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Shape memory polyurethanes based on recycled polyvinyl butyral. I. Synthesis and morphology

Research Article

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Abstract: Shape memory polyurethanes (SMPUs) were synthesized by 4,4′-diphenylmethane diisocyanate (MDI), hexane-1,6-diol (HD), polypropylene glycol (PPG), and recycled polyvinyl butyral (PVB). Dynamic mechanical analysis, differential scanning calorimetry and Fourier transformation infrared attenuated total reflection spectroscopy was used to characterize the poly (vinylbutyral-urethanes). Micro-phase domain separation of hard and soft segments and phase inversion were investigated. Increasing the hard segment content, *i.e.*, average hard segment molecular weight, leads to an increase in the degree of micro-phase separation, hard domain order and crystallinity. The crystalline hard segment structures combined with the elastic nature of soft segment matrix provide enough physical and chemical crosslinks to have shape memory effect.

Keywords: *Polyvinyl butyral • Shape memory • Polyurethanes • Thermal analysis • IR spectroscopy*

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1. Introduction

The first recognition of the polymer shape memory effect (SME), as suggested by Mather et al., can be traced back to a patent in the 1940's in which "elastic memory" was mentioned [1]. The well-known heat shrinkage tubing that appeared in the 1960's, on the other hand, represents a commercial application of SMPs even before the terminology became used. Probably the first official use of the shape memory polymers (SMP) term started in 1984, with the development of the poly (norbornene) based SMP by CDF Chimie Company (France) [2]. Despite the long history of SMPs, however, the phenomenon of polymer SME had remained little known and the number of scientific papers in this area had been rather limited until the 1990's. Along this time frame, the discovery of segmented polyurethane with shape memory effect by Mitsubishi Heavy Industries Ltd. has stimulated significant interest in shape memory polyurethanes (SMPUs), due to the versatility of urethane chemistry that allows easy structural tuning and the industrial significance of polyurethanes.

Segmented polyurethanes (PU) are considered to be composed of a flexible soft segment and a rigid hard segment. Soft segments are formed from a long chain polydiol, and the hard segments are based on an aromatic diisocyanate and chain extender such as low molecular weight diols [3,4]. In segmented PU phase separation and formation of hard and soft segment domains are caused by repellent interactions between the dissimilar segments [3] and thermodynamic incompatibility [5]. Domain morphology affects the mechanical and thermal properties of the PUs. Monomers chemical structure, composition and stoichiometric ratio [6-8], the sequence length distribution of the hard and soft segments [9], the molecular weight and molecular weight distribution, processing conditions, and thermal history [10] could affect the morphology of the PUs [11]. Koberstein *et al.* proposed a morphological model which considered the length and distribution of the hard segment [10,11]. They assumed that hard segment, shorter than a critical sequence length, should be dissolved in the soft segment matrix and longer hard segment would tend to fold or coil forming the hard-segment rich phase. The

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hard segments and their chain length distribution lead to different morphologies formations. Glass transition and PUs properties are considered to be affected by the hard segment content.

Increasing growth of raw material prices, environmental aspects and landfill fees bring about the increasing interest encountered with plastic waste recycling. The main use of polyvinyl butyral (PVB) is in safety glass laminates, particularly in automotive, aerospace and architectural glass. Worldwide 65% of all PVB is used in automotive applications. An alternative to disposal in landfills is to recycle by mechanical means leading to variation in molecular structure of PVB and its effect on material properties and end use [12]. Only a few economically or practically feasible fields of uses have been discovered for material of PVB, which may contain glass particles, pure or mixed with other materials. PVB film for use in windscreens is designed to prevent glass from splintering. Modern equipment for automatic separation of glass and PVB film has been developed, so that most of the glass can be recycled into new products.

In this paper we propose a new approach for PVB waste utilization. Series of segmented polyurethanes based on polypropylene glycol and PVB as the soft segment and 4, 4'-diphenylmethane diisocyanate (MDI), and hexane-1,6-diol (HD) in different proportions as the hard segment were studied. The hard to soft segment ratio in the PU component was varied systematically, and for each specific PU composition their thermo-mechanical properties were compared to find the optimum combination.

2. Experimental procedure

2.1. Materials

Polypropylene glycol (PPG, M_w= 1100 g mol^{-1}, under the trade name Lupranol®1100, kindly supplied by Elastogran, Germany) and hexane-1, 6-diol (HD, M_w= 118.2 g mol^{-1}, supplied by Alfa Aesar, Karlsruhe, Germany) were used as received. Reagent grade 4, 4'-diphenylmethane diisocyanate (MDI, M_w= 250 g mol^{-1}, as Desmodur® 44 M, Bayer Material Science, Germany) was melted at 45°C and used after removing the white precipitates in the melts. Polyvinyl butyral (PVB, M_w= 25000 g mol^{-1}) was kindly supplied by Johann Schirmbeck Glasrecycling GmbH, Schierling, Germany. Recycled material was recovered from the delamination of car windshields from known commercial products and received as mixed scrap wastes.

2.2. Synthesis

Four polyurethane samples of varying composition were synthesized with PVB, MDI, PPG, and HD as the chain extender. To understand the effect of the content of the hard segment on the properties of the PUs, the mol ratios of MDI and HD were varied to synthesize PUs with different contents of hard segments. The compositions of the materials are listed in Table 1. A modified two-step polymerization was used. The NCO-terminated prepolymer was prepared by reacting MDI and the polyol at a specified NCO/OH molar ratio by using the following procedure: in a 500 mL four-neck flask equipped with magnetic stirrer, thermometer, heating nest and a gas inlet and outlet for continuous flow of nitrogen, an appropriate amount of the diisocyanate was melted at 45°C. PPG was added and the mixture was stirred vigorously at 80°C under nitrogen. The course of the reaction was followed by infrared absorption of the isocyanate stretching band at 2260 cm^{-1} and the reaction was considered to be complete when the band intensity remained constant for at least three distinct measurements. SMPUs synthesis was carried out in a Brabender® Plasti-corder® coupled with mixer model W350E. The desired amount of PVB was added into the mixing chamber at 140°C and homogenized for 10 minutes, followed by the addition of premixed hexane-1, 6- diol and prepolymer. The mixing time was determined as the time to reach the plateau of torque vs. mixing time plot. All samples were prepared by compression molding. A Servitec Polystat 400S hydraulic press, equipped with 200×200 mm steel frame, was used for compression molding. Samples were pressed at 170°C and 2.4 MPa for 10 minutes and subsequently cooled down to room temperature before de-molding.

2.3. Infrared spectroscopy (IR)

Fourier transform infrared attenuated total reflection spectroscopy (FTIR-ATR) was used to investigate hydrogen bond formation. Measurements were performed with a Varian 620 IR FTIR spectrometer equipped with GladiATR. Single beam spectra of the samples were obtained after averaging 16 scans between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were carried out in the absorbance mode.

2.4. Differential Scanning Calorimetry (DSC)

The thermal properties of SMPUs were measured by a Netzsch Phoenix 204 DSC, purged with nitrogen gas, and quenched with liquid nitrogen. The specimens were scanned from -150°C to 250°C with a heating rate of 10 K min^{-1}. The weight of the sample was 10–12 mg.

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Table 1. SMPUs molar composition.

Sample	MDI/PPG/PVB/HD molar ratio (mol)	Hard segment content (wt %)
SMPU30	4/1/0.08/2.92	30
SMPU35	4/1/0.055/2.945	35
SMPU40	5/1/0.058/3.942	40
SMPU45	5/1/0.04/3.96	45

2.5. Dynamic Mechanical Analysis (DMA)

DMA measurements were carried out with a Myrenne ATM3 DMA. Dynamic mechanical properties were measured in the tensile mode at a fixed frequency of 1 Hz under nitrogen gas purging. The measured specimens were heated from -150°C to 250°C using a heating rate of 5 K min^{-1}. The data of the storage modulus G′, loss modulus G″ and loss factor tan δ were recorded.

3. Results and discussion

3.1. Infrared spectroscopy

The urethane carbonyl C=O stretching region (Amide-I) is well known and widely studied. It is considered that infrared absorbance of hydrogen bonded urethane carbonyl appears at lower wavenumbers than that of the free urethane carbonyl [10,11,13,14]. Generally two C=O amide-I stretching bands are observed: H-bonded carbonyl groups in ordered designated as ''crystalline'' hard domains (1695- 1706 cm^{-1}) and non H-bonded designated as ''free'' carbonyl groups (1731- 1733 cm^{-1}). Fig. 1 displays the PUs infrared spectra. The peak at 1730 cm^{-1} was due to stretching of the hydrogen-bonded carbonyl and the one at 3320 cm^{-1} was due to the N–H stretching of the urethane linkage suggesting that with increasing hard segment content more aggregated domains are formed in the PU block copolymer. Such domain formation has a major impact on the mechanical and thermo- mechanical properties of the PUs. Increasing hard segment content gives a rise to hydrogen bonding between hard segments as well as dipole–dipole interaction between carbonyl groups affecting the C=O stretching vibration, and shifting the carbonyl stretching peak to lower wavenumbers [15]. Thus, the peak observed at 1730 cm^{-1} could be associated with the carbonyl of isolated hard segments and less influenced by the inter- or intra-chain interactions. Strong interactions in the hard segments probably have led higher degree of physical crosslinking and thus to phase separation or domain formation, an effect quite desirable in terms of shape memory polyurethanes [16,17].

In this work, the carbonyl peak in the FTIR spectra can be attributed to both urethane linkages in hard segments and ester linkages in PVB soft segments. Thus, it was not possible to unequivocally determine the degree of phase separation of hard segment domains.

3.2. Differential Scanning Calorimetry

Thermal properties, characteristic ranges and temperatures such as the glass transition range and temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_m) were measured using differential scanning calorimetry (DSC). DMA was used to determine the behavior of the hard segments within the macromolecular structures.

The thermal properties of the polymers were analyzed by DSC (Fig. 2). Generally, polyurethanes tend to segregate into hard and soft domains due to thermodynamic incompatibility and the aggregation of the hard segments consisting of the isocyanate and chain extender molecules (here MDI and HD) [18]. The arrangement of the segments and the degree of domain formation strongly depend on the polyol component used, the amount of isocyanate and chain extender used, mode of sample preparation, and the curing conditions. Thus, the glass transition temperature depends on the hard segment content and its quality of segregation– higher hard segment content and high degree of segregation lead to an increase in glass transition temperature.

The polymer material described here has a few peculiarities due to the material employed. The PVB used is a mixture of PVB and at least two plasticizers, *i.e.*, a phthalate as the major component and a sebacate [12]. This complicates the structure formation process. The chain extension employed by MDI and HD is not typical for PUs but was chosen because of the tendency of this combination to result in crystallinity. The reaction proceeds at the processing temperatures of 140°C and 170°C respectively, nearly complete as seen from the FTIR data where no isocyanate band appears (at 2260 cm^{-1}). Under these conditions, the MDI prepolymer first reacts with the primary hydroxyl groups of the HD forming rather small hard segments (MDI:HD-2:1 to 3:2). Before a reaction occurs with the secondary hydroxyl groups of the PVB, most of the primary hydroxyl groups have reacted resulting in pre-formed hard segments which are, in a second step, attached to the PVB backbone while the plasticizers are moving out of the phase between the PVB chains into smaller units and interacting with the hard segments *via* intermolecular interactions. Thus, the complicated reaction mixture processed in a one-stage process is reflected by the DSC curves. Fig. 2 shows the curves

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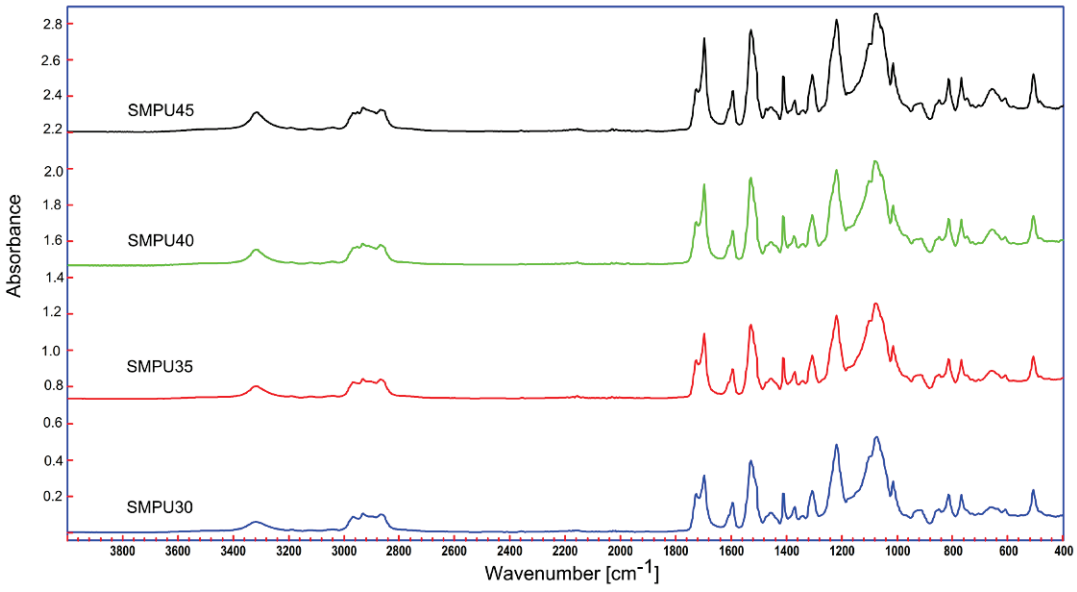

Figure 1. FTIR spectra of SMPUs with varying hard segment content.

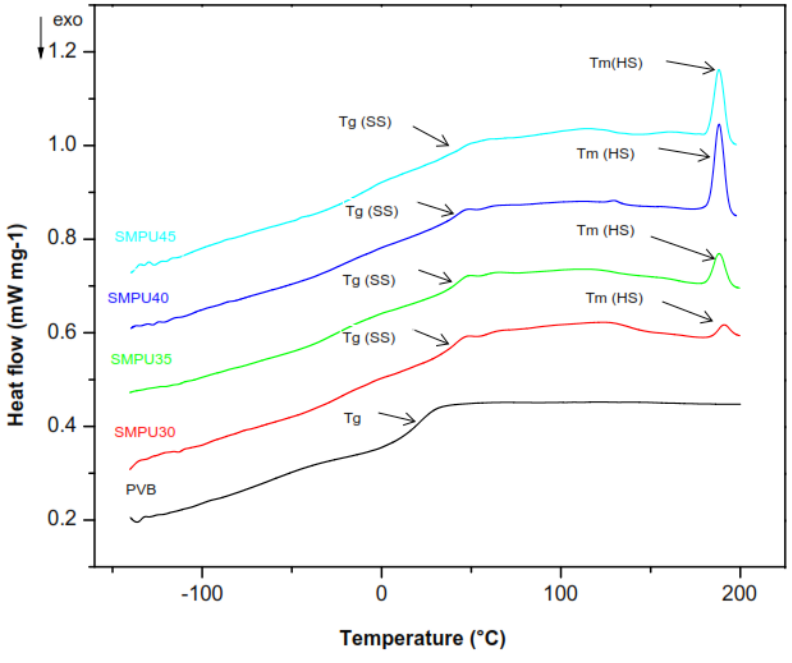

Figure 2. DSC heating curves of SMPUs with varying hard segment content.

of PVB and the polymers with varied hard segment content in the range between 30% and 45% b. w. and the glass transition temperatures of the soft segments, heat of fusion and melting temperatures of the PU block copolymers having 30, 35, 40, and 45 wt.% of hard segment can be depicted.

First glass transition is recognizable in the original PVB sample at about -50°C which is assigned to the plasticizers. This transition is shifted to higher temperatures with increasing hard segment content, suggesting a mixed phase is formed of the hard segments and the plasticizer which is growing when increasing the amount of the MDI and HD. Second transition is suggested to be the main transition in the region of 20°C at PVB but increasing to 48°C when 45% of hard segments are incorporated. The increase in the main transition reflects the interaction of the MDI and HD with the PVB backbone and the cross-linking of the

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Table 2. Thermal analysis data.

Sample	T_g (SS) (°C) *DSC*	T_g (SS) (°C) *DMA*	T_m (HS) (°C) *DSC/DMA*	ΔH_m (HS) (J g^{-1}) *DSC*
SMPU30	42	1/45	188/191	1.104
SMPU35	45	0/48	188/180	3.196
SMPU40	45	3/44	188/177	7.577
SMPU45	48	10/49	191/175	5.79

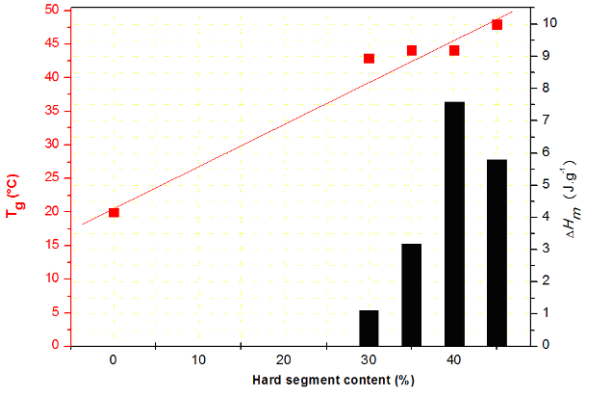

Figure 3. Dependence of T_g and heat of fusion on hard segment content.

chains. The molecular weight between these cross-links does not decrease to the really hard structure so that the difference between the polymers containing 30 and 45% b. w. of hard segments is only 5°C (Fig. 3).

The increase in cross-linking and the increase of mixing of some non-segregated hard segments into the soft segment being the PVB backbone are seen as the origin of the T_g increase. The step of the main transition region in the curves is followed by a small endothermic peak suggesting that the material is in non-equilibrium. This view is supported by the slight maximum between 80°C and 120°C which shows that during this heating period of the material in the DSC, the non-equilibrium state tends to equalize at that very moment.

At temperatures between 180°C and 195°C, there is a sharp melting region. This region is not present in the pure PVB but increases in area with increasing hard segment content (Fig. 3).

The increase in the hard segment content leads to a melting point at temperatures of about 200°C. The melting peak of these highly ordered domains increases with increasing content of isocyanate and chain extender forming well aggregated crystalline rigid domains. With increasing the hard segment content, obviously a higher degree of phase segregation occurs and better-ordered polymer morphology compared to those with a lower percentage of hard segment content also occurs. It is further seen that the curve seems to have a maximum at 40% of hard segment content, suggesting that, between 40% and 45% of hard segment, a phase inversion occurs. It is to be considered that the PVB phase at 40% hard segment content actually contains approximately 52% b. w. of hard segment when not considering the plasticizer that may be neglected in this discussion. At 45% b. w. hard segment, the actual content is more than 58% in relation to PVB and clearly beyond the 50% threshold.

The transition temperatures of the region of about 40°C to 50°C can be used as an indication of the relative purity of the soft segment regions while the peak area at the 188°C peak reflect the quality and degree of crystallinity of the MDI/HD hard segments. The more the soft domains are contaminated with integrated high glass transition temperature hard segments and the higher the crosslink density, the higher will be the T_g. and the transition region in DSC broader.

3.3 Dynamic Mechanical Analysis (DMA)

The DMA of the molded polyurethanes provides information on their viscoelastic properties, which can be related to micro-domain thermal transitions to obtain information about micro-domain purity or micro-domain degree of segregation, *i.e.*, the presence of the hard segments in the soft phase and *vice versa*. Dynamic mechanical properties (G' and tan δ) of polyurethanes with different hard segment contents are shown in Fig. 4.

As Fig. 4 shows, G′ and tan δ vary markedly in the vicinity of T_g in the range of 42°C to 49°C. As seen in the G′ curves, there are at least two transitions in the main transition region. This suggests that there are at least two different phases built up of the main polymer PVB and some addition of short hard segments, which are "dissolved" in the PVB. The increase in the magnitude of the plateau module beyond about 25°C shows the increase in hard segment content. Also, this region is characterized by some structure. The plateau refers to chemical and physical cross-linking. The shorter hard segments are either as singular components of the hard domains or as part of the PVB matrix will start to melt at much lower temperatures than the longer ones, shown *e.g.* with the weak peaks in the region between 120°C and 150°C. The longer the chains of the hard segments, the higher will be their melting temperature which finally reaches 192°C. Furthermore, the structural units of the hard segments are able to interact with other structural units, *e.g.* the carboxyl ester group of the plasticizer or the oxygen atoms of the PVB *via* the hydrogen atoms of the urethane groups. The longer hard segments melt at

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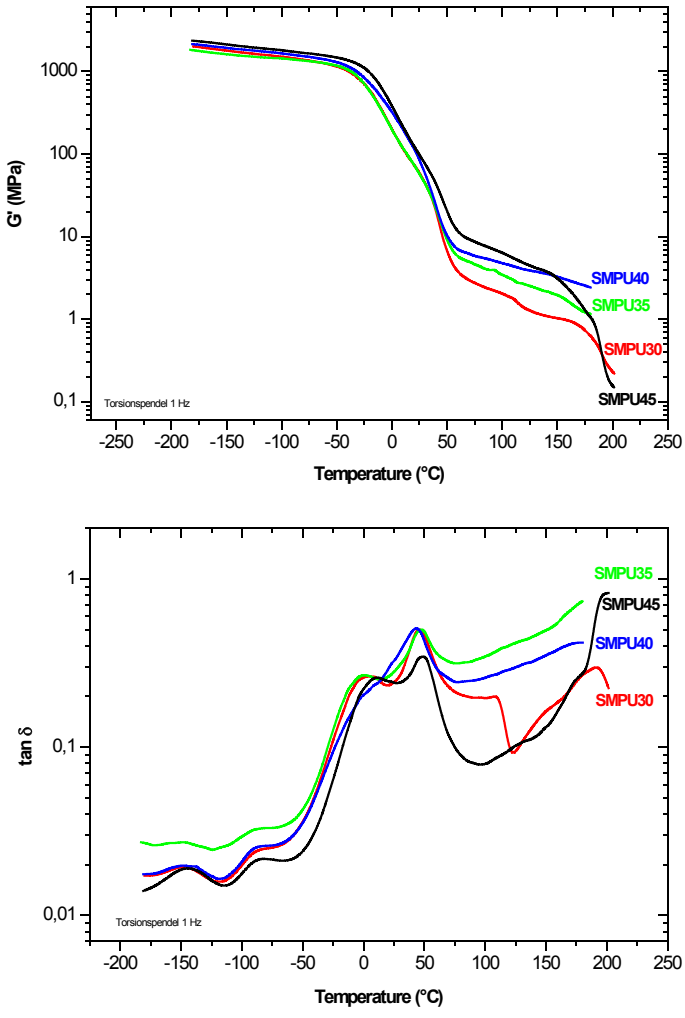

Figure 4. DMA scans of SMPUs with varying hard segment content.

temperatures exceeding 170°C. This is depicted in the curve of the sample with 45% of hard segments showing two distinct transitions. This and the comparison with the 40% sample again point to a phase inversion of the material from a PVB dominated matrix to a hard segment dominated matrix.

The loss modulus curves (tan δ) are to be considered while keeping in mind that the curve of the 35% sample is somewhat deteriorated in the temperature region between -185°C and -50°C due to a failure in the sample at the clamps of the DMA. The first maximum at about -150°C is dedicated to the mobility of small groups of side chains. The second maximum at about -85°C shows the transition of the pure plasticizer phase and which is nearly independent of the composition. The glass transition region is split into two maxima between 0°C and 50°C showing the two-phase structure of the soft segments. The first maximum at about 0°C to 10°C corresponds to the glass transition temperature of the soft segments based on PPG 1100 (T_g (PPG 1100)= –67°C) [19]. The shift of the glass transition of about 70°C is attributed to better phase separation in the soft matrix. The highest phase separation is observed at the sample SMPU45 (highest HSC). The second maximum at about 40°C shows that both phases have a different composition but have high entropy elasticity and point to the fact that a nearly perfect network is produced, *i.e.*, the PVB chains are interconnected by the MDI/HD hard segments.

The higher temperature region reflects again the complex structure of the material. In SMPU30, there can be seen another phase at about 120°C (which is the same as in the DSC curves) showing the melting of short MDI/HD chains (2:1). The longer MDI/HD chains are reflected in the peak at about 175°C. In SMPU35 and SMPU40, the melting of the hard segment domains

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occurs above 180°C, *i.e.*, in the same region as was shown in DSC. The SMPU40 curve depicts, at its highest temperature, the start of the melting process.

The two-stage process of sample preparation is to be discussed in terms of the stepwise polyaddition process. During the course of the polyaddition, first the most reactive groups react to form small oligomers [20]. A lot of oligomers combine in the second stage to form longer chains or entangled aggregates. These duplicate and react with reactive groups of lower reactivity or even such being sterically hindered because of the generally decreased rate of reaction, the more difficult diffusion due to higher viscosity of the mixture. Thus, there is always a broad distribution in the chain length of the single hard segment molecules and the reaction with the secondary hydroxyl groups of the PVB will start at a late stage of the process [21].

The ratio of G′ at temperatures above and below T_g (T_g + 20°C to T_g – 20°C) is very large, being about 100. This indicates that the material is easily deformed at high temperatures and, furthermore, that deformation resistance is larger at low temperatures. On the other hand, tan δ becomes very large at temperatures in the vicinity of T_g and tan δ is about 0.3 to 0.5 at T_g. As already stated, the material developed shows very good entropy elasticity. This suggests that the function as a high damping material is superior at temperatures in the vicinity of T_g.

4. Conclusion

The morphological investigation of the shape memory PUs was carried out using DSC, DMA, and FTIR. The change in soft and hard segment domains' quality of the PUs depends on the content of hard segments (MDI/HD) and the processing conditions. The greater the amount of MDI and HD used, (i) the higher the T_g and (ii) the lower the modulus ratio of the PUs obtained. It is seen that the compatibility of the soft-segment domains and the hard-segment domains is better in cases where the content of the hard segment is increased, as indicated by the DMA and FTIR data but, at a content between 40% and 45%, there is a phase inversion from the PVB matrix determining the properties to the MDI/HD domains determining them. The distribution of the hard segments is broad and short MDI HD oligomers that are dispersed in the PVB matrix, which melts at lower temperatures. The results also indicate that the reversible phase of SMPUs was the soft segment rich phase containing PVB and short hard segments. The fixed phase was the hard segment rich phase. SMPUs with high T_g show high recovery temperature. The combination of a rather wide network between two pure carbon chains and crystallized hard segments, both being able to react to external forces and adopt other shapes, are able to recover their original shape upon removal of the external force.

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