

SHAPE MEMORY POLYURETHANES BASED ON RECYCLED POLYVINYL BUTYRAL II. MECHANICAL AND SHAPE MEMORY PROPERTIES

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ABSTRACT

Shape memory polyurethanes (SMPUs) based on recycled polyvinyl butyral and 4,4'-diphenylmethane diisocyanate, hexane-1,6-diol, and polypropylene glycol of varying hard segment content were investigated. Their mechanical properties and shape memory effect in particular were examined defining the amorphous soft segment domain as a reversible phase, while the crystalline hard segment domain as a frozen phase. Effects of hard segment content (30 - 45 %) and maximum strain on the cyclic tensile and mechanical properties below (25°C) and above (70°C) material glass transition temperatures were studied. The properties reversibility observed on repeated deformation was improved by decrease of the deformation magnitude and the increase of the hard segment content.

Keywords: recycled polyvinyl butyral, shape memory, polyurethanes, mechanical properties.

INTRODUCTION

Shape memory polymers (SMPs) have rapidly developed over the last two decades [1-3]. Shape memory polyurethanes (SMPUs) have recently attracted much attention due to their unique properties, such as a wide range of shape recovery temperatures (-30 to 70°C) as well as high shape recoverability, good processing ability and excellent biocompatibility [4-7]. Their main advantages refer to their low cost and light weight when compared to shape memory alloys. SMPUs consist basically of two phases, a frozen phase and a reversible one. Crystalline, glassy state, entanglement network or crosslinking network can be used as a fixed structure memorizing the original shape. The thermally reversible phase is generally designed to have a large drop in the elastic modulus in case of heating up above the shape recovery temperature (T_s). The melting temperature (T_m) of the crystalline phase or the glass transition temperature (T_g) of the amorphous phase can be used as T_s [8-11].

In segmented polyurethanes, the physical aggregation of crystalline hard segments forming domains of a size usually less than 100 Å [12]. These domains can be viewed as the component forming the fixed structure. The glass-transition temperature of the soft segment which forms the reversible phase can be designated by T_g . Rubber elasticity is observed in the temperature range between T_s and the melting temperature of the hard segment domains in such polyurethanes. This is so because of the restricted molecular motion of the soft segments in the space around the crystalline hard-segment phase. Once deformed at temperatures between T_s and T_m and subsequently cooled below T_s under a constant strain, the deformed shape is fixed because of its frozen their mobility. When they are reheated to a temperature above T_s , a shape-memory effect is observed, i.e. the original shape is recovered by the elastic stress stored during the deformation.

We synthesized [13] segmented polyurethanes based on polypropylene glycol (PPG) and recycled polyvinyl

butyral (PVB) as soft segments (SS) using 4, 4'-diphenylmethane diisocyanate (MDI) and hexane 1,6-diol as chain extenders to form the hard segments (HS). The present communication reports the results obtained in studying their mechanical properties and shape memory effect.

EXPERIMENTAL

Details on the synthesis and the sample preparation are given in ref. [13]. The sample coding and the chemical composition of the materials used are given in Table 1.

Tensile test samples specimens molded to 2-mm thickness at 170°C were prepared by pressing 24 hours prior to the tensile tests. The latter were performed at room temperature and at 70°C using a universal testing machine (Zwick Z020, Ulm, Germany) with a dumbbell-type specimen. The gauge length and the crosshead

speed were 25 mm and 100 mm/min, respectively. The same machine equipped with a controlled thermal chamber was used to measure the shape memory effect. The samples were conditioned for 15 minutes to a specified temperature, T_1 (70°C), which was above the glass transition temperature of the soft segments, T_g . Then they were elongated to a maximum deformation of 50, 100 and 150 % of the original length with a rate of 100 mm min⁻¹.

The samples were then cooled below the glass transition temperature of the soft segments T_0 (25°C) and the force was brought back to zero. Finally, the samples shape was recovered by heating for 15 minutes at T_1 . The strain maintained after force removal and the residual strain measured after each cycle completion were used to calculate the shape fixing (R_f) and shape recovery (R_r) in accordance with the following equations:

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100 \% \quad (1)$$

$$R_r = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100 \% \quad (2)$$

where ε_m is the maximum strain achieved in the cycle, ε_u is the residual deformation after strain removal, while ε_p is the residual deformation after shape recovery.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of SMPUs were mea-

Table 1. SMPUs sample coding and chemical composition.

Sample	MDI/PPG/PVB /HD molar ratio [mol]	Hard segment content [mass %]
SMPU30	4/1/0.08/2.92	30
SMPU35	4/1/0.055/2.94 5	35
SMPU40	5/1/0.058/3.94 2	40
SMPU45	5/1/0.04/3.96	45

Table 2. Tensile analysis data of the SMPUs.

Sample	Room temperature [25°C]			70°C		
	Modulus, MPa	Tensile strength, MPa	Elongation at break, %	Modulus, MPa	Tensile strength, MPa	Elongation at break, %
SMPU 30	79	11.4	333	6.4	3.3	331.4
SMPU 35	95.9	10.5	249.9	10	2.8	209.1
SMPU 40	132.4	15.1	365.6	13.7	4.5	167.9
SMPU 45	164.6	16.7	483.5	22.9	6.7	423.7

sured at two temperatures, i.e. at room temperature (25°C) and at a higher value of 70°C (see Table 2). The room temperature values correspond to those of the glassy state, whereas the higher one - to those of the elastic state of state of the SMPUs. In fact these two temperature values correspond to T_0 and T_1 . The tensile test data of the samples investigated are summarized in Table 2.

Generally, the modulus, the tensile strength and the elongation at break measured at room temperature increase with the increase of the hard segment content. It is also evident that at high temperatures the modulus and the tensile strength increase, while the elongation at break decreases with hard segment content increase. The soft segment phase in these SMPUs is assumed a continuous matrix phase because of the predominating soft segments. That is why in case of imposing an external force the matrix soft phase deforms preferentially and the soft-segment domain containing low amounts of rigid hard segment shows lower values of the modulus and the tensile strength, while higher values of the elongation at break. The effect of hard segment content (HSC) on the tensile strength is not a linear one. Usually a maximum is observed in the range between 40% and 60% hard segment content depending on the structure and the morphology [14]. The maximum of elongation at break is found at 45 % HSC.

Shape memory effect

The results of the cyclic tensile tests characterizing the shape memory effect of the samples studied are shown in Figs. 2, 3 and 4. The sample is first elongated at 70°C to ϵ_m of 50 % (Fig. 2), 100 % (Fig. 3) and 150

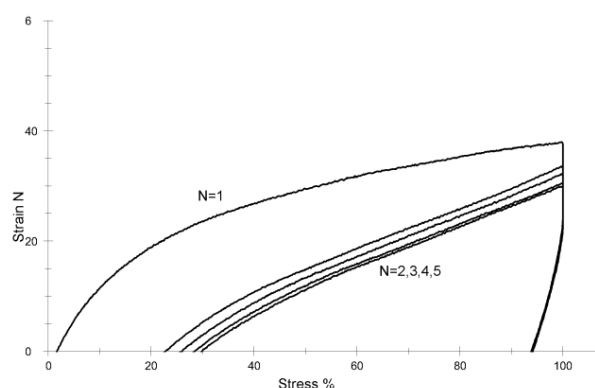


Fig. 1. Representative stress versus strain graph for the testing of shape memory behavior.

% (Fig. 4) at a constant elongation rate of 100 mm/min. The samples were cooled to 25°C, while maintaining the strain at ϵ_m . Then the strain was removed. A small recovery of the strain to ϵ_u occurred when the latter step proceeded at 25°C. The sample was subsequently heated to 70°C over for 15 min aiming a deformation recovery. Thus a thermomechanical cycle ($N = 1$) is completed. It leads to a residual strain, ϵ_p , which becomes the starting point for the subsequent cycle ($N = 2$). Fig. 1 depicts a model of the curves recorded during the thermal cycles.

Figs. 2-4 illustrate how the shape is preserved or recovered in dependence on the maximum strain and

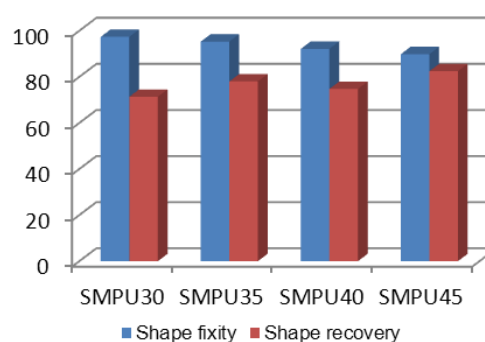


Fig. 2. Shape fixity and recovery at maximum strain of 50 %.

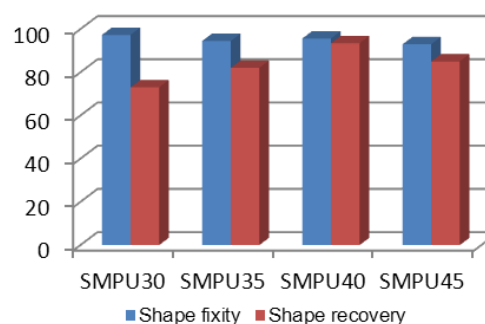


Fig. 3. Shape fixity and recovery at maximum strain of 100 %.

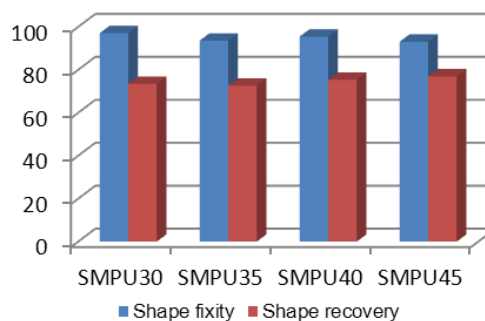


Fig. 4. Shape fixity and recovery at maximum strain of 150 %.

HSC. The shape recovery is almost unaffected by the maximum strain and the hard segments amount in the range between 90 % and 97 %. The shape recovery increases with the increase of the hard segment content.

CONCLUSIONS

It is found that shape memory effect can be achieved with the application of a new composition of polyurethane polyvinyl butyral copolymers where the PVB is crosslinked by polyether urethane bridges containing crystallizing hard segment domains. The shape memory effect is determined in the course of stress/strain and cyclic loading experiments providing the parameters required. The shape preservation reaches the maximum value of 97 %. It is not affected by maximal deformation applied and the HSC amount. The shape recovery increases with increase of the hard segment content and the maximum strain. In case of 150% strain the recovery starts to decrease probably due to damage of the structural elements responsible for the recovery mechanism. It is assumed that the combination of slight crosslinks, crystallizing hard segments (of MDI and hexane-1,6-diol origin), and the rather weak urethane bonds formed between the hydroxyl groups of the PVB and the MDI are responsible for this behavior. It is assumed that certain weak urethane groups can be temporarily destroyed by the mechanical forces applied and then recover on the removal of the latter. Furthermore, the hydrogen bond network is not as strong as in case of regular polyurethane elastomers. That is why the physical rupture of these bonds is also possible. Both phenomena act in the same direction leaving the shape memory effect restricted to certain ranges of the values of mechanical force and the temperature.

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