Shape memory polyurethane foams

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Abstract. Molded flexible polyurethane (PU) foams have been synthesized from polypropylene glycol (PPG) with different molecular weights (M_w) and functionalities (f), and 2,4/2,6-toluene diisocyanate (TDI-80) with water as blowing agent. It was found that the glassy state properties of the foam mainly depended on the urethane group content while the rubbery state properties on the crosslink density. That is, PPG of low MW and low f (more urethane groups) provided superior glass state modulus, strength, density, shape fixity and glass transition temperature (T_g), while that of high M_w and high f (higher crosslink density) showed high rubbery modulus and shape recovery. Consequently shape fixity of low M_w PPG decreased from 85 to 72% while shape recovery increased from 52 to 63% as the content of high M_w PPG increased from 0 to 40%.

Keywords: smart polymers, polyurethane foam, dynamic mechanical properties, shape memory properties, density

1. Introduction

Shape memory polymers (SMPs) respond to stimuli such as temperature, electricity, pH, ionic strength and light [1–4], and have many advantages like low density, good shape recovery and easy processing [5–9]. Thermally actuated SMPs have found broad applications in actuators, smart textiles and coatings, sporting goods [10, 11] and in biomedical devices [12]. Recently, triple shape effect and two way shape memory behavior which are largely based on thermal triggering have also been suggested. [13–15]. Excellent reviews have also been published along with recent developments [6, 16, 17].

Molded flexible polyurethane foams are used in a broad range of applications including transportation seating and trim parts, packaging, furniture, and novelty items. The greatest advantage is that the foam is molded into the desired intricate shape and the need for cutting is eliminated [18, 19]. If high shape fixity and high shape recovery are endowed to such foam products, precision molding with high durability will be implemented.

Shape memory effects of polyurethane foam have also been reported with regard to the thermomechanical properties [20, 21], laser-activated foam device [22], effect of shape holding conditions [23], and for biomedical application [24, 25] Most of these studies use commercially available polyurethane foams. Consequently, the basic structure-property relationships of the shape memory foam have not been reported perhaps except those by the present groups [26, 27].

In this work molded flexible polyurethane foams have been synthesized from polypropylene glycol (PPG) with various molecular weights (M_w) and functionalities (f), and 2,4/2,6-toluene diisocyanate with water as blowing agent. The reactivity, mechanical and dynamic mechanical and shape memory properties of the foams were analyzed along with basic structure- property relationship of the foam.

2. Experimental
2.1. Raw materials

Two types of polypropylene glycol (PPG), viz. SR-240 and GP-3000 (KPX, Korea) with different

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molecular weights (M_w) and functionalities (f) were used. SR-240 has the number average molecular weight (determined by gel permeation chromatography) of 240, and functionality of 2, while $f = 3$ and number average $M_w = 3000$ for GP-3000. The Toluene diisocynate (TDI-80) was provided by Dow Chemical whereas TA-350 as a cell-opener by KPX Chemicals. The water used as chemical blowing agent was distilled in our laboratory. L-626 (silicon surfactant), A1 (bis(2-dimethylaminoethyl) ether, amine catalyst) and methylene chloride (MC, blowing catalysts) and T-9 (stannous octoate, organometallic gelling catalyst) were provided by Air Products (USA) and used as received.

2.2. Preparation of polyurethane foam

The flexible foams were synthesized by one-shot method. All raw materials were first put into a 500 ml beaker and mixed for 20 s at 3000 rpm using a dispersing turbine type impeller of 2.5 cm diameter at 25°C and 70% relative humidity. Then the mixtures were discharged to an open mold ($200 \times 200 \times 200$ mm) and the foam cake was cured for 48 h at room temperature. The NCO index (isocyanate equivalents/polyol equivalents) was fixed at 1.00. We designed and synthesized six types of molded flexible polyurethane foams having various ratios of the two polyols giving different average M_w and f values. The basic formulations are given in Table 1.

2.3. Characterizations

Kinetics of the foam formation was followed by the physical change of the properties. The cream time corresponds to the start of bubble rise and hence color of the mixture becomes creamlike from milk due to the formation of foam bubbles. Rise time is the starting point of stable network formation by intensive formations of urethane and urea linkages

and crosslinkings by allophanate and biuret reactions. The two characteristic times were measured by a digital stop watch.

The density of the foam was measured according to ASTM D 1622 with sample size of $30 \times 30 \times 30$ mm (width × length × thickness), and an average of at least five measurements was taken to report. The cell structure of the foam was studied with a polarized optical microscope (POM) at a magnification of 120. For the measurement, central part of the foam was cryogenically fractured in liquid nitrogen. The total number of cells was countered to report the number average size of the cell. Dynamic mechanical properties of the foam were measured using a dynamic mechanical thermal analyzer (DMTA, Rheometrics MK-IV) in tension mode. Samples were heated from –100 to 150°C at 5°C/min, 10 Hz and 2% strain.

Tensile properties of the foam were measured at room temperature with an universal testing machine (UTM, Lloyd, UK) at 2.00mm/min with the specimen dimension of $4 \times 25 \times 0.3$ mm (width × length × thickness). To measure the compressive strength, samples were cut into dimensions of $50 \times 50 \times 50$ mm (width × length × thickness) and placed between metal plates and compressed to 50% of the original thickness.

Shape memory properties were characterized using a temperature controlled universal testing machine. The sample was first heated to a loading temperature ($T_g + 20$°C) at 4°C/min before it was loaded to a maximum strain (ε_m) of 100%, followed by cooling to ($T_g - 20$°C) at a rate of 7°C/min under constant strain. Then the sample was unloaded, giving a substantial amount of shrinkage (ε_u) depending on the molecular and shape parameters of the foam. Then the sample was reheated to the loading temperature ($T_g + 20$°C) to recover the strain, leaving a substantial amount of permanent strain (ε_p). These

Table 1. Formulations to synthesize the polyurethane foams, T_g, and $G°_n$ (unit: pphp)

	SR-240	GP-3000	TA-350	L-626	Water	A1	T9	M.C	TDI-80	T_g [°C]	$G°_n \cdot 10^6$ [dyne/cm²]
S10	100	–							52.81	49.8	2.3
S08	80	20							47.06	39.6	3.6
S06	60	40	2	1	1.6	0.2	0.1	3	41.30	26.5	4.1
S04	40	60							35.64	–12.3	4.1
S02	20	80							29.92	–15.1	4.7
S00	–	100							24.21	–49.2	5.1

pphp: part per hundred polyol

three steps complete one thermomechanical cycle [28]. Shape fixity and shape recovery are defined by Equations (1) and (2) respectively:

$$\% \text{ shape fixity} = \frac{\varepsilon_u}{\varepsilon_m} \cdot 100 \tag{1}$$

$$\% \text{ shape recovery} = \frac{\varepsilon_r}{\varepsilon_m} \cdot 100 \tag{2}$$

where $\varepsilon_r = \varepsilon_u - \varepsilon_p$ is the recovered strain.

3. Results and discussion
3.1. Reactivity and foam density
Reactivity of the foaming reaction caused measuring the cream time and rise time. Table 2 shows that the two characteristic times monotonically increase with the increases of average molecular weight and functionality of the polyol mixture. This implies that both gelling and blowing reactions become slower. The reactivity decrease is primarily due to the decreased concentration of OH group which reacts with the isocyanate. This is seen from the decreased amount of the diisocyanate used in Table 1.

Typical POM morphologies of the foam are shown in Figure 1 and the details are summarized in Table 1 where the cell size increases from 0.3 (S10) to 0.45 mm (S04) with increasing molecular weight and functionality of the polyol. In accordance with the increased cell size, foam density decreases from about 59 (S10) to 52 (S04) [kg/m^3] (Figure 2). The smaller cell size with low M_w polyol is due to the fast gelling reaction over the foaming reaction.

Table 2. Reactivity and cell size

		S10	S08	S06	S04
Cream time	[s]	9	11	14	18
Rise time	[s]	189	200	219	235
Cell size	[mm]	0.30	0.36	0.37	0.45

Figure 2. Density of the polyurethane foams

Then the cell becomes strong enough before it is blown keeping the cell small. Density is a most important parameter to control the mechanical properties of the foam. The decreased foam density is related to the decreased urethane group content and glass transition temperature of the foam to be discussed with the dynamic mechanical measurements to follow.

3.2. Mechanical properties
It is seen that the tensile stress-strain curves are almost linear regardless of polyol type (Figure 3).
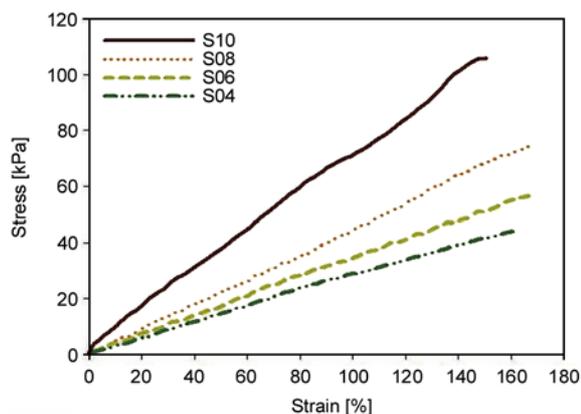
Figure 3. Tensile behaviors of the polyurethane foams

Figure 1. Typical POM morphologies of the foams (×120)
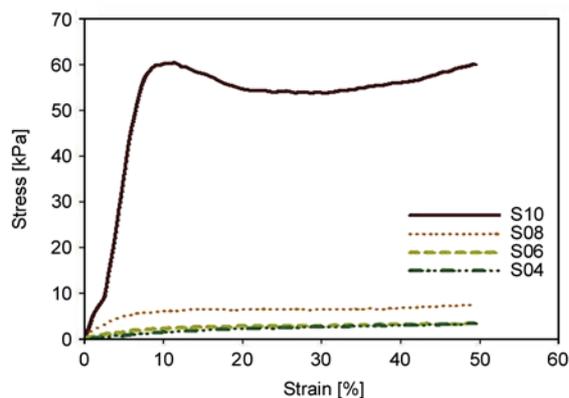
Figure 4. Compressive behaviors of the polyurethane foams

The initial modulus and break strength monotonically decrease with increasing molecular weight and functionality of the polyol while keeping the elongation at break almost constant. For example, the modulus of S10 is over 72 while that of S04 is about 25 kPa. The decrease is mainly due to the decreased T_g which on the other hand is introduced by the high molecular weight polyol which provides high chain flexibility and less urethane group. The two factors contribute to the lower T_g of the foam. It is mentioned that S02 and S00 showed insufficient loading capability to measure at room temperature. Figure 4 shows the compressive strength of the foam. The strength at 50% deformation of the original thickness was taken as the compressive strength of the foam. As expected the compressive modulus and strength decreases with increasing molecular weight and functionality of the polyol. Only S10 shows compression yield, necking-like behavior and strain hardening. It is noted that the compressive strength of S10 is greater than the tensile

strength while those of others are lower than the tensile strength when compared at the same deformation (50%). This is an indication that the S10 is in glassy state and others are in rubbery state.

3.3. Dynamic mechanical properties

The dynamic mechanical properties of the foams are given Figure 5 and Table 1 as a function of temperature. It is seen that the T_g of the foam which is seen in terms of tanδ peak decreases and the peak width broadens as the molecular weight and functionality of the polyol increases. The peak temperature ranges from about –50°C (S00) to 50°C (S10). Since the broad peak is an indication of broad damping and heterogeneity of the sample, lower molecular weight polyol augments the homogeneity of PU by the increased more hydrogen bonding between the urethane groups.

It is of interest to note that the glassy state modulus decreases while the rubbery state modulus increases with increasing molecular weight and functionality of the polyol. The decreased glassy modulus is a direct response of the decreased density of the foam. Density should decrease with decreasing intermolecular force which in this case is the hydrogen bonding between the urethane groups. On the other hand, increasing rubbery modulus is due to the increased crosslink density of the foam. Crosslink is introduced mainly by the tri-functional polyol. It is also introduced by the biuret reactions between the free isocyanate and urea groups, as noted from the existence of the rubbery plateau for S10 having no tri-functional polyol. Urea groups are introduced by the foaming reaction between the free isocyanate and water.
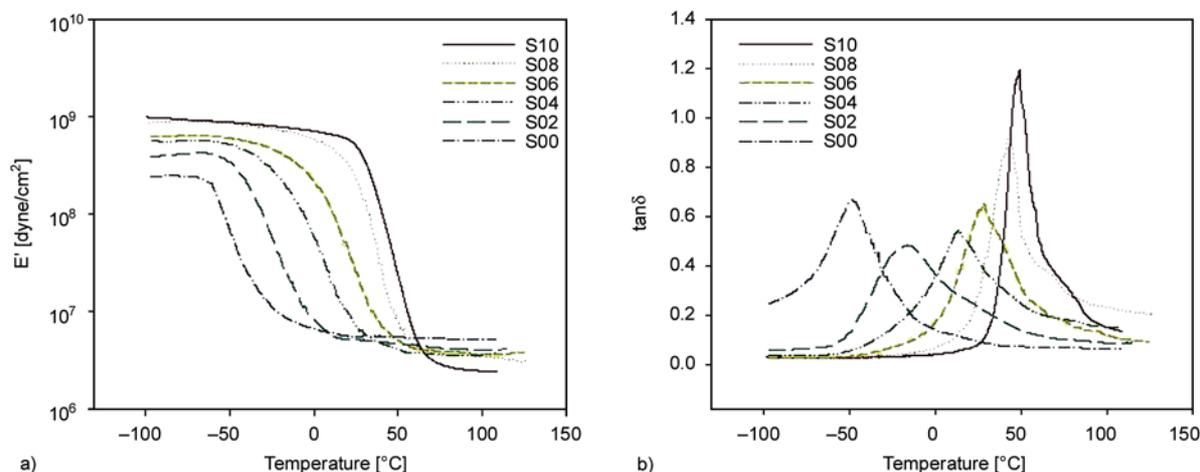
Figure 5. Dynamic mechanical properties of the polyurethane foams: storage modulus (a) and loss tangent (b)

It is noted that rubbery plateau modulus increases as the functionality of the polyol increases in accordance with the ideal rubber theory as shon by Equation (3) [29]:

$$G^{\circ}_{n} = \frac{\rho RT}{M_c} \tag{3}$$

where ρ is the density, R the gas constant, T the absolute temperature and M_c the molecular weight between the crosslinks. This implies that crosslink introduced by the tri-functional polyol of high molecular weight governs the rubbery state modulus while in glassy state the secondary force mainly governs the physical and mechanical properties of the foam.

3.4. Shape memory properties

Figure 6 shows the cyclic loading and unloading behavior of the foam for the first four thermomechanical cycles. It is seen that the shape fixity decreases from about 84 (S10) to 72% (S06) while shape recovery increases from 52 (S10) to 63 % (S06) with increasing molecular weight and functionality of the polyol [27]. This indicates that shape fixity depends on the glassy state modulus and shape recovery on the rubbery state modulus. This seems reasonable since shape is fixed during cooling where the slope of cooling step is the glass modulus [12] while the strain is recovered in rubbery state via the rubber elasticity which increases with increasing crosslink density. It is worth mentioning that the elastic strain energy viz. the area under the stress-strain curve is smaller with higher molecular weight polyol, thus the retractive force is maximum with S10. Regardless of polyol type, the cyclic hysteresis, viz. the reduction of area upon further cycling is mostly confined to the first cycle implying most chain breakages and chain slips are confined to the first cycle. However, it should be mentioned that the cyclic hysteresis of the foam is more serious than that of the elastomeric material [5, 28] due to the physical breakage of the cell structure, implying that foam is inherently more vulnerable to chain breakage upon tensile loading as compared with elastomeric materials.

4. Conclusions

The effects of molecular weight and functionality of polyol on the properties of molded flexible
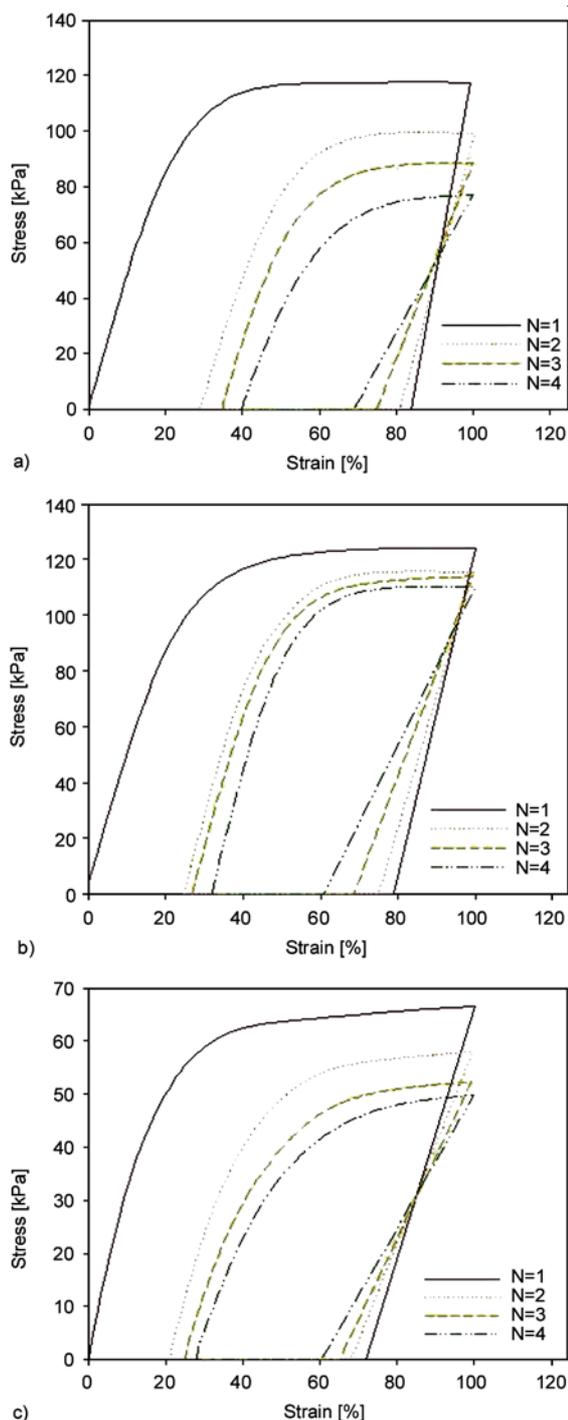
Figure 6. Thermomechanical cyclic behaviors of the polyurethane foams: (a) S10, (b) S08, (c) S06. *N* is the number of cycle.

polyurethane foam were studied and the following conclusions were drawn.

The cream time and rise time monotonically increased with the increases of average molecular weight of the polyol mixture due to the decreased concentration of OH group.

The glassy state properties of the foam mainly depended on the urethane group content, i.e., lower molecular weight polyol gave smaller cell size, higher foam density, strength and glass modulus. On the other hand, the rubbery state properties mainly depended on the crosslink density of the polyurethane, i.e., high crosslink density of high molecular weight of polyol gave high rubbery modulus according to the rubber elasticity. Consequently, high shape fixity of low molecular weight polyol is due to the high glassy state modulus while the high shape recovery of high molecular weight polyol due to the great rubber elasticity.

Acknowledgements

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