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Test Method

Evaluating shape memory behavior of polymer under deep-drawing conditions

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ABSTRACT

Thermoplastic polyurethanes (TPU) are a popular family of shape memory polymers (SMP) due to their excellent abrasion & weather resistant, and mechanical strength. However, conventional processing operations or their combination with other polymers by adhesion or blending can affect their unique shape memory behavior. Currently, there are no effective methods to study and quantify the shape memory behavior of SMP based polymer laminates as they would respond to deep drawing operations. In this paper, a new method was introduced to effectively quantify the recovery behavior of TPU based polymer laminates undergoing simultaneous stretching and bending operations at different processing temperatures. The results presented show the value of developing a shape recovery characterization method that resembles the stresses of thermoforming to properly assess formability of shape memory polymers used in laminate constructions.

1. Introduction

Recently, polyurethanes (TPU) have garnered a great amount of attention as a significant group of shape memory polymers (SMP). Generally, the morphology of a typical shape memory TPU should contain a reversible soft segment phase and a fixed hard segment phase. A thermally responsive shape memory behavior can arise due to this unique morphology [1,2]. In addition to the excellent shape memory effect, because of their versatility of chemical structure, easy processing, and low cost, shape memory TPUs are widely used in the automotive, aerospace, medical and commercial sectors for applications such as paint protection films, actuators, biomedical materials and smart fibers [3–5]. Particularly interesting to this study are films developed to be a functional layer for paint protection and paint replacement, benefiting from their high level of strength, abrasion & weather resistant, and flexibility [6,7]. However, at certain working temperatures, the shape fixity of a formed part with these TPU can be affected by the shape memory effect. To broaden the structural applications of shape memory TPU, laminates may be introduced whereby the film is adhering to a rigid polymer substrate which reinforces the shape fixity of the formed shape. However, new knowledge of how a bonding agent and substrate will influence shape recovery is required. Depending on the operating conditions, different levels of shape fixity of formed laminate part are foreseen.

To date, few studies have been carried out that characterize the shape fixity of deformed shape memory polymers. Typically, a cyclic thermo-mechanical tensile test is frequently employed to investigate the recovery behavior and shape fixity of SMPs. As described in the study by *Ohki et al* in 2004 [6], a uniaxial load is applied in the test on a SMP specimen at elevated temperature, T_h (where $T_h > T_g$, T_g being a glass transition temperature of the polymer), and the load is not removed until the extended sample is quenched to a temperature below its transition temperature. The shape fixity is then quantified by the method using the strain variation before and immediately after the unloading process. That deformed SMP is then re-heated to T_h and the recovered strain is measured to quantify the shape memory effect. The effect of temperature and testing cycling on the shape fixity and recovery effect are commonly investigated for SMP.

Other than the uniaxial test mentioned above, a bending recovery test of shape memory behavior for TPUs and their composites was introduced by Zheng et al., [8]. In their test, one end of a SMP laminate is fixed by a clamp to outer surface of a cylinder with

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specified angle. The bent specimen was heated and its shape memory quantified by measuring the difference between the initial and recovered deflection of its free end. A similar bending recovery test was performed by Lan et al. [9], where the sample was deformed around a cylindrical shaft. In their case, the shape memory effect was characterized by the change of angle, Θ.

However, most polymer forming operations consist of simultaneous stretching and bending deformational modes, such as thermoforming, which are not effectively captured by the tests given above. This paper proposed a new method modified from the bending recovery test method of Lan et al. [9].

2. Recovery measurement method

The newly introduced measurement method was developed to characterize the recovery behavior of a SMP based polymer laminate intended for complex forming processes. Laminated samples are deformed under this method using a lab-scaled matched-mold thermoforming process conducted in a universal mechanical testing system (UMTS) fitted with an environmental chamber. As indicated in Fig. 1, the arch shaped laminate is formed with a set of conforming die plates having a semi-circular shape with an arc radius of 25 mm and a peak height of 15 mm; spacers were used when a draw depth of less than 15 mm was desired. Three specimens are clamped into the lower female mold at a time and the environmental chamber is heating to a typical forming temperature for the laminate. The male mold with a peak height of 15 mm is lowered into the female mold using the crosshead of the UMTS which allowed control over the out-of-plane strain as well as the strain rate that the laminate samples experienced. As the results will show, for our polymer laminate system deep drawing was not possible to the full 15 mm depth without tearing the film.

Once the three specimens are deformed to the desired out-of-plane strain and at the selected strain rate dictated by the crosshead speed of the UMTS, both molds and samples are removed from the environmental chamber and immediately stored in a deep freezer to cool. The specimens remain clamped in place within the molds while being cooled to 10 °C (i.e. $T < T_{g,SMP}$) over a span of 20 min and then the specimens were quickly removed from the mold in order to be affixed in a mounting rig. One end of each specimen was cut at the bend edge in order to removed the flat section that had been in the clamp of the mold, and its other flat section was used to mount the specimen in the rig. A two-component epoxy was applied to seal the tip of free end with a cure time of 7 min; sealing the ends of the specimens minimized inter-layer shear contributions in the recovery behavior of the SMP laminate. It should be noted that the specimen preparation procedures including removal from the mold, trimming and clamping were all performed in the low temperature environment of the freezer to minimize any rise in temperature and at no time were the specimens exposed to body heat.

Three mounted laminate specimens laying horizontally on their edges within the rig are transferred to a small environmental chamber partially submerged in a water-circulating bath with temperature control (VWR International; PA, USA). The set temperature of the chamber was determined by the experiment, which for the present studies produced an equilibrium specimen temperature of either 45 °C or 65 °C (which above the T_g of the studied SMP). The mounted specimens were placed atop of printed patterns of a recovery curve (discussed below) on the base of the chamber showing its central angle during recovery, as displayed in Fig. 2(a); the end of sample at position (0,0) was fixed with a clamp. The specimens were kept dry and free from any influence of friction by avoiding contact with the base of the chamber. An acrylic lid was initially placed over top of the water bath to allow direct viewing of the three specimens as they recovered.

According to the recovery mechanism of a shape memory TPU, restorative stresses will develop once its soft segment phase exhibits increased molecular mobility which occur above its corresponding glass transition temperature. As a rigidly affixed film in a laminate, there was no possibility for the stretched and bent TPU film to recover back to the original shape along with the rigid substrate without strain release. Thus, the recovery stress is consistently applied as a shear stress across the interface between TPU and substrate to produce a bending moment that intends to flatten the deformed laminate. Based on two assumptions, namely (1) the arc length of the formed laminates remained constant during recovery; and (2) the end of a recovering specimen traversed a circular arc with decreasing central angles, a recovery curve which indicates the path of the free end of a specimen could be calculated by MATLAB, as shown in Fig. 2(b). The free end of a specimen is initially located at position (X_i, Y_i). As recovery proceeds, the position of the free end can be found at (X, Y) at time t, till finally reaching position (X_f, Y_f) for its recovered shape. By visually comparing the location of the specimen relative to the recovery curve, it was possible to quantify the recovery of the SMP laminate.

During a typical recovery test, three digital timer-operated cameras are placed atop of the transparent acrylic lid of the chamber, each focusing on an individual specimen to minimize the parallax error in reading the central angle from the printed recovery curves. The initial central angle of a specimen is recorded as soon as it is placed in the chamber, and then the recovery behavior of the specimen is captured every 15 s for first 30 min. The span increased to every 60 s for the next 30 min. After the first hour recording, the transparent acrylic lid had to be replaced with an insulated lid (supplied with the circulating bath) to prevent the water in the bath from evaporating. With the insulated (non-transparent) lid in place now, observations are carried out less

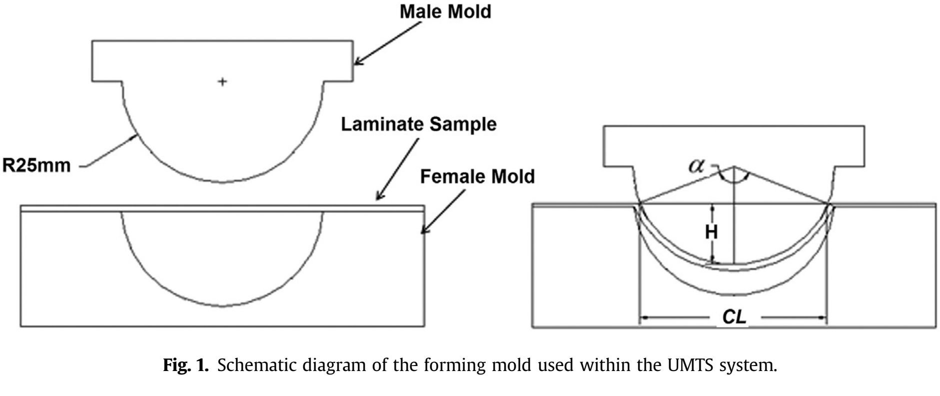

Fig. 1. Schematic diagram of the forming mold used within the UMTS system.