyurethane (PU) in alternating layers with volume compositions of 25/75, 50/50 and 75/25 [6]. The shape memory effects of the layered PCL/PU films were examined in macro-scale with a switching temperature of 70 °C. The shape memory effects of the layered PCL/PU films were found to be much better than the PCL/PU blend films with the same compositions. Armstrong et al. further investigated the layer thickness contribution to the shape memory effects by changing the layer thickness of the PCL/PU layered films from micro to nano scale [7]. In addition, a recent work reported by Shanjuo Ji et al. showed the development of triple shape memory multilayer films, which is another indication of novelty of force assembly coextrusion method [8].

Another key feature of this work is to imprint micro/nano-scale information on multilayer films, which involves intricate process of understanding the role of hardness, visco-elastic deformation, and time-pressure-temperature optimization [9]. Programming of micro/nano-scale information stems from the bulk shape memory of the polymer film. Such programming of patterns is also known as surface shape memory [10]. Shape memory surfaces extend the shape memory effects from macro-scale in the bulk SMPs to the micro or nano-scale on their surfaces based on the same molecular principles [10–13]. The shape memory surfaces were programmed to switch the micro or nano-scale structures or patterns as well as the rendered unique properties such as optical, adhesive, wetting, etc. [14–17]. Xu et al. designed a switchable optical device by programming optical patterns on the surface of SMPs [14]. These patterns can range from the micro-scale (i.e. microprism, microlens) to the nano-scale (i.e. gratings, holograms). Schauer et al., developed tunable diffractive gratings with a period in micro-scale and a height in nano-scale on the surface of a shape memory thermoplastic polyurethane film and studied the recovery mechanism. The diffraction property can be tuned by programming the surface micro and nano-scale structure [15]. Reddy et al. programmed micro-pillars on shape memory films to switch the adhesion of the surface through shape memory effects [16]. Wu et al. developed a thermal stimuli-responsive microstructured surface that can change a film's wetting properties [17].

Our previous work has demonstrated that surface patterning of micro-scale patterns can be carried out above the softening point of a high molecular weight glassy polymer, PVAc [9]. However, the SM behavior of the monolith is largely limited by the brittleness and ageing at room temperature. In this paper, forced assembly coextrusion technique was used to produce multilayer transparent shape memory film, which after surface embossing are tunable in their optical properties. Highly transparent multilayer films were produced with alternating polyvinyl acetate (PVAc) and polyurethane (PU) layers. The similar refractive indices of the PVAc ($n = 1.47$) and the PU ($n = 1.50$) ensured high transparency in the co-extruded multilayered films. Two different types of micro-scale patterns including a sharp microprismatic pattern and a smooth microlens pattern were permanently embossed on the surface of the multilayer PVAc/PU films by a PDMS replica mold using a reported soft lithography method [24–26]. By programming the micro-scale pattern on surface, the optical property of the film switches as the surface microstructures change through compression and recovery when acted on by thermal stimuli [14,18,19]. This

switchable optical property can be employed for the fabrication of micro-optical devices such as a thermal sensor [14], a smart label for anti-counterfeiting [27] or an encoded information storage medium [28]. The PVAc/PU multilayer film is demonstrated to have enhanced shape memory effects compared to the high molecular weight PVAc film that has been studied previously [9]. In addition, PVAc/PU film is more elastic than the monolith. This paper also investigates the effects of composition, compression pressure, recovery temperature, and geometry of the microstructures on the shape memory behavior of PVAc/PU multilayer films by utilizing the Burgers viscoelastic model.

2. Materials and methods

Polyvinyl acetate (Vinnapas UW 4fs) was obtained in bead form from Wacker Chemie AG. Polyurethane (Carbothane PC-3595A) was obtained in pellet form from Lubrizol. Prior to co-extrusion, the PVAc beads and the PU pellets were dried under vacuum at room temperature (25 °C) and at 80 °C respectively for at least 48 h to remove any water absorbed during storage.

Two-component multilayer films with alternating PVAc and PU layers in an ABABA layered structure were produced by using a forced assembly multilayer co-extrusion process as previously described elsewhere, shown in Fig. 1a [20,21]. The co-extrusion was conducted at 200 °C for the viscosity matching of the two materials, as determined by using a Kayeness Galaxy 1 melt-flow indexer at a shear rate that is similar to extrusion condition (10 s^{-1}). Two sacrificial polyethylene (PE) skin layers were laminated on the outside of the multilayer or control films to improve the surface quality. These sacrificial PE skin layers were removed prior to post processing and testing of the multilayer or control films. The films were extruded through a 14" die and collected on a film casting takeoff roll set at 60 °C. Films consisting of 257 layers, with PVAc as the outer layers, were produced with volume compositions of 30/70, 50/50 and 70/30. In addition, PVAc control film was extruded using the same setup for comparison.

The films produced were 60 μm thick, with layer thicknesses ranging from 141 to 328 nm depending on their composition. Thick film stacks having a total thickness of 330 μm were made by consolidating 6 as-extruded films with identical composition on a hydraulic press (Carver Inc. US) at 90 °C under 4450 N of force. The nominal layer thickness as well as the transparency of these films are shown in Table 2.

Cross sections of the PVAc/PU multilayer films were imaged by using an atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments, US). The as-extruded multilayer samples were first embedded in epoxy, cured overnight at room temperature (25 °C) and then sectioned at $-180\text{ }^\circ\text{C}$ using a Leica Microsystems (Buffalo Grove, US) EM FC6 ultra-microtome. The polished cross section of the multilayer samples were imaged by using the AFM operating in the tapping mode. The phase images were analyzed to evaluate the layer structure of the PVAc/PU multilayer films shown in Fig. 1b, c and 1d. The sharp interface indicates the immiscibility between PVAc and PU.

Differential scanning calorimetry (DSC, TA Q2000, TA Instruments Inc. US) was used to determine the switching temperature of the PVAc/PU multilayer films shown in Table 1. The DSC analysis was conducted under nitrogen. The temperature range was between -50 and $150\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}/\text{min}$ and the sample mass was between 5 and 10 mg. A second round of heating scans (Figure S1) was conducted to ensure identical thermal histories. The DSC measurements show a glass transition temperature (T_g) associated with PVAc at 44 °C and with PU at $-30\text{ }^\circ\text{C}$ as well as a melting point of PU at around 118 °C.

Thermo-mechanical tests were carried out on the PU and PVAc

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