



# Influence of molecular architecture on the isothermal time-dependent response of amorphous shape memory polyurethanes

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## ABSTRACT

The thermomechanical response of a series of thermally activated shape memory polyurethanes (SMPUs), determined by dynamic mechanical analysis (DMA), has been adjusted by systematic modification of the molecular architecture. It is argued that the free recovery behavior of these SMPUs at temperatures in the vicinity of the calorimetric glass transition temperature is dependent not only on the recovery temperature, but also on the form of the corresponding peak in  $\tan \delta$  in DMA temperature scans at constant frequency. On the basis of simple correlations between recovery rates and the width and shape of the  $\tan \delta$  peak, it is suggested that DMA may provide a relatively simple and rapid means of assessing the potential of the SMPUs with respect both to recovery and shape fixity at a given storage temperature. This in turn allows establishment of a direct link between the shape memory performance and molecular architecture.

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## 1. Introduction

Shape memory polymers (SMPs) are able to transform from a deformation-induced temporary shape to a “primary” shape characteristic of the equilibrium conformation of a molecular network defined by entanglement and physical and/or chemical cross-linking [1]. While such a transformation may occur in response to various types of stimulus, it is usually triggered by raising the temperature,  $T$ , above a softening temperature, e.g. a glass transition temperature,  $T_g$ , or a melting point, below which the temporary shape is effectively frozen-in, owing to the limited mobility of the polymer molecules.

SMPs are typically designed to show well-defined recovery temperatures [2], and a high level of reproducibility of the recovered shape [3] within a relatively short time [4]. However, many potential applications, particularly in the biomedical field, also require adequate control of the shape recovery kinetics, e.g. to avoid damaging body tissue [5] or to ensure well-defined flow rates in microfluidic de-

vices [6]. Moreover, if a passive source of thermal energy such as the human body is used to actuate the SMP, it may be important to limit the sensitivity of the recovery rate to fluctuations with respect to the targeted actuation temperature.

At  $T$  well above  $T_g$ , i.e. in the rubbery state, the segmental mobility of a glassy polymer is high, so that the molecular network is able to rearrange quasi-instantaneously to reach a new equilibrium configuration in response to an applied stress, resulting in a quasi-instantaneous (macroscopic) elastic strain [7]. Well below  $T_g$ , on the other hand, the polymer is in a non-equilibrium state, conformational rearrangements are extremely slow, and brittle failure may intervene prior to any significant stress relaxation. If intermediate recovery rates are required, the recovery temperature should therefore be in the vicinity of  $T_g$  [8]. However, the relaxation and retardation times associated with conformational rearrangements in this regime generally show a strong temperature dependence [7], which implies the recovery rate also to be strongly dependent on  $T$ .

One strategy to reduce the temperature sensitivity of the free recovery rate might be to compensate the temperature dependence of individual retardation times by

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broadening the retardation time spectrum, bearing in mind that too broad a transition may compromise shape fixity at low  $T$  (indeed, for this reason the actuation temperature in most commercial SMPs, which are designed for rapid deployment, tends to be associated with a sharp transition in the mechanical response). In the present work, we therefore examine the effect of molecular architecture on the free recovery behavior of a series of amorphous shape memory polyurethanes (PUR) based on a formulation described previously by Buckley et al. [9], for which the retardation time spectrum is relatively broad. The results are compared with data from a commercial thermoset SMPU and discussed in the light of results from low strain dynamic mechanical analysis (DMA) temperature sweeps at constant frequency, which allow relatively rapid characterization of the linear viscoelastic response in the transition zone.

## 2. Materials and methods

### 2.1. Specimen preparation

A range of thermoset SMPUs was synthesized following Buckley et al. [9], based on a polytetrahydrofuran (PTHF) macrodiol with two weight average molar masses,  $M_w = 650$  and  $1000$  g/mol, 4,4'-diphenylmethane diisocyanate (MDI), and trimethylolpropane (TMP) as a cross-linker. The chain extender 1,4-butanediol (BDO) was also included in certain formulations. All chemicals were purchased from Sigma–Aldrich, Switzerland and were used without further purification.

1 mm thick sheets of the SMPUs were prepared as follows. First, the PTHF was vacuum-dried at  $110^\circ\text{C}$  and a pressure of less than 50 mbar for one and a half hours and then cooled under vacuum to  $70^\circ\text{C}$ . At the same time, the TMP was vacuum-dried at  $70^\circ\text{C}$  and a pressure of less than 50 mbar. Where BDO was included in the formulation, it was mixed with the TMP and the mixture vacuum-dried as for the TMP. The MDI was introduced to the PTHF at  $70^\circ\text{C}$ , followed by vigorous hand mixing for 30 s. The TMP or TMP/BDO was then added to the resulting pre-polymer and hand mixing continued for 30 s. A reaction temperature of  $70^\circ\text{C}$  was preferred to that of  $90^\circ\text{C}$  used elsewhere [9], so as to increase the pot life of the reaction mixture and hence facilitate subsequent liquid injection molding. The injection molding apparatus comprised a sealed steel chamber connected to a closed aluminum mold, which was preheated to  $90^\circ\text{C}$  for 1 h, a vacuum pump and a compressed air supply. This allowed rapid switching from the very low pressure required for efficient degassing (50 mbar for 45 s) to the pressure of 2 bar necessary to inject the reactive mixture into the mold within its 3 min pot-life. Once the mold was filled, the oven temperature was increased to  $110^\circ\text{C}$  and the specimen cured at this temperature for 24 h at 2 bar, after which the mold was left to cool to room temperature. All specimens were stored in a desiccator at ambient temperature prior to testing.

To study the effect of the cross-link density on the thermomechanical properties of the SMPUs, two formulations

were considered: PTHF (650 g/mol):MDI:TMP = 2:5:2 and 1:4:2, corresponding to TMP concentrations  $n_c = 0.71$  mol/kg and 1.04 mol/kg, respectively,  $n_c$  providing a measure of the cross-link density [9]. These will be referred to as P650-lowCD and P650-highCD in what follows. A blend of PTHF with weight average molar masses of  $M_w = 650$  and  $1000$  g/mol was also used to produce an SMPU with an increased degree of polydispersity of the molar mass between cross-links, which will be referred to as P650 + 1000. Finally, the chain extender BDO was used to modify the mobility at the junction between the PTHF and the TMP, and between 2 TMPs, in a formulation that will be referred to as P650 + CE. These formulations and the corresponding  $n_c$  are summarized in Table 1. A schematic representation of the morphology of the SMPUs is given in Fig. 2.

A two-part thermoset SMPU resin purchased from SMP Technologies (Japan) with the trade name MP5510 and a relatively narrow glass transition in the cured state was also investigated for comparison. The two components of the resin were degassed at room temperature under vacuum (50 mbar) for 1 h. They were then thoroughly hand-mixed for 30 s in the ratio 40:60 by mass, giving a reactive mixture with a pot life of about 5 min. The mixture was injected as described above, with a mold temperature of  $70^\circ\text{C}$  and a curing time of 4 h, following the manufacturer's recommendations. The final  $T_g$ , measured by differential scanning calorimetry (DSC) at a heating rate of  $10^\circ\text{C}/\text{min}$  was  $65^\circ\text{C}$ . All the specimens were post-cured at  $110^\circ\text{C}$  ( $70^\circ\text{C}$  for MP5510) and slowly cooled to room temperature immediately before testing in order to erase any effects of physical aging during storage. This precaution was important for the reproducibility of the experimental results owing to the proximity of the  $T_g$  to room temperature in certain of the SMPUs investigated here.

### 2.2. Dynamic mechanical analysis (DMA)

DMA measurements were made using a TA Instrument Q800 DMA calibrated with steel standards.  $1 \times 5 \times 10$  mm<sup>3</sup> rectangular specimens cut from the molded sheets were tested in tensile mode in dry air at a heating rate of  $2^\circ\text{C}/\text{min}$ , a frequency of 1 Hz and a dynamic strain of 0.01%, after equilibration at  $-50^\circ\text{C}$ . 1 Hz was chosen to be the measurement frequency in order to provide data consistent with the timescale of the shape memory tests described in the next section, i.e. so that processes occurring at fixed  $T$  in the time domain between 1 and 100 min corresponded to processes occurring immediately above this temperature in the DMA sweeps.

### 2.3. Tensile shape memory tests

Rectangular SMPU strips of  $1 \times 10 \times 100$  mm<sup>3</sup> (ASTM standard D 882) were tested using a Universal Testing System (UTS, Walter + Bai AG, Switzerland) equipped with a 1 kN load cell and an environmental chamber (Noske-Kaesser, Germany), capable of raising and lowering  $T$  under controlled conditions. A K-type thermocouple placed on a dummy specimen close to the test specimen was used to provide a precise indication of the specimen temperature.

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