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# Contribution of soft segment entanglement on the tensile properties of silicone–urea copolymers with low hard segment contents

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ABSTRACT

Novel, segmented thermoplastic silicone–urea (TPSU) copolymers based on rather high molecular weight aminopropyl terminated polydimethylsiloxane (PDMS) soft segments ($<M_n>$ 10,800 and 31,500 g/mol), a cycloaliphatic diisocyanate (HMDI) and various diamine chain extenders were synthesized. Copolymers with very low urea hard segment contents of 1.43–14.4% by weight were prepared. In spite of very low hard segment contents, solution cast films showed very good microphase separation and displayed reasonable mechanical properties. Tensile strengths of TPSU copolymers showed a linear dependence on their urea hard segment contents, regardless of the structure of the diamine chain extender used. The modulus of silicone–urea copolymers is dependent on the urea concentration, but not on the extender type or PDMS molecular weight. When silicone–urea copolymers with identical urea hard segment contents were compared, copolymers based on PDMS-31,500 showed higher elongation at break values and ultimate tensile strengths than those based on PDMS-10,800. Since the critical entanglement molecular weight ($M_e$) of PDMS is about 24,500 g/mol, these results suggest there is a significant contribution from soft segment chain entanglement effects in the PDMS-31,500 system regarding the tensile properties and failure mechanisms of the silicone–urea copolymers.

## 1. Introduction

Segmented thermoplastic polyurethanes and polyureas (TPUs) are obtained by the chemical combination of soft (such as aliphatic polyethers, polyesters, polycarbonates, polydimethylsiloxane, etc.) and hard (urethane or urea) segments along a macromolecular backbone. Conventionally soft segment oligomers with number average molecular weights ($M_n$) in 1000–5000 g/mol range are employed in TPU synthesis. In most cases however, preferred soft segment molecular weight is around 2000 g/mol. Depending on the properties desired and specific applications, urethane or urea hard segment contents of TPUs generally range from 15 to 40% by weight. Such a combination of soft and hard segments usually leads to a microphase morphology and results in TPUs with excellent thermal and mechanical properties [1,2].

Specialty TPUs based on polydimethylsiloxane (PDMS) soft segments have been extensively studied during the last 25 years [3–5]. PDMS based TPUs have unique combination of properties, which mainly stems from the characteristics of the PDMS soft segments. These include extremely low glass transition temperatures around −120 °C, good oxidative and thermal stability, water repellency, physiological inertness and high gas permeability. High molecular weight PDMS with $M_n$ values above 3000–4000 g/mol crystallizes and has a melting point around −50 °C. Therefore the useful range for elastomeric properties of PDMS containing copolymers starts at ca. −50 °C and not −120 °C which is the $T_g$. High molecular weight silicone–urea copolymers with good thermal and mechanical properties can be prepared: (i) by the stoichiometric reactions of diisocyanates and aminopropyl terminated PDMS oligomers, without any chain extenders [5,6], or (ii) by the conventional prepolymer method through the use of chain extenders [7]. Due to substantial differences between the solubility parameters of PDMS and urea hard segments, which are 15.6 and 45.6 $(J/cm^3)^{1/2}$ respectively, even at very low hard segment contents of 5–6% by weight silicone–urea copolymers display microphase morphology. In copolymers obtained by the stoichiometric reactions average molecular weight of the PDMS oligomer determines the urea hard segment content of the system. Similar to conventional polyether and polyester based TPUs, in silicone–urea copolymers also PDMS oligomers with ($M_n$) values in 1000–5000 range are widely utilized. At this point we would like to note that an important factor, which plays a critical role in determining/influencing several properties of a polymer including its melt viscosity and several mechanical properties of the bulk state is the critical

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entanglement molecular weight, which is denoted as ($M_e$) or ($M_c$) (here we will use $M_e$). Soft segment molecular weights ($M_n$) typically used in silicone–urea copolymers (1000–5000 g/mol) are much lower than ($M_e$), which is reported to be 24,500 g/mol reported for PDMS [8,9].

In segmented polyurethanes and silicone–urea copolymers strong hydrogen bonding between hard segments resulting in physical crosslinking is believed to be more predominant in determining the morphology and properties than the critical entanglement molecular weight of the soft segments. To our knowledge there are no detailed reports in the open literature where the effect of soft segment entanglements on the properties of TPUs was investigated. Since there are no significant intermolecular interactions between PDMS soft segments and the urea hard segments [10], silicone–urea copolymers are excellent models for the investigation of the effect of soft segment entanglement on the mechanical properties, which is the main aim of this study. Another aim is to determine the effect of the structure of the diamine chain extender on the thermomechanical properties of silicone–urea copolymers.

## 2. Experimental

### 2.1. Materials

$\alpha,\omega$-Aminopropyl terminated polydimethylsiloxane (PDMS) oligomers with ($M_n$) values of 10,800 and 31,500 g/mol were kindly supplied by Wacker Chemie, Munich, Germany. They were free of cyclic species, which were removed under vacuum. Number average molecular weights were determined by end group titration in isopropanol with standard HCl. Bis(4-isocyanatocyclohexyl)-methane (HMDI) with a purity better than 99.5% was supplied by Bayer Turk, Istanbul and used as received. Chain extenders 2-methyl-1,5-diaminopentane (Dytek A, DY) (DuPont) and ethylene diamine (ED) (Aldrich) and reagent grade reaction solvents, isopropyl alcohol (IPA) (Merck) and tetrahydrofuran (THF) (Merck) were all used as received.

### 2.2. Polymer synthesis

Polymerization reactions were carried out in three-neck, round bottom, Pyrex reaction flasks equipped with an overhead stirrer and an addition funnel. All reactions were performed at room temperature. Typical concentrations of the reaction solutions were about 12–15% solids by weight. All polymers were prepared by using the “prepolymer” method. A typical reaction procedure was as follows: The desired amount of HMDI was dissolved in THF in the reactor. The calculated amount of PDMS oligomer was dissolved in a separate flask in a THF/IPA (50/50) mixture, introduced into the addition funnel and added dropwise into the HMDI solution under strong agitation. After the prepolymer formation, stoichiometric amount of diamine chain extender (ED or DY) was dissolved in IPA, introduced into the addition funnel and added dropwise into the prepolymer solution in the reactor. The progress and completion of the reactions were followed by FTIR spectroscopy in monitoring the disappearance of the strong isocyanate absorption peak at 2265 $\text{cm}^{-1}$. Silicone–urea copolymers obtained had fairly high molecular weights, well above 200 kDa as determined by GPC in a THF/IPA mixture.

### 2.3. Characterization methods

FTIR spectra were recorded on a Nicolet Impact 400D FTIR spectrometer using solution cast films on KBr discs, which were dried using a heat gun. 20 scans were taken for each spectrum with a resolution of 2 $\text{cm}^{-1}$.

Films for thermal and mechanical tests were obtained by casting polymer solutions into Teflon molds. Solvent was evaporated in an air oven at 50 °C and then in a vacuum oven at 50 °C until constant weight was reached. Films obtained at a thickness of 0.2–0.5 mm were kept in sealed polyethylene bags until testing.

A TA model Q800 instrument was used for dynamic mechanical analysis (DMA). The test specimens (approximately $30 \times 5 \times 0.6$ mm) were cut from the solution cast films described above. Measurements were performed in the tensile mode, between −150 and 250 °C. The frequency was 1 Hz and the heating rate was 3 °C/min. Tests were carried out under a dry nitrogen atmosphere. Tan $\delta$ and storage modulus, $E'$, values were obtained.

Stress–strain tests were performed on an Instron model 4411 tester, controlled by Series IX software. Dog-bone shaped specimens (ASTM D 1708) were cut from solution cast films ($L_o = 24.0$ mm). Tests were conducted at room temperature using a 25.0 mm/min cross-head speed. For each polymer at least three samples were tested and the average values of Young’s modulus, ultimate tensile strength and elongation at break values were obtained.

## 3. Results and discussion

Silicone–urea copolymers which display excellent microphase separation between the soft PDMS matrix and urea hard segments are important materials as model systems for the investigation of the structure–property behavior of segmented copolymers. As stated earlier, two main goals of our study were: (i) the investigation of the influence of urea hard segment structure and (ii) the effect of PDMS soft segment molecular weight on the tensile properties of silicone–urea copolymers with very low hard segment contents. For this purpose two different diamine chain extenders, short and symmetrical ethylene diamine (ED) and longer and branched 2-methyl-1,5-diaminopentane (DY) and two different PDMS oligomers with $M_n$ values of 10,800 and 31,500 g/mol were utilized.

### 3.1. Influence of the structure of the chain extender on the tensile properties of silicone–urea copolymers based on PDMS-10,800 or PDMS-31,500

In conventional polyurea copolymers based on aliphatic polyethers, the structure of the diamine chain extender plays an important role on polymer properties. Poly(ether-ureas) prepared by using compact and symmetrical ED generally leads to better microphase separation and superior thermomechanical properties when compared with polyureas chain extended with longer and asymmetrical diamines [11]. Urea groups based on ED have smaller molar volumes and as a result higher cohesive energy densities, compared with longer and branched diamines. This leads to better

**Table 1**
Effect of the structure of the chain extender and polymer composition on the tensile properties of PDMS-10,800 and HMDI based silicone–urea copolymers.

| Polymer code | Chain extender | Molar composition[a] | HS content (wt%) | Modulus (MPa) | Tensile str. (MPa) | Elong. (%) |
|---|---|---|---|---|---|---|
| PSU-11-2.3 | – | 1.0/1.0/0.0 | 2.32 | 0.70 | 0.50 | 800 |
| PSU-11-ED-3.8 | ED | 1.0/1.5/0.5 | 3.77 | 0.95 | 1.10 | 270 |
| PSU-11-ED-5.1 | ED | 1.0/2.0/1.0 | 5.14 | 1.10 | 1.40 | 210 |
| PSU-11-ED-7.8 | ED | 1.0/3.0/2.0 | 7.75 | 1.60 | 2.10 | 230 |
| PSU-11-DY-5.3 | DY | 1.0/2.0/1.0 | 5.31 | 1.20 | 1.65 | 280 |
| PSU-11-DY-8.6 | DY | 1.0/3.0/2.0 | 8.62 | 1.30 | 2.60 | 310 |
| PSU-11-DY-11.4 | DY | 1.0/4.0/3.0 | 11.4 | 1.50 | 3.30 | 280 |
| PSU-11-DY-14.4 | DY | 1.0/5.0/4.0 | 14.4 | 2.20 | 3.60 | 225 |

[a] [PDMS]/[HMDI]/[CH EXT] ratio.

**Table 2**
Effect of the structure of diamine chain extender on tensile properties of PDMS-31,500 and HMDI based silicone–urea copolymers.

| Polymer code | Chain extender | Molar composition[a] | HS (wt.%) | Modulus (MPa) | Tensile str. (MPa) | Elong. (%) |
|---|---|---|---|---|---|---|
| PSU-32-ED-1.8 | ED | 1/2/1 | 1.82 | 0.50 | 0.80 | 400 |
| PSU-32-ED-2.8 | ED | 1/3/2 | 2.80 | 0.60 | 1.25 | 350 |
| PSU-32-ED-3.7 | ED | 1/4/3 | 3.73 | 0.75 | 1.80 | 500 |
| PSU-32-ED-4.7 | ED | 1/5/4 | 4.70 | 0.90 | 2.20 | 500 |
| PSU-32-DY-2.0 | DY | 1/2/1 | 1.99 | 0.60 | 0.70 | 300 |
| PSU-32-DY-3.1 | DY | 1/3/2 | 3.13 | 0.70 | 1.20 | 600 |
| PSU-32-DY-4.3 | DY | 1/4/3 | 4.25 | 0.80 | 1.65 | 420 |
| PSU-32-DY-5.3 | DY | 1/5/4 | 5.34 | 0.90 | 2.10 | 400 |
| PSU-32-DY-7.4 | DY | 1/7/6 | 7.35 | 1.40 | 3.00 | 290 |

[a] ([PDMS]/[HMDI]/[CH EXT] ratio).

packing and stronger intermolecular hydrogen bonding between ED based urea hard segments. ED chain extended polyureas display better microphase separation and superior elastomeric properties, such as in LycraSpandex [12,13]. On the other hand, in PDMS based polyureas due to the substantial differences in the solubility parameters of PDMS and urea groups (15.6 and 45.6 $(J/cm^3)^{1/2}$ respectively), no significant competitive hydrogen bonding or interaction between PDMS and urea are expected, leading to excellent microphase separation. Therefore, the structure or the symmetry of the diamine chain extender may not be as important or critical in determining the microphase separation in PDMS-ureas as it is in polyether-ureas [14,15].

Chemical compositions and tensile properties of the silicone–urea copolymers prepared by using PDMS-10,800 or PDMS-31,500, HMDI and use of either the ED or DY chain extenders are provided on Tables 1 and 2 respectively. The abbreviation used to identify the copolymers was as follows: PSU indicates the silicone–urea copolymer; the following number indicates the $M_n$ value of PDMS in kg/mole; the next two letters (ED or DY) indicate the chain extender used respectively; the final numbers indicate the urea hard segment content of the copolymer in weight percent. For example, the PDMS-10,800, HMDI and DY based silicone–urea copolymer with 8.62% by weight hard segment content was coded as: PSU-11-DY-8.6.

Before going into the detailed discussion of the tensile behavior of the silicone–urea copolymers described on Tables 1 and 2, representative experimental stress–strain curves obtained for PSU-11-ED-3.8 and PSU-32-ED-3.7 are reproduced in Fig. 1. These copolymers have identical hard/soft segment ratios. The only difference between them is the molecular weight of the PDMS oligomer used during synthesis. It is interesting to note some significant differences between the two stress–strain curves. PSU-11-ED-3.8 has a slightly higher initial modulus but much lower ultimate tensile strength and elongation at break than that of PSU-32-ED-3.7. While PSU-32-ED-3.7 extends to about 500% elongation at break, PSU-11-ED-3.8 fails much earlier at around 270% elongation. As we have discussed in our earlier publication [15] silicone–urea copolymers which were based on 3000–7000 g/mol PDMS oligomers also showed fairly low elongation at break values. We explained this to be due to poor stress transfer between soft and hard segments. In fact when small amounts of polyether modifiers were incorporated into the copolymers, this leads to remarkable increases in the elongation at break [15]. Premature failure of PSU-11-ED-3.8 may be due to the same reason. However, fairly surprisingly no premature failure is observed in PSU-32-ED-3.7. We believe these results are particularly interesting. We suggest that they may indicate a different basis for the failure for these homologous silicone–urea copolymers and the important effect of PDMS molecular weight on tensile behavior as will be discussed in the paragraphs below.

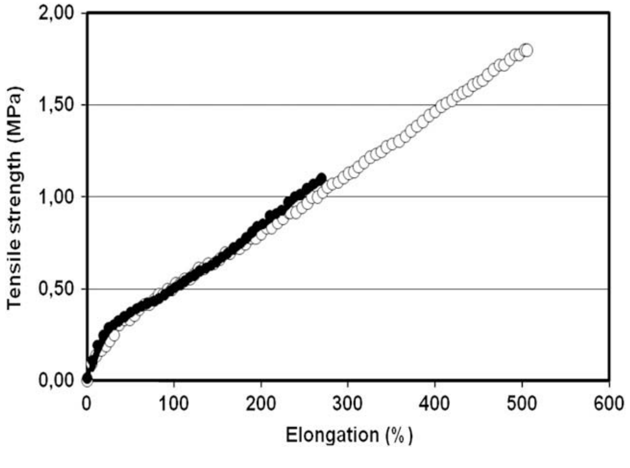

**Fig. 1.** Comparative stress–strain curves for PSU-11-ED-3.8 (●) and PSU-32-ED-3.7 (○).

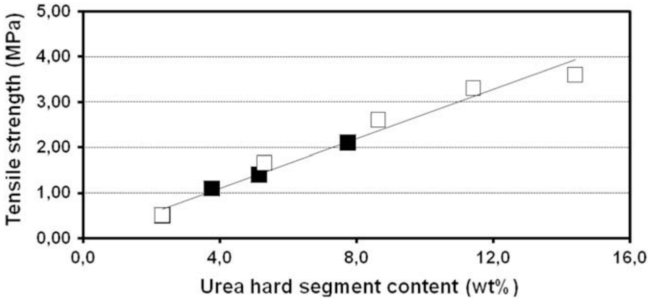

**Fig. 2.** Effect of the chain extender structure and urea hard segment content on the ultimate tensile strengths of silicone–urea copolymers based on PDMS-10,800 (■) ED (□) DY.

Chemical compositions and tensile properties of the silicone–urea copolymers based on PDMS-10,800 are reported on Table 1. Very interestingly, even the non-chain extended silicone–urea copolymer based on PDMS-10,800, which contains only 2.3% by weight urea hard segments (PSU-11-2.3) forms a very nice, non-tacky film with reasonable tensile properties, such as 0.70 MPa modulus, 0.50 MPa tensile strength and 800% elongation at break. As expected, when the urea hard segment content of the copolymers is

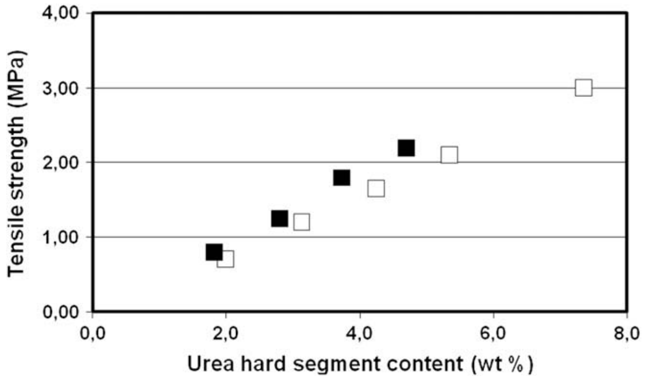

**Fig. 3.** Effect of the chain extender structure and urea hard segment content on the ultimate tensile strengths of silicone–urea copolymers based on PDMS-31,500 (■) ED (□) DY.

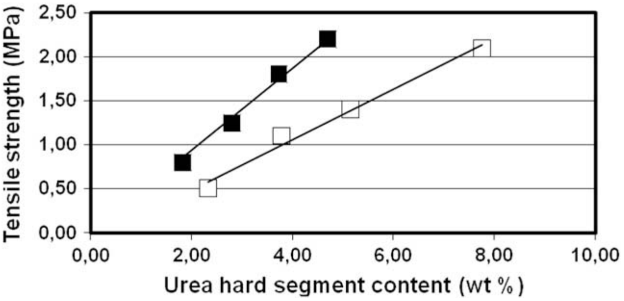

**Fig. 4.** Effect of the PDMS molecular weight on the ultimate tensile strength of silicone–urea copolymers based on HMDI and ED chain extender (■) PDMS-31,500 (□) PDMS-10,800.

increased through the use of chain extenders such as ED or DY, an increase in the modulus and tensile strength and a substantial decrease in the elongation at break values are observed (Table 1).

As shown on Fig. 2, when the tensile strength values of silicone–urea copolymers based on PDMS-10,800 are plotted as a function of their urea hard segment contents, a linear relationship is observed regardless of the type of the chain extender (ED or DY) used, similar to our earlier observations [6,7]. Since properties of segmented copolymers are strongly dependent on their microphase morphology, these results indicate that the chemical structure or symmetry of the diamine chain extender do not have a significant effect on the nature and extent of microphase separation in these specific silicone–urea copolymers.

For comparison, the effect of the chain extender structure on the properties of HMDI and PDMS-31,500 based silicone–urea copolymers was also investigated. Similar to the PDMS-10,800 based copolymers, the chain extenders used were ED and DY. Table 2 gives the chemical compositions and tensile properties of these copolymers. The copolymers reported in Table 2 are very unusual since they are based on extremely high molecular weight PDMS soft segments. They also have extremely low urea hard segment contents that vary from 1.82 to 5.34% by weight. Nevertheless all copolymers formed clear and reasonably strong films. As can be seen from Table 2, as the hard segment content is increased, an increase in the modulus and tensile strength values of the copolymers are observed to be similar to the PDMS-10,800 based copolymers. On the other hand, very interestingly there is no change or even slight increases in the elongation at break values are also observed for the PDMS-31,500 based silicone–urea copolymers. Since the critical entanglement molecular weight of PDMS is reported to be 24,500 g/mol [8,9], we believe the increase in elongation is mainly due to the presence of entanglements of the PDMS soft segments, preventing the premature failure of the material. When the tensile strengths of PDMS-31,500 based silicone–urea copolymers are plotted as a function of their urea hard segment contents (Fig. 3), regardless of the chain extender structure, they also fall on the same trend-line, indicating no significant effect of the chain extender structure on tensile properties, within the range of the experimental error, similar to that of PDMS-10,800 based copolymers and others reported in the literature [6,7].

### 3.2. Influence of the PDMS molecular weight on the tensile properties of silicone–urea copolymers based on PDMS-10,800 or PDMS-31,500

As we stated earlier and briefly discussed above, in this study one of our goals was to investigate the influence of the chain extender structure on the tensile properties of silicone–urea copolymers. Another, more important goal was to find out if there is any influence of the entanglements in PDMS soft segments on the tensile properties. To find out whether there was any effect of PDMS entanglements on the tensile strengths of silicone–urea copolymers, in Fig. 4 we plotted the tensile strengths of the homologous PDMS-10,800 and PDMS-31,500 based silicone–urea copolymers chain extended with ED as a function of their urea hard segment contents. As can be clearly seen in Fig. 4, the slope of the line for PDMS-31,500 based silicone–urea copolymers is much higher than that of PDMS-10,800 based systems. These results are somewhat surprising at first glance; however we believe they clearly demonstrate that in addition to the strong hydrogen bonding between urea hard segments, chain entanglements within the PDMS matrix seem to have a synergistic effect on the tensile strengths of these silicone–urea copolymers. As can be seen in Tables 1 and 2 as well as in Fig. 4, the copolymers based on PDMS-31,500 display tensile strengths almost double of those based on PDMS-10,800 with identical urea hard segment contents. We believe this is the first report on the existence of a synergistic effect of soft segment entanglements on the tensile strength in segmented silicone–urea copolymers. Interestingly, we also observed the same soft segment molecular weight dependent tensile behavior in poly(propylene oxide) based polyurethaneureas. These results will be published later. A simplified sketch of the morphological texture of the silicone–urea copolymers with and

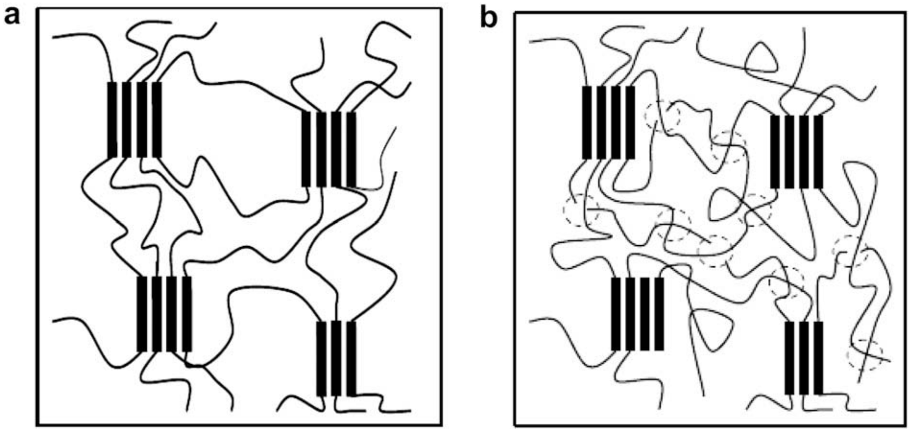

**Fig. 5.** Schematic representation of intermolecular entanglements in the PDMS soft segment matrix in silicone–urea copolymers: (a) No entanglements ($M_n < M_e$), (b) Entanglements ($M_n > M_e$).

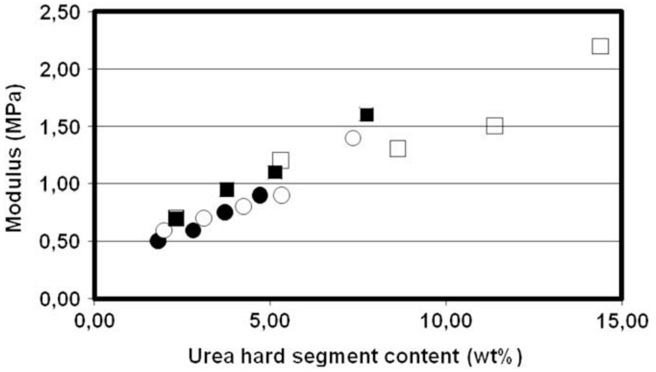

**Fig. 6.** Young's modulus as a function of the urea hard segment content in silicone–urea copolymers based on PDMS-10,800 and PDMS-31,500, chain extended with ED or DY. (■) PDMS-10,800 and ED, (□) PDMS-10,800 and DY, (●) PDMS-31,500 and ED, (○) PDMS-31,500 and DY.

without soft segment entanglements is provided in Fig. 5a and b respectively, for a better illustration of the system.

### 3.3. *Dependence of modulus on the urea content and modulus–temperature behavior of silicone–urea copolymers based on PDMS-10,800 and PDMS-31,500*

Fig. 6 provides a plot of the Young's or the initial modulus as a function of the urea hard segment content in copolymers based on PDMS-10,800 and PDMS-31,500, chain extended with ED or DY. As expected, the modulus values increase as a function of the urea hard segment content. However, it is interesting to note that average molecular weight of the PDMS segments or the chemical structure of the chain extender do not seem to have an influence on the modulus.

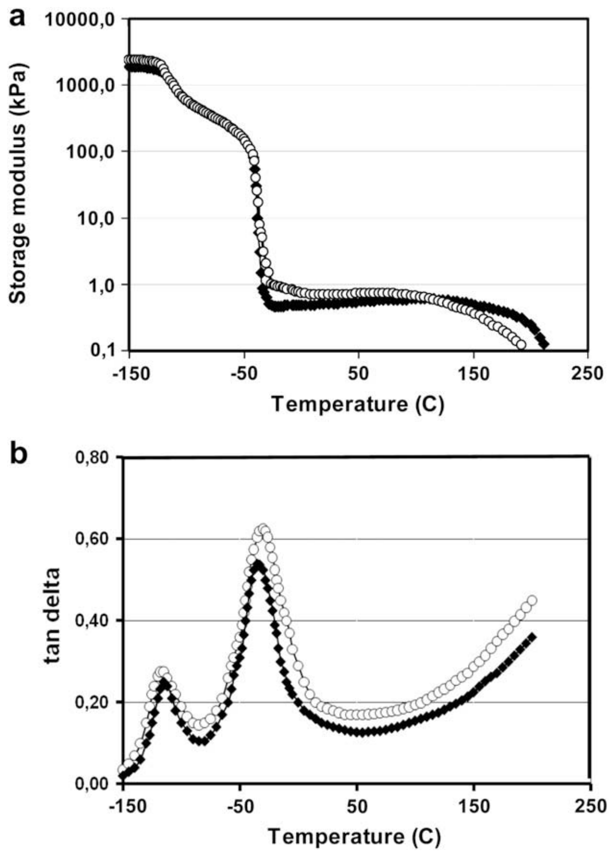

**Fig. 7.** Comparative storage modulus–temperature curves for PDMS-10,800 and PDMS-31,500 based silicone–urea copolymers with similar compositions (○) PSU-11-ED-3.8 (■) PSU-32-ED-3.7.

Fig. 7 provides the storage modulus–temperature (7a) and tangent delta–temperature (7b) profiles for silicone–urea copolymers based on HMDI, PDMS-10,800 and PDMS-31,500 and chain extended with ED. Both copolymers (PSU-11-ED-3.8 and PSU-32-ED-3.7) have almost identical hard segment contents. In spite of their very low hard segment content, as shown on Fig. 7a and b, both copolymers display two phase morphologies with a well defined PDMS glass transition with ($T_g$) at about $-120$ and melting ($T_m$) at $-40$ °C, typical for high molecular weight PDMS. In both cases the PDMS melting transition is followed by a long and temperature insensitive rubbery plateau (Fig. 7a), extending up to about 150 °C. Due to weakening and breaking of the hydrogen bonded urea network, both polymers show flow in the 150–200 °C region, typical for silicone–ureas [5]. Although not provided here, the modulus–temperature curves for the Dytek A (DY) chain extended silicone–urea copolymers based on PDMS-10,800 and PDMS-31,500 are very similar to those shown on Fig. 7.

## 4. Conclusions

Novel silicone–urea copolymers containing very high molecular weight PDMS soft segments with $M_n$ values of 10,800 and 31,500 g/mol were prepared and characterized. Our main goals in this study were to investigate the effect of: (i) the structure of the diamine chain extender and urea hard segment content, and (ii) the average molecular weight of PDMS oligomer incorporated on the tensile properties of these silicone–urea copolymers. The critical entanglement molecular weight of PDMS is reported to be 24,500 g/mol [8,9], therefore it was possible to determine the effect of soft segment entanglements on the tensile behavior of silicone–urea copolymers by comparing homologous samples prepared with PDMS-10,800 and PDMS-31,500. We can summarize the major conclusions of this study as follows:

(i) In the range of compositions investigated, the structure of the chain extender does not seem to influence the modulus–temperature behavior (microphase morphology) or tensile properties of the silicone–urea copolymers synthesized.
(ii) There is a linear relationship between the tensile strength and urea hard segment content of silicone–urea copolymers based on PDMS-10,800 and PDMS-31,500.
(iii) When homologous PDMS-10,800 and PDMS-31,500 based copolymers are compared, an important contribution of soft segment entanglements on the elongation at break values and ultimate tensile strengths of silicone–urea copolymers is observed.
(iv) The modulus of silicone–urea copolymers seems to be dependent on the urea concentration, but not on the extender type or PDMS molecular weight.

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