Dynamic-mechanical and differential scanning calorimetry measurements on crosslinked poly(ester-siloxane)-urethanes

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Dedicated to Professor Cristofor I. Simionescu on his 80th anniversary.

Abstract

Various crosslinked poly(ester-siloxane)-urethanes containing hard and soft segments, were prepared by a one-step melting/polyaddition. Thus, soft sequences based on poly(ethylene glycol adipate)diol (PEGA) or poly(diethylene glycol adipate)diol (PDEGA) as ester components, α,ω-poly(dimethylsiloxane)diol (PDMS) and/or polybutadienediol (PBD), were built. The hard segments were composed from diglycerin maleate tetrol (DGMA) and two aromatic diisocyanates, 4,4′-diphenylmethane diisocyanate (MDI) and 2,4-tolylene diisocyanate (TDI). Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were employed to characterise crosslinked polyurethane materials. The obtained data revealed that the thermal curves are influenced significantly by the soft and hard segment structures in the temperature range studied. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Crosslinked polyurethanes; Dynamic-mechanical properties; Differential scanning calorimetry

1. Introduction

It is well known that the poly(dimethylsiloxane) elastomers present important physical and chemical properties, previously discussed [1–4]. They are considered to have very good resistance at temperature and oxidant agents, ultraviolet radiation, very low glass transition, good gas permeability and biocompatibility, but they exhibit rather poor mechanical properties [5,6]. On the other hand, the polyurethanes show superior mechanical properties but a reduced thermostability [7–14]. Preparing block copolymers with hard segments based on polyurethanes, polyamides, polycarbonate–polyurethanes and soft segments based on polybutadiene, polyisobutylene and polydimethylsiloxane can exceed these disadvantages of siloxanic elastomers and polyurethanes [15–18]. The increasing interest in multiphase copolymers based on polydimethylsiloxane is mainly due to their unique combination of properties, which is related to their chemical structure and macromolecular architecture [19–23]. These compounds are a very important group of materials that opened a range of new applications.

According to the recent development of medical technology, it is desired to create polymer materials having a wide variety of functions [21,24]. In the case of polymers used for medical design antithrombogenicity is one of the most important factors to be taken into account, as well as suitable mechanical properties. Polyurethanes and poly(urethaneurea)s are widely used materials for these purposes, particularly for the artificial heart and blood vessels, where elastic properties similar to those of muscle are required as well as antithrombogenicity [25,26].

The structural and compositional diversity of polyurethane elastomers represent a useful way to study the properties and the structure of these materials.

The previous publications [27–32] presented the syntheses of some new segmented and crosslinked polyurethane elastomers containing very flexible chains. The influence of polymer structure on the thermal stability, the behaviour in different organic solvents, the structure and the morphology of these compounds were analysed. The goal of the present work is to investigate the correlation between the molecular structure, the dynamic-mechanical properties and the differential scanning calorimetry behaviour of the crosslinked poly(ester-siloxane)urethanes (PUS).

2. Experimental

2.1. Polymer syntheses

The starting materials were poly(diethylene glycol adipate)

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Table 1
Chemical composition of the crosslinked poly(ester-siloxane)-urethanes samples containing hard and soft segments

Sample	Soft segment			Hard segment		Weight ratio
	R_1	R_2	R_3	R_4	Ar	R_1:R_2:R_3:(R_4 + Ar)
PUS1	PEGA	PDMS	–	DGMA	MDI	52.5:12:0:35.5
PUS2	PDEGA	PDMS	–	DGMA	MDI	52.0:12:0:36.0
PUS3	PEGA	–	–	DGMA	TDI	73.0:0:0:27.0
PUS4	PEGA	PDMS	–	DGMA	TDI	60.5:12:0:27.5
PUS5	PDEGA	PDMS	–	DGMA	TDI	60.0:12:0:28.0
PUS6	PDEGA	PDMS	PBD	DGMA	TDI	46.0:12:12:30.0

diol (DPEGA) with $M_n = 2500$, α,ω-poly(dimethylsiloxane)-diol (PDMS) with $M_n = 10,000$, and diglycerin maleate tetrol (DGMA) obtained as described in our previous works [27,31]. We also used poly(ethylene glycol adipate)diol (PEGA) with $M_n = 2000$ (supplied by Fibrex SA, Savinesti, Romania), 4,4′-diphenylmethane diisocyanate (MDI), 2,4-tolylene diisocyanate (TDI, Riedel) and polybutadienediol (PBD, Aldrich), with $M_n = 2400$. The samples of chemically crosslinked poly(ester-siloxane)urethanes were obtained by one-step melting/polyaddition [27,31] at a molar ratio NCO/OH = 1:1. The chemical compositions of the considered samples are shown in Table 1.

The optimum concentration of urethane groups in the PUS was found to be 2×10^{-3}–2.11×10^{-3} moles per gram of polymer [31]. According to these results, a concentration of urethane groups of 2×10^{-3} moles per gram of polymer was considered for all the synthesised samples.

2.2. Measurements

Dynamic mechanical tests were carried out in air atmosphere by means of Du Pont Instruments, Dynamic Mechanical Analyser 983 (Nemours & Co. (Inc.), Concord Plaza-Quillen Building, Wilmington, DE 19898) on samples of following sizes: 26 mm:2 mm:7 mm. The tests

at 0.060, 0.125, 0.250, 0.5, 1 and 2 Hz frequencies, and the temperature range 25–100°C, with a heating rate of 2°C / min were accomplished.

The differential scanning calorimetry (DSC) curves were determined in air atmosphere by a Du Pont DSC 9900 at a heating rate of 10°C/min, in temperature range from 20 to 250°C on samples of 10 mg, using the aluminium open pans.
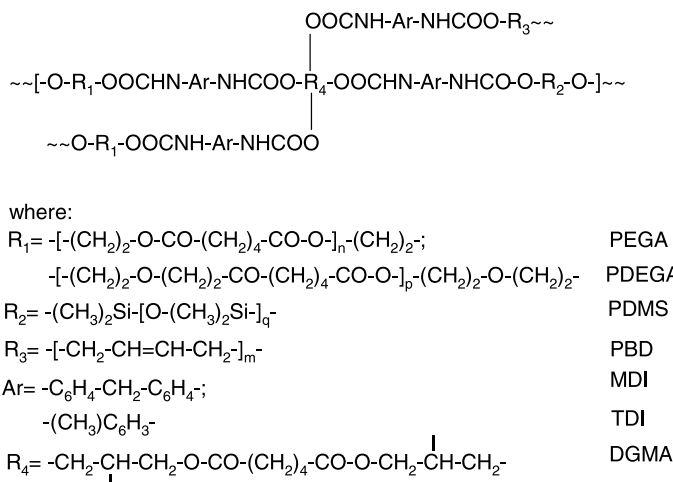
3. Results and discussion

The general structure of the poly(ester-siloxane)urethanes discussed in the present work is presented in Scheme 1.

The cumulative effects of the all components from the soft and hard segments, in the rubbery phase were studied.

3.1. Dynamic mechanical analyses

The dynamic mechanical tests offer the possibility to follow the change in both the elastic and viscous properties of a material as a function of temperature and morphology of the polymers [33–37]. If a polymer is semicrystalline, the height of the rubbery plateau is governed by the degree of crystallinity. This is due to two factors: first, the crystalline regions tend to behave as a filler phase, and second, because the crystalline regions also behave as a kind of physical crosslink, binding the chains together [38].

In conformity with previous data ([31], Fig. 5), the rubbery region of the studied samples starts from the approximately 25°C, when all the flexible segments are in the high elastic state, while the hard segments are in the glassy state. It is known that the hard segments are destroyed without passing through the high elastic state. In the rubbery plateau region, crosslinked poly(ester-siloxane)urethanes exhibit long-range rubber elasticity, i.e. the elastomer can be stretched, even several hundred percents, and snap back to its original length when being released. Properties varying from that characteristic to tough plastics

OOCNH-Ar-NHCOO-R₃~~
|
~~[-O-R₁-OOCHN-Ar-NHCOO-R₄-OOCHN-Ar-NHCO-O-R₂-O-]~~
|
~~O-R₁-OOCNH-Ar-NHCOO

where:
R₁= -[-(CH₂)₂-O-CO-(CH₂)₄-CO-O-]ₙ-(CH₂)₂-;   PEGA
     -[-(CH₂)₂-O-(CH₂)₂-CO-(CH₂)₄-CO-O-]ₚ-(CH₂)₂-O-(CH₂)₂-   PDEGA
R₂= -(CH₃)₂Si-[O-(CH₃)₂Si-]_q-   PDMS
R₃= -[-CH₂-CH=CH-CH₂-]ₘ-   PBD
Ar= -C₆H₄-CH₂-C₆H₄-;   MDI
     -(CH₃)C₆H₃-   TDI
R₄= -CH₂-CH-CH₂-O-CO-(CH₂)₄-CO-O-CH₂-CH-CH₂-   DGMA

Scheme 1.

to very soft rubbers can be obtained, depending on the soft segment length and concentration.

3.1.1. Effect of frequency

Fig. 1a–c present data concerning dynamic-mechanical properties of PUS1 at six frequencies in the 0.060–2.000 Hz domain and in the 25–100°C temperature range. As the frequency increases, the tensile storage modulus, E', and tensile loss modulus E'', increases.

A useful parameter, which is dimensionless and conveys no physical magnitude but is a measure of the ratio of energy lost to energy stored in a cyclic deformation, is the loss tangent, tan δ. For the investigated domain 0.060–2.000 Hz, one can observe that the loss tangent generally increases with increasing of frequency. This behaviour is confirmed by literature data for the crosslinked polymers [38]. Also, for the studied temperature range, which corresponds to the usual utilisation domain of these polymers, the tan δ do not exhibit damping peaks which correspond to $T_g(S)$ of soft segments at lower temperature and to $T_g(H)$ of hard segments at higher temperature. Thus, in a previous paper [31] we showed that the PUS samples manifest the transitions corresponding to the soft segments at $T_g = -124$ up to $-90°C$, assigned to PDMS segments and at $T_g = -25$ up to 45°C, assigned to PDEGA units. Because above 250°C begins the degradation of these samples, T_g transitions for the hard segments could not be determined [29].

3.1.2. Effect of soft and hard segment structure on tensile properties

The E', E'' and tan δ versus temperature curves of the crosslinked poly(ester-siloxane)urethanes analysed are shown in Fig. 2a–c. One can conclude that the structures of diisocyanates and crosslinks agents have a strong effect on the domain morphology and the mechanical resistance of polyurethane materials. Symmetric isocyanates form crystallising hard segments with good packing ability, producing materials with high mechanical resistance. Usually diisocyanates have been compared only at certain specific hard segment concentration, thus the conclusions presented in the literature could not be general enough. It has been shown [38] that the structure of the diisocyanate affects tensile strength, modulus and hardness of elastomers. The following diisocianates are listed in decreasing order of tensile strengths: MDI > p-phenylene diisocyanate > 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate (DMDI) > TDI > 3,3'-dimethyl-4,4'-diphenyl diisocyanate (TPDI) > 4,4'-diphenylisopropylidene diisocyanateee (DPDI). Diisocyanates with methyl substituents, such as TDI, DMDI and DPDI, favourites lower modulus than those with an analogous structure but without substituents. Samples containing MDI is believed to possess significant chain rigidity because of the high cohesive energy and bulkiness of the benzene ring [38].

In the present work the influence on the mechanical properties of MDI or TDI together with DGMA as hard segments, was taken into account. The effect of DGMA on physical properties of crosslinked polyurethanes determines an increased number of urethane connections, and an increase interchain interaction caused by the hydrogen bonds and chemical crosslinks between diisocyanates and DGMA. Typically for crosslinked polyurethanes, the elastic properties are mainly governed by the polyol, and the mechanical strength by the hard domains. The above characteristics mainly contribute to the mechanical strength. The presence of DGMA as chain extender, determined an increase of the tensile storage modulus, E' as well as the T_g of soft segment. This again is a clear indication of increased chain rigidity with DGMA presence.

All the analysed samples have DGMA as one of the hard components, the other one being either MDI or TDI. The highest tensile storage modulus was obtained for PUS1, which contains in hard segments MDI, followed by the samples PUS3, PUS6 and PUS5, which contain as hard segments TDI components (Fig. 2a), in good agreement with literature data. Moduli at deformations reflect the tendency of the soft blocks to crystallise under stress. Thus, sample PUS1 based on MDI are crystallisable, causing the higher moduli than the corresponding samples with TDI.

Tensile strength is also highly dependent on the type of chain extender used. A comparison of various diol chain extenders showed [38] that 1,4-butanediol gives superior tensile strength and rebound elasticity but inferior compression value as related to ethylene glycol. In the present work, an increase of the effects manifested by the 1,4-butanediol is achieved by replaced with DGMA.

The influence of soft segment structure on the tensile storage modulus is related to the intermolecular association and crystallisation during stretching. The effect of the soft segment is pronounced mainly in polymers with a continuous soft phase, i.e. above 50%.

For the same composition of hard segment, replacing PEGA with PDEGA as one of the soft components determines the decreasing of tensile storage modulus (e.g. samples PUS1 and PUS2, Fig. 2a). This effect increases when the amount of PDEGA is increased (samples PUS5 and PUS6, Fig. 2a). Also, PUS6 based on PDEGA–PDMS–PBD as soft segment reveals a higher tensile storage modulus than PUS5 based only on PDEGA–PDMS. This behaviour is probably due to some additional effects in PUS6, such as the supplementary crosslinkings. The same effects were observed in the literature too [34,39] for the PBD/TDI/BD segmented polyurethanes.

From Fig. 2b one can observe that the influence on tensile loss modulus is approximately the same for all the studied samples. This proves that the energy lost as heat is not modified by the structure of crosslinked copolymers for the temperature range 40–100°C. Higher differences appear for temperatures below 40°C. Also, the curves corresponding of the loss tangent versus temperature (Fig. 2c) show the same form.
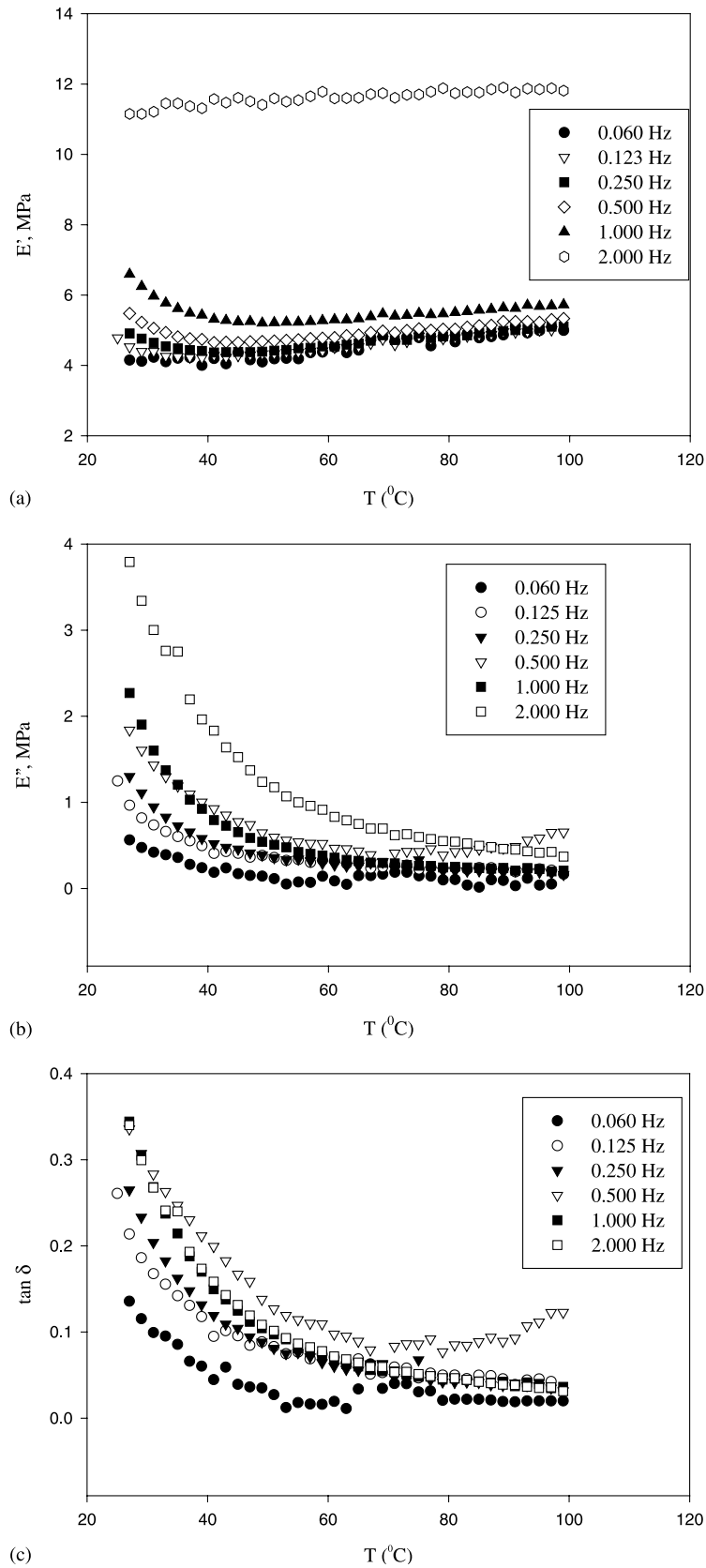
Fig. 1. (a) Plot of tensile storage modulus (E') as a function of temperature and frequency for PUS1. (b) Plot of tensile loss modulus (E'') as a function of temperature and frequency for PUS1. (c) Plot of tan δ as a function of temperature and frequency for PUS1.
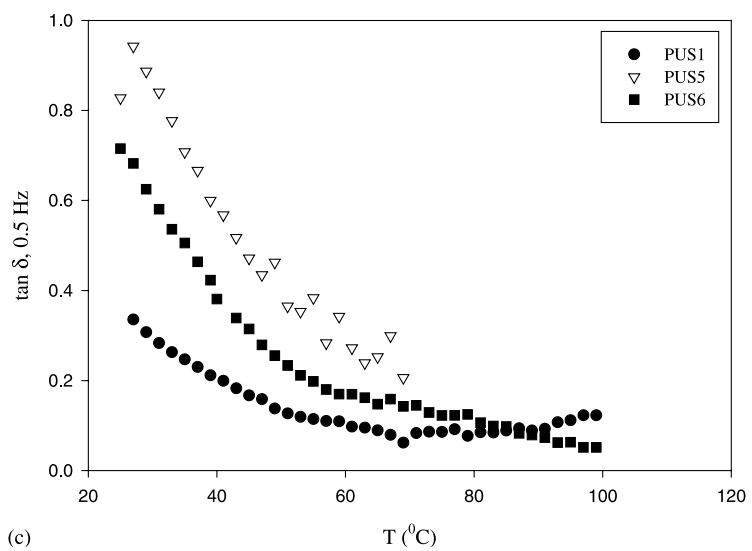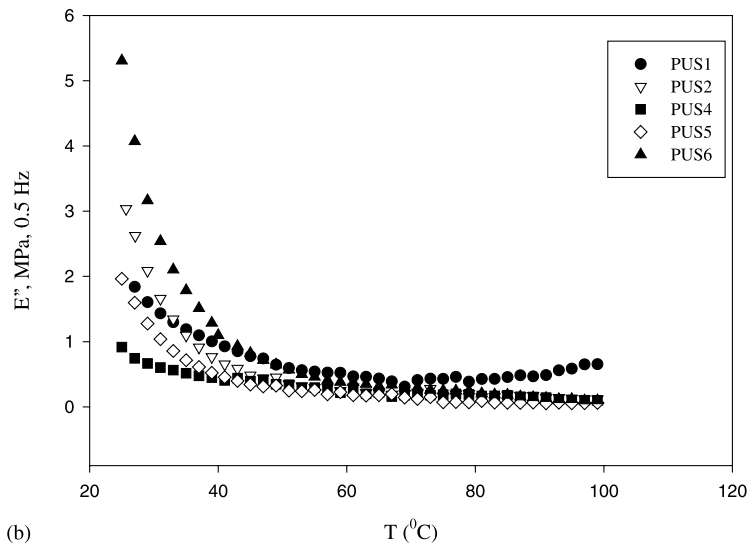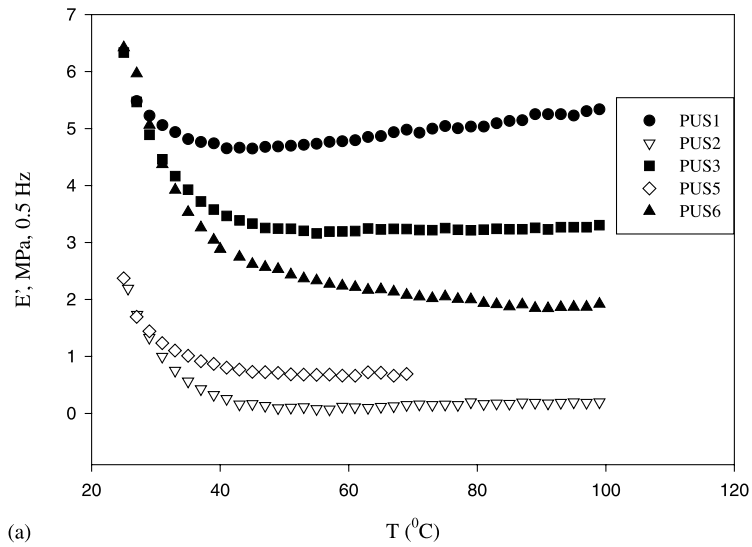
Fig. 2. (a) Plot of tensile storage modulus (E') as a function of temperature at 0.500 Hz for crosslinked poly(ester-siloxane)-urethanes with different hard and soft components (PUS1, PUS2, PUS3, PUS5, and PUS6). (b) Plot of tensile loss modulus (E'') as a function of temperature at 0.500 Hz for crosslinked poly(ester-siloxane)-urethanes with different hard and soft components (PUS1, PUS2, PUS4, PUS5 and PUS6). (c) Plot of tan δ as a function of temperature at 0.500 Hz for crosslinked poly(ester-siloxane)-urethanes with different hard and soft components (PUS1, PUS5 and PUS6).
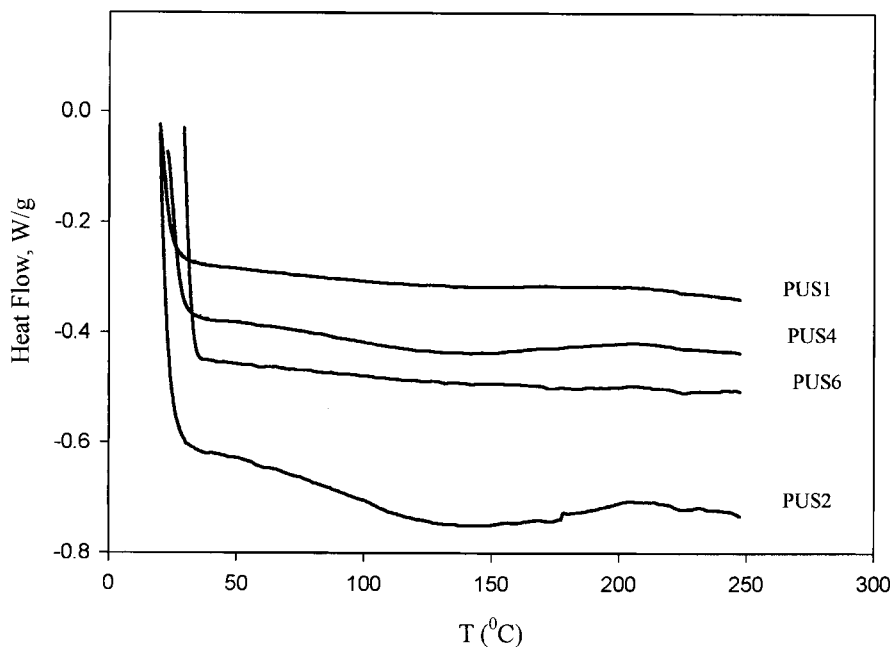
Fig. 3. DSC heating curves of crosslinked poly(ester-siloxane)-urethanes materials, PUS1, PUS2, PUS4 and PUS6.

3.2. Differential scanning calorimetry

Polyurethane elastomers are used in the temperature range limited by $T_g(S)$, corresponding to the soft segment (low temperature limit) and $T_g(H)$ corresponding to the hard segment (upper temperature limit). Below the $T_g(S)$ of the soft segment, polyurethanes are glassy materials, loosing their elastomeric properties. Their high intermolecular secondary bonds can explain the higher mechanical resistance of glass materials as compared with elastomers. The strength of polyurethane elastomers exponentially decreases as the temperature is increase above the $T_g(S)$ of the soft segment.

DSC measurements of phase separation are based on the fact that the glass transition temperatures of homogeneous mixtures generally obey to the copolymer equation [38]:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (1)$$

where w_1 and T_{g1} are weight fraction and glass transition temperature of the component 1, and w_2 and T_{g2} the same for the component 2. Thus, the interphase layer should have a T_g which is between those of the components and which would depend on the relative amounts of the present components. Since phase mixing is partial, i.e. there are pure soft and hard phases as well as mixtures of two of them, three separate glass transitions are expected. In practice, the amount of mixed material is small compared to the mass of pure phases so that the third T_g is not readily observable. Usually some increase of the soft segment $T_g(S)$ and decrease of hard segment $T_g(H)$ is observed. Similar, the melting transition may be interpreted as due to the presence of mixed regions of soft and hard segments.

In our case, we can not exclude the possibility to have interactions between the soft and the hard segments. The siloxane and the ester can not interact, the both having the same side groups (i.e. –OH), but they can easily react with the diisocyanate components, having as a result a slight modification of Eq. (1). The experimental trial of Eq. (1) is hard to realise, due to impossibility to detect $T_g(H)$, which appears in the temperature range when the hard segments are destroyed.

Fig. 3 presents the DSC heating curves for the temperature range of 20–250°C, corresponding to four crosslinked polyurethane materials (PUS1, PUS2, PUS4 and PUS6 from Table 1).

The DSC heating curves of segmented poly(ester-siloxane)urethanes) based on MDI and TDI exhibit a large endothermic peak at a temperature of about 40–60°C corresponding to the melting temperature of soft segments [28].

It was observed that for all crosslinked studied samples in the present work, the endotherm corresponding to the melting transition of the soft segments was not detected, due to crosslinked networks which obstructs the melting process. The distribution of the curves from Fig. 3 show a higher specific heat for samples with TDI in hard segments or for samples with PDEGA instead PEGA in soft segments. So, we can conclude that these results are in good agreement with the dynamic mechanical properties.

4. Conclusions

The Dynamic mechanical analysis (DMA) and DSC data show that the thermal curves of crosslinked poly(ester-siloxane)-urethanes are influenced by the soft and hard segments structures.

Crosslinked poly(ester-siloxane)-urethanes with MDI and DGMA as hard segments manifest a higher energy elastically stored than the corresponding ones with TDI and DGMA as hard segments. The presence of DGMA in the soft segments determines an increase of the tensile storage modulus caused by the increased interchain interaction between hydrogen bonds and chemical crosslinks of diisocyanates and DGMA, respectively.

The presence of PDEGA and PDMS in the soft segment determined a decreasing of tensile storage modulus much less than for the presence of PEGA and PDMS. Also, introduction of PBD in soft segments reveals a higher tensile storage modulus, probably due to some additional effects in PUS6, such as the supplementary crosslinks in presence of TDI.

For four crosslinked polyurethane materials, the DSC heating curves in the temperature range of 20–250°C did not evidence the endotherm corresponding to the melting transition because of crosslinked networks which hinder the melting process.

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