ELSEVIER

Polymer 42 (2001) 7953–7959

polymer

www.elsevier.nl/locate/polymer

Hydrogen bonding: a critical parameter in designing silicone copolymers

Emel Yılgör, İskender Yılgör*

Koç University, Rumelifeneri yolu, Sariyer, TR-80910 Istanbul, Turkey

Received 10 January 2001; received in revised form 17 April 2001; accepted 22 April 2001

Abstract

Structure–property relations in polydimethylsiloxane (PDMS) containing segmented copolymers with model hard segments capable of forming hydrogen bonding, such as urea, *N*-methylurea and urethane have been investigated. High molecular weight silicone containing copolymers with these hard segments were prepared from PDMS oligomers with number average molecular weights ranging from 890 to 3750 g/mol. Due to major differences in the solubility parameters between PDMS and polar hard segments, all copolymers are expected to display good microphase separation. It was demonstrated that mechanical and thermal properties of these copolymers are directly linked to the strength of the hydrogen bonding in the hard segments. As expected, siloxane–urea copolymers displayed much higher tensile strengths when compared with siloxane–*N*-methylurea and siloxane–urethane copolymers with similar compositions.

Keywords: Hydrogen bonding; Silicone copolymer; Siloxane

1. Introduction

High molecular weight silicone homopolymers, especially polydimethylsiloxanes (PDMS), display a combination of very interesting properties. These include very low glass transition temperatures (−123°C), high thermal, UV and oxidative stability, low surface energy, hydrophobicity, high gas permeability, good electrical properties and physiological inertness or biocompatibility [1]. In spite of these attractive properties, PDMS homopolymers exhibit very poor mechanical properties at room temperature, even at very high molecular weights [1,2]. This is a direct result of their very low T_g (at room temperature, they are about 150°C above their T_g) and very low intermolecular forces between polymer chains [3]. In order to have reasonable mechanical properties, PDMS must be highly cross linked and in many cases filled with finely divided reinforcing fillers, such as silica [4].

Another effective technique to improve the thermal and mechanical properties, while still retaining the desired chemical and physical properties of PDMS polymers, is through the controlled synthesis of block or segmented copolymers [5,6]. In these copolymers, PDMS can be combined with a wide range of organic hard segments, resulting in thermoplastic elastomers, where ultimate properties depend on the type and nature of the hard segments, relative segment molecular weights and the backbone compositions [5,6]. We have already reported that [7,8], when urea groups (which can form very strong hydrogen-bonding) are chosen as the hard segments, the resulting silicone copolymers display excellent elastomeric properties with very good mechanical strengths. In these copolymers, extremely nonpolar PDMS soft segments, with very low solubility parameters of 15.6 $(J/cm^3)^{1/2}$ or 7.6 $(cal/cm^3)^{1/2}$ show almost complete phase separation from the urea hard segments, which are fairly polar, as indicated by their high solubility parameters of around 45.6 $(J/cm^3)^{1/2}$ or 22.3 $(cal/cm^3)^{1/2}$ [9,10]. This leads to very strong hydrogen bonding in the urea hard segments and excellent mechanical properties in silicone–urea copolymers.

Due to the availability of a wide range of reactive PDMS oligomers and organic monomers, it is possible to synthesize well-defined silicone copolymers with controlled hydrogen bonding capabilities in the hard-segments and use them as model systems to study the influence of hydrogen bonding on the properties of resultant thermoplastic elastomers. This cannot be easily achieved in conventional polyether or polyester based urethane or urea type elastomeric systems because of extensive phase mixing between hard and soft segments due to hydrogen bonding between urethane or urea groups and the ether or ester linkages in the soft segments [11–13].

In this study, PDMS copolymers containing urea,

* Corresponding author.
E-mail address: iyilgor@ku.edu.tr (İ. Yıgör).

0032-3861/01/$ - see front matter
PII: S0032-3861(01)00293-2

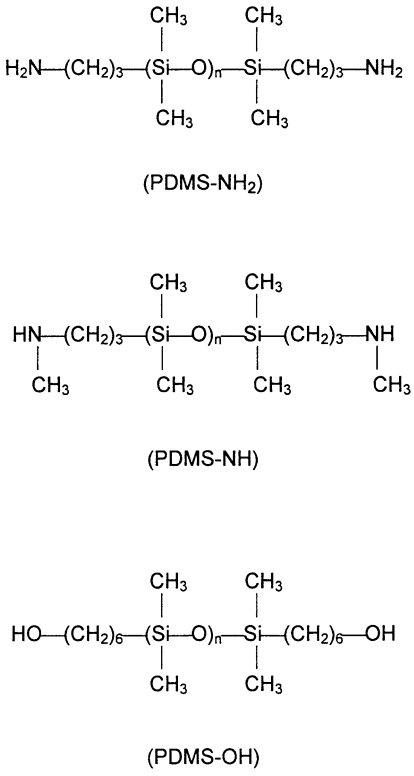


Fig. 1. Chemical structures of α,β-organofunctionally terminated polydimethylsiloxane oligomers.

N-methylurea and urethane type hard segments were prepared and characterized. The strength of hydrogen bonding in these copolymers was controlled by the type and the amount of hard segment in the system. In addition, model urea and urethane hard segments, with similar structures and compositions to those in the copolymers, were also prepared and characterized. A good correlation was found between the hydrogen bonding capacities of the hard segments and thermal and mechanical properties of the siicone copolymers.

2. Experimental

2.1. Materials

α,ω-Aminopropyl (PDMS–NH_2), α,ω-*N*-methylaminopropyl (PDMS–NH) and α,ω-hydroxyhexyl (PDMS–OH) terminated PDMS oligomers (Fig. 1) with number average molecular weights ranging from 890 to 3750 g/mol were either obtained from Th. Goldschmidt AG, Essen, Germany, or prepared in our laboratories [14]. Molecular weights of amine-terminated oligomers were determined by the titration of the end groups with standard hydrochloric acid. Number average molecular weights of hydroxyhexyl terminated PDMS oligomers were determined by ^{1}H NMR spectroscopy [15]. Bis(4-isocyanatocyclohexyl)methane (HMDI) with a purity greater than 99.5% was supplied by Bayer AG. *n*-Butanol, *n*-butylamine, urea and 1,3-dimethylurea with purities better than 99.5% were purchased from Aldrich and used as received. Chromatographic grade reaction solvents, tetrahydrofuran (THF) and dimethylformamide (DMF) were obtained from Carlo Erba and used without further purification. Dibutyltindilaurate (DBTDL) catalyst was obtained from Witco.

2.2. Preparation of model compounds

Detailed procedures for the preparation and characterization of HMDI based model urethane and urea hard segments bis(4-butylcarbamatecyclohexyl)methane (HMDI–urethane) and bis(4-butylureacyclohexyl) methane (HMDI–urea), which are shown in Fig. 2, are provided elsewhere [13].

2.3. Polymer syntheses

Siloxane–urea and siloxane–*N*-methyl urea copolymers were prepared by the reaction of stoichiometric amounts of amine terminated PDMS oligomers and HMDI, in THF solution, under dry nitrogen atmosphere. During the reactions, PDMS–NH_2 or PDMS–NH solutions (25% by weight in THF) were slowly added from an addition funnel, into the reaction flask containing stoichiometric amounts of diisocyanate (HMDI) solution (25% by weight in THF). The reactions were conducted at room temperature. After the completion of siloxane addition, the system was heated to 50°C for 3 h. Completion of the reactions was determined by FTIR (Fourier Transform Infrared) spectroscopy, following the disappearance of strong isocyanate peak at 2260 cm^{-1}. When PDMS–NH_2 oligomers with M_n 900 and 1150 g/mol were used, as the urea content in the copolymer formed increased, the reaction mixtures became extremely viscous due to very strong hydrogen-bonding in the system and therefore were diluted with DMF for effective mixing and also to prevent the premature precipitation. The products obtained were coagulated in isopropanol/water (90/10) mixture, washed with isopropanol, filtered and dried to constant weight in a vacuum oven at 50°C.

Siloxane–urethane copolymers were prepared by the reaction of equimolar amounts of PDMS–OH and HMDI

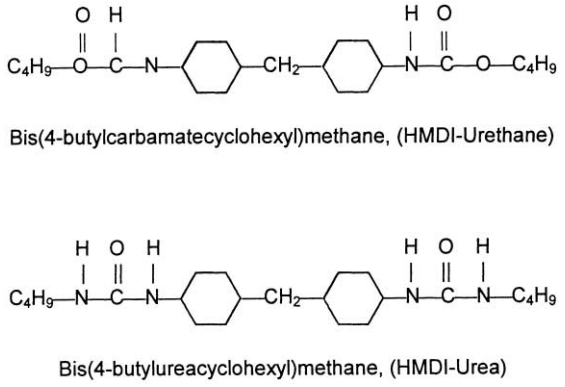


Fig. 2. Chemical structures of model urethane and urea hard segments.

Table 1
Chemical compositions of segmented PDMS copolymers

Polymer code	PDMS oligomer			HMDI weight (g)	$[\eta]^{25°C}$ THF (dl/g)
	End group	M_n (g/mol)	Weight (g)		
PSU-1	NH_2	890	77.3	22.7	0.39
PSU-2	NH_2	1150	81.4	18.6	0.47
PSU-3	NH_2	1675	86.5	13.5	0.45
PSU-4	NH_2	2480	90.4	9.6	0.73
PSU-5	NH_2	3750	93.5	6.5	0.93
PSNU-1	NH	900	77.5	22.5	0.57
PSNU-2	NH	1650	86.3	13.7	0.69
PSNU-3	NH	2400	90.2	9.8	0.62
PSPU-1	OH	900	77.5	22.5	0.35
PSPU-2	OH	2400	90.2	9.8	0.59

in toluene at 80°C under the catalytic action of DBTDL. Completion of the reactions was again followed by monitoring the disappearance of strong isocyanate peak at 2260 cm^{-1} using FTIR spectroscopy. Table 1 gives the compositions of silicone copolymers synthesized together with the values of their intrinsic viscosities, which indicate the formation of high molecular weight polymers. Polymer codes denote the following systems: poly(siloxane–urea), PSU, poly(siloxane–*N*-methylurea), PSNU and poly(siloxane–urethane), PSPU.

2.4. Polymer characterization

Structural characterization of copolymers was obtained by FTIR spectroscopy, using a Nicolet Impact 400D spectrometer. For FTIR studies, thin polymer films were cast on KBr disks from THF or THF/DMF solutions and dried in vacuum oven. GPC curves were obtained on a Polymer Laboratories PL-110 GPC, equipped with PL-gel columns of 500, 1000 and 10 000 Å and a refractive index detector. Measurements were done at 23°C, with a flow rate of 1 ml/min. Intrinsic viscosities were determined in Ubbelohde viscometers, at 25°C, in THF. Differential scanning calorimetry (DSC) analyses of the products were obtained on a Rheometrics PL-DSC Plus instrument, under nitrogen atmosphere with a heating rate of 10 K/min. Temperature and enthalpy calibration of DSC was obtained by using indium, lead and tin standards. Thermogravimetric analysis of the products was obtained using Schimadzu TGA 50H, under nitrogen atmosphere, with a heating rate of 10 K/min. TMA (Thermomechanical analysis) penetration curves were obtained on a Perkin Elmer TMS-2, with a heating rate of 10 K/min. The load applied was varied between 10 and 30 g depending on the type and amount of hard segments in the sample. Thickness of the films were around 1.0–1.5 mm. Stress–strain tests were carried out on an Instron Model 4411 Universal Tester, at room temperature, with a crosshead speed of 20 mm/min. Films for TMA and stress–strain tests were prepared by compression molding at 200°C using a Carver, hydraulic press.

3. Results and discussion

Polydimethylsiloxane containing segmented copolymers with urea, *N*-methylurea and urethane hard segments were used as model systems to investigate and understand the influence of hydrogen bonding on the thermal and mechanical properties of these copolymers. All of these copolymers were obtained by the reaction of stoichiometric amounts of HMDI and organofunctionally terminated PDMS oligomers, structures of which are shown in Fig. 1. M_n values of the oligomers varied between 890 and 3750 g/mol. No chain extenders were used. Therefore, all copolymers of the same family (e.g. urea, *N*-methylurea or urethane) have exactly the same hard segment structure and molecular weight.

It is well known that hydrogen bonding plays critical roles in determining the thermal and mechanical properties of block and segmented copolymers [16,17]. High molecular weight, multiphase thermoplastic elastomers such as segmented polyurethanes, polyureas and semi-crystalline polyamides owe their thermal and mechanical properties to mainly three major factors. These are (i) the extent of microphase separation between soft and hard segments, (ii) the nature and the extent of intermolecular hydrogen bonding in their hard segments, and (iii) the extent of crystallization in the hard segments. In general, the first two are related to each other, where highly polar hard segments, such as urea, with high solubility parameters, promote better phase separation in the system, while at the same time providing more effective hydrogen bonding in the hard segments [18–20]. On the other hand, if the soft segments have polar groups such as ether oxygen or carbonyl, there may also be substantial interaction between urea hard and polyether or polyester soft segments. For siloxane containing systems, due to very large differences between the solubility parameters of PDMS and urea, urethane or

N-methylurea hard segments, it is expected that there will be very good phase separation [1,2,5,6]. Therefore, homologous siloxane–urea, siloxane–urethane and siloxane–*N*-methylurea copolymers can be used as models to quantitatively determine the influence of hydrogen bonding capacity in the hard segments on the thermal and mechanical properties of the resultant systems.

3.1. Cohesive energy densities and solubility parameters (δ)

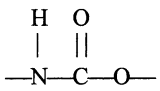
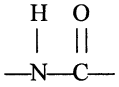
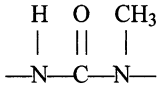
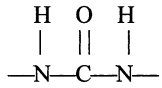
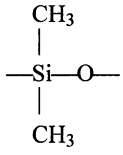
For an organic group, traditionally, a good measure of the capacity to form hydrogen bonding and other intermolecular forces can be obtained from the value of their cohesive energy densities (CED) or solubility parameters (δ), where $\delta = (\mathrm{CED})^{1/2}$ [9,10]. A high value for CED or δ means that the group or the molecule is highly polar. The solubility parameter, δ, consists of three components, with each component representing a molecular interaction force of different kind. These components are, (δ_d), due to dispersive (London) forces, (δ_p), due to dipole forces and (δ_h), due to hydrogen bonding. The relationship between solubility parameter and its components is given in Eq. (1).

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

For many small organic molecules, and especially for solvents, values of solubility parameters and their components are experimentally determined and are given in the literature [10]. For molecules or groups where these values are not available, it is possible to calculate CED, δ, or its components by using group interaction modeling based calculations [10,21,22]. Table 2 gives values for CED, solubility parameter, δ, and hydrogen bonding component of solubility parameter, δ_h, for urethane, *N*-methylurea and urea groups, calculated from group contributions. As a comparison, these values are also provided for dimethylsiloxane groups. Results of these calculations indicate that, in terms of increasing polarities, these groups have the following order: urethane, *N*-methylurea and urea. A similar order is also valid for the hydrogen bonding capacities of these groups. As a simple comparison, the experimentally determined solubility parameters of formamide, *N*-methylformamide and *N*,*N*-dimethylformamide are 36.6, 32.9 and 24.8 $(\mathrm{J/cm^3})^{1/2}$, respectively [10], which clearly show the influence of methyl substitution on polarity of the molecule and its solubility parameters. As for the hydrogen bonding component, the values are 19.0 and 11.3 $(\mathrm{J/cm^3})^{1/2}$ for formamide and DMF, respectively [10]. It is interesting to note the dramatic reduction in the hydrogen bonding capacity by replacement of amide hydrogens with methyl groups in the formamide molecule.

Although CED and δ_h values given in Table 2 provide a basis for the relative strengths of expected hydrogen bonding between these groups, which constitute the hard segments in silicone copolymers, they are far from giving a complete picture. As can be seen from Table 2, although there is a trend, the difference between δ and δ_h values for different groups are not very significant. This may indicate that siloxane copolymers with these hard segments are expected to show some differences in their thermal and mechanical properties, but these may not be very substantial. However, as the results of tensile tests (Table 3 and Fig. 3) and thermomechanical characterization (Fig. 5) clearly show, the overall performance of homologous siloxane copolymers, with urea, urethane and *N*-methylurea groups are significantly different from each other.

Table 2
Cohesive energy density and solubility parameter values for urethane, amide, *N*-Methylurea, urea dimethylsiloxane groups calculated by using group contribution method [9,21,22]

Group structure	CED $(\mathrm{J/cm^3})$	δ $(\mathrm{J/cm^3})^{1/2}$	δ_h $(\mathrm{J/cm^3})^{1/2}$
	1385	37.2	25.4
	1862	43.2	28.0
	1573	39.7	27.8
	2079	45.6	34.2
	243	15.6	0

3.2. Mechanical properties of copolymers

As can be seen in Table 3, the first significant and somewhat surprising observation in tensile test results is that the siloxane–urethane copolymer with 39.9% urethane hard segment content (PSPU-1), shows essentially no mechanical strength at room temperature. This film is very soft and sticky and shows viscous flow at room temperature. On the other hand, films of other homologous copolymers, siloxane–urea (PSU-1) and siloxane–*N*-methylurea (PSNU-1), even with slightly lower hard segment contents than that of PSPU-1, show very good mechanical integrity. Siloxane–urea copolymers, as expected, show higher modulus and tensile strengths than siloxane–*N*-methylurea copolymers with similar compositions. However, the

Table 3
Tensile properties of segmented PDMS copolymers

Polymer code	Hard segment content (wt%)	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)
PSU-1	32.8	157.3	20.1	430
PSU-2	26.8	115.0	16.5	550
PSU-3	19.5	19.3	10.2	700
PSU-4	13.8	6.9	7.9	900
PSU-5	9.4	4.9	4.8	950
PSNU-1	34.9	35.9	8.1	650
PSNU-3	15.3	4.8	2.1	750
PSPU-1	39.9	–	–	–

difference in the actual values of tensile properties are much higher than that can be explained by CED values or by the hydrogen bonding component (δ_h) of the solubility parameters given in Table 2. As given in Table 3, the ultimate tensile strength of PSU-1 is about 2.5 times higher than that of PSNU-1. The difference in the moduli values are even more dramatic, PSU-1 showing a modulus value, about 4.5 times that of PSNU-1. Fig. 3 clearly shows the difference between the tensile behavior of siloxane–urea and siloxane–*N*-methylurea copolymers. It is clear that the replacement of one hydrogen on urea nitrogen by a methyl group substantially diminishes the hydrogen bonding capability of the resulting structure.

Another interesting observation regarding siloxane–urea copolymers is the direct relationship between their ultimate tensile strengths and hard segment contents. As given in Fig. 4, when ultimate tensile strengths of siloxane–urea copolymers are plotted against their urea hard segment, a straight line (assuming no deviation from linearity below 10% urea content) passing through the origin is obtained. This, we believe is a dramatic observation and first to be reported for a block copolymer system, where soft segments have no contribution to the tensile strength of a copolymer. Such a linear relationship shown in Fig. 4 also suggests that, the urea hard segments are very-well phase separated and homogeneously distributed in the PDMS soft matrix. We also believe that the domain sizes of these hard segments are fairly uniform since all hard segments have the same structure and molecular weight (the hard segments in these siloxane copolymers consist of HMDI end-capped by the organofunctional end groups of PDMS oligomers, whereas, soft segment consists only of PDMS). In addition, these hard segment domains in siloxane–urea copolymers are also held together with very strong hydrogen bonding.

Another interesting observation is the logarithmic relationship between the modulus and the urea content of silicone–urea copolymers as shown in Fig. 5. Although we cannot quite explain this behavior, it is identical to the behavior of semi-crystalline nylon-6,10, where amide hydrogens are partially replaced with *t*-butyl groups [13,23]. Net results of such a modification in the polyamide backbone are (i) dramatic reduction in the hydrogen bonding between amide groups and (ii) disruption of the crystallinity of the system, both of which are expected to reduce the modulus of the system. When the straight line (assuming no deviation from linearity below 10% urea content) in Fig. 6, given for the siloxane–urea copolymers, is extrapolated to 'zero urea content', a negative log(modulus) value is obtained. This indicates extremely low modulus, typical for liquid-like materials. This interesting observation very clearly explains the expected behavior of siloxane–urea copolymers, with 'no' urea groups! Such a system would consist of pure PDMS soft segments (oligomers), which are known to be very low viscosity liquids at room temperature, since at room temperature they are about 140°C above their T_gs. Tensile data displayed in Figs. 3–5 very clearly

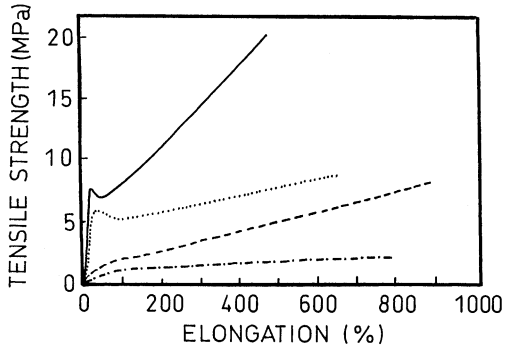


Fig. 3. Comparison of Stress–strain behavior of polydimethylsiloxane copolymers containing urea and *N*-methylurea hard segments (—: PSU-1; ···: PSNU-1; - - -: PSU-4; -·-·-: PSNU-3).

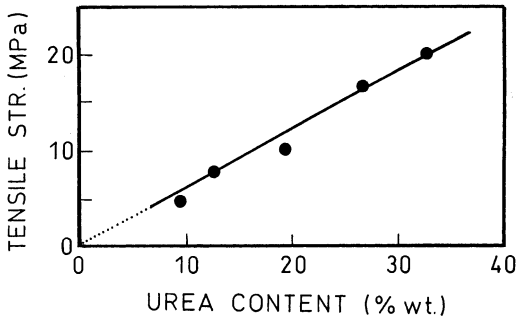


Fig. 4. Ultimate tensile strengths of siloxane–urea copolymers as a function of their urea hard segment contents.

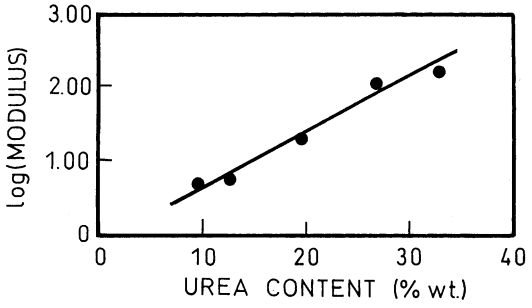


Fig. 5. Relationship between tensile modulus and urea content in siloxane–urea copolymers.

demonstrate the very critical role played by hydrogen bonding in determining the mechanical behavior of siloxane copolymers.

3.3. Thermomechanical behavior of copolymers

Fig. 6 gives the thermomechanical behavior of representative siloxane copolymers between −150 and +200°C. These curves are obtained by measuring the penetration of a quartz probe into a polymer film as a function of temperature. As can be seen in Fig. 6, penetration-temperature curves are qualitatively identical to modulus-temperature curves of polymeric systems. Therefore, by this experiment, glass transition temperatures, rubbery plateau and rubbery and viscous flow regions of amorphous polymers can be easily determined. In all copolymers tested (PSU-1, PSNU-1 and PSPU-1), sharp penetrations are observed around −120°C. This is due to the glass transition temperature of PDMS. The degree of penetration at this region may be a good indication of the mechanical integrity of the copolymer or the strength of the hydrogen bonding in the matrix. As expected, siloxane–urea copolymer shows the least penetration and siloxane–urethane, the most in this region. As the temperature is increased dramatically, different penetration profiles are observed for different copolymers. For siloxane–urethane copolymer, there is a fairly short plateau, followed by the complete penetration of the probe. For siloxane–*N*-methylurea copolymer, the rubbery plateau extends up to about 50°C. Complete penetration of the probe into the film takes place in the range between 80 and 100°C. For siloxane–urea copolymers, thermomechanical behavior is quite different after the glass transition region of PDMS. Unlike other copolymers, for PSU-1, there is a very long plateau region, where no penetration is observed. This clearly shows the integrity of the matrix, which is a direct result of very strong hydrogen bonding in these systems. Around +120°C, there is another small penetration, which most probably indicates the glass transition temperature of the urea hard segments. This is followed by another plateau region. Complete penetration of the probe takes place above 160°C. TMA curves given in Fig. 6 provide a very clear picture about the relative strengths of hydrogen bonding in the hard segments of these siloxane copolymers. By using these temperature values in the flow regions (where there is complete penetration of the probe), it may also be possible to calculate approximate thermal energies required to break up the hydrogen bonding in different hard segments.

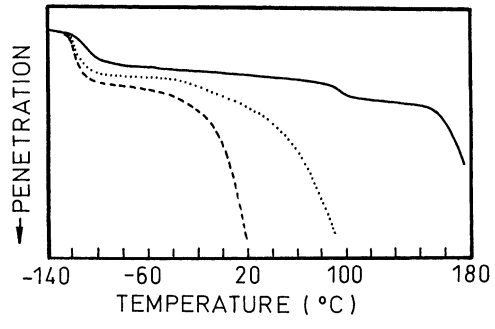
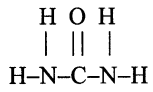
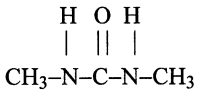


Fig. 6. Comparison of the thermomechanical behavior of siloxane copolymers with different hard segments (—: PSU-1; ···: PSNU-1; - - -: PSPU-1).

3.4. Thermal properties of model compounds

In order to have a better understanding of the dramatic differences observed in the thermomechanical behavior of siloxane copolymers with urea, *N*-methylurea and urethane hard segments, melting behavior of urea, 1,3-dimethylurea and model HMDI–urethane and HMDI–urea compounds were investigated by DSC. As expected, there are substantial differences both in the melting temperatures and more importantly in the enthalpy of fusion values of these compounds as provided in Table 4. Urea has a melting point of 133°C, which is about 27°C higher than that of 1,3-dimethylurea. This is expected because of stronger hydrogen bonding in the urea than *N*-methylurea. As for the enthalpy of fusion, urea and 1,3-dimethylurea show values of 242.4 and 141.6 J/g respectively, or urea showing a value about 70% higher than that of *N*-methylurea. We believe these values provide a more quantitative explanation than that of CED values, to the difference between the hydrogen bonding strengths in these compounds. There is also very good correlation between DSC results, TMA behavior and stress–strain properties. DSC scans of HMDI based model urethane and urea compounds are provided in Fig. 7, together with the TGA curve of the HMDI–urea compound. In these DSC scans, obtained with a heating rate of 10 K/min, HMDI–urethane shows a fairly sharp melting peak starting at 110 and ending at 130°C, with peak minimum at 120.6°C. The enthalpy of fusion (obtained from the area under the peak) is 87.0 J/g. For the HMDI–urea compound, the melting peak starts at 180°C, as expected at a much higher temperature than that of the homologous urethane compound. However, then it becomes somewhat complicated showing double peaks with minima at 227 and 243°C, respectively, followed by another major endothermic peak. When the sample is scanned for the second time, the melting behavior changes completely. These results led us to believe that the HMDI–urea compound was thermally

Table 4
Melting behavior of model compounds determined by DSC

Compound	T_m (°C)	ΔH fusion (J/g)
	133	242.4
	106	141.6
HMDI–urethane	120	87.0
HMDI–urea	> 180	Decomposes

decomposing while melting. When thermal stability of this compound was studied by TGA, in line with our expectations, it showed decomposition after 200°C. Therefore, it was not possible to compare its enthalpy of fusion with that of model HMDI–urethane. The curve plotted as a solid line in Fig. 7, represents the TGA behavior of HMDI–urea model compound, where weight left is plotted against temperature. We believe these DSC results provide a better explanation to the differences observed in the strength of hydrogen bonding and resulting mechanical properties in siloxane–urea and siloxane–urethane copolymers than simple comparison of the solubility parameters. The most important information comes from the enthalpy data, since the enthalpy of fusion is the energy needed to break up all the attractive forces between molecules and the order (crystallinity) in the solid system. In all of the model compounds studied, this basically corresponds to overcoming the hydrogen bonding in the system. DSC results also demonstrate that hydrogen bonding between urea groups is much stronger than those of urethanes or *N*-methylureas as expected. These experimental results are in very good agreement with the hydrogen-bond energies obtained by quantum mechanical calculations on similar model compounds [13,24]. Unlike the model compounds, interestingly, no high temperature transition (T_g or T_m) was observed in siloxane–urea copolymers up to 300°C [7,8].

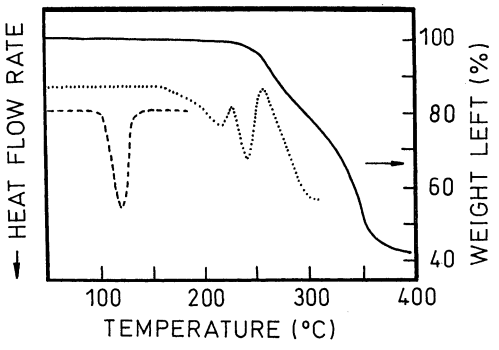


Fig. 7. TGA curve for HMDI–urea (—) and DSC thermograms for HMDI–urea (···) and HMDI–urethane (- - -).

4. Conclusions

A series of segmented siloxane copolymers containing urea, *N*-methylurea and urethane hard segments were prepared and characterized. It was demonstrated that, in these homologous siloxane copolymers, which display very good microphase separation, thermal and mechanical properties are dictated mainly by the strength of the hydrogen bonding between their hard segments, with urethanes showing the weakest, ureas showing the strongest thermal and mechanical properties and *N*-methylureas in between. Strong supporting evidence to the thermal behavior of these copolymers and substantial differences in the hydrogen bonding strengths between different hard segments were also provided by DSC studies of model compounds.

References

[1] Noll W. Chemistry and technology of silicones. New York: Academic Press, 1978.
[2] Polmanteer KE. Rubber Chem Technol 1981;54:1051.
[3] Voronkov MG, Mileshkevich VP, Yuzhelevskii YuA. The siloxane bond. New York: Consultants Bureau, 1978.
[4] Warrick EL, Pierce OR, Polmanteer KE, Saam JC. Rubber Chem Technol 1979;52:437.
[5] Noshay A, McGrath JE. Block copolymers: overview and critical survey. New York: Academic Press, 1977.
[6] Yılgör İ, McGrath JE. Adv Polym Sci 1988;86:1.
[7] Yılgör İ, Sha'aban AK, Steckle Jr WP, Tyagi D, Wilkes GL, McGrath JE. Polymer 1984;25:1800.
[8] Tyagi D, Yılgör İ, McGrath JE, Wilkes GL. Polymer 1984;25:1807.
[9] Grulke EA. In: Brandrup J, Immergut EH, editors. Polymer handbook. New York: Wiley, 1989. p. 519–59.
[10] Van Krevelen DW. Properties of polymers. Amsterdam: Elsevier, 1990. Chapter 7.
[11] Lelah MD, Cooper SL. Polyurethanes in medicine. Boca Raton, FL: CRC Press, 1986.
[12] Abouzahr S, Wilkes GL. J Appl Polym Sci 1984;29:2695.
[13] Yılgör E, Burgaz E, Yurtsever E, Yılgör İ. Polymer 2000;41:849.
[14] Riffle JS, Yılgör İ, Tran C, Wilkes GL, McGrath JE, Banthia AL. In: Bauer RS, editor. Epoxy resin chemistry II, ACS symposium series, vol. 221. 1983 Chapter 2.
[15] Yılgör E, Yılgör İ. Polym Prepr 1998;39(1):465.
[16] Yılgör İ, Tyagi D, Wilkes GL, McGrath JE. ACS 123rd Rubber Division Meeting. Paper No 47, 1983; Toronto, Canada.
[17] Cooper SL, Tobolsky AV. J Appl Polym Sci 1966;10:1837.
[18] Bras W, Derbyshire GE, Bogg D, Cookie J, Elwell MJ, Komanschek BU, Naylor S, Ryan AJ. Science 1995;267:996.
[19] Elwell MJ, Ryan AJ, Grunbauer HJM, VanLieshaut HC. Polymer 1996;37:1353.
[20] Naylor S, Terrill NJ, Yu GE, Tanodekaew S, Bras W, King SM, Booth C, Ryan AJ. Polym Int 1997;44:371.
[21] Van Krevelen DW. In: Bicerano J, editor. Computational modeling of polymers, New York: Marcel Dekker, 1992. Chapter 2.
[22] Porter D. Group interaction modeling of polymer properties. New York: Marcel Dekker, 1995 (Part 1.2).
[23] Zimmerman J. Polyamides, Encyclopedia of polymer science technology, vol. 11. New York: Wiley, 1984.
[24] Yılgör E, Metin B, Gördeslioğlu M, Yılgör İ. Polym Prepr 2000;41(1):375.