

# Comparison of hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea copolymers

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## Abstract

Hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea type segmented copolymers was investigated by infrared spectroscopy, differential scanning calorimetry and quantum mechanical calculations. Hydrogen bonding in model urethane and urea compounds was compared with those of the copolymers, in order to determine the extent of interaction and resulting phase mixing between hard and soft segments in these copolymers. Quantum mechanical calculations were also used to determine the interaction energies due to hydrogen bonding in model urethane and urea compounds. Further, similar calculations were also performed to quantify the interactions between silicone and ether type soft segments, and urea and urethane type hard segments. As expected, these calculations clearly indicated the absence of any interaction between silicones and urea groups, while there was substantial hydrogen bonding between urea groups and the oxygen in the ether type soft segments. Results of FTIR studies and quantum mechanical calculations were in good agreement with thermomechanical behavior and mechanical properties of these copolymers. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Hydrogen bonding; Siloxane; Polyether

## 1. Introduction

Hydrogen bonding plays very critical roles in determining the morphology and overall properties of polyamides, polyurethanes, polyurethaneureas [1–4] and other polymers which have pendant functional groups capable of forming hydrogen bonding, such as polyvinyl alcohol, poly(acrylic acid), polyhydroxyethers and their copolymers [5,6]. This is due to medium to strong hydrogen bonding interactions between amide, urethane, urea groups in these polymers, or due to hydroxy or acid type pendant groups. Hydrogen bonding energies usually range between 12 and 36 kJ/mol [7,8].

It has been reported that in polyamide-6,10 when some of the hydrogens in the amide groups are selectively replaced by tertiary butyl groups, there is a dramatic reduction in the modulus of these materials [9–11]. This is a direct result of the reduction in the hydrogen bonding capacity of the system. Interestingly, if the logarithm of the modulus is plotted against the level of substitution in these polyamides, as shown in Fig. 1, a straight line is observed. More interestingly, if this line is extrapolated to 100% substitution, as shown by the dotted line in Fig. 1, it intersects the  $x$ -axis at

around 95% substitution and goes to negative  $\log(\text{modulus})$  values. This is a clear indication that the actual value of the modulus is very small (almost zero) for the material, where amide hydrogens are all substituted leading to the elimination of the hydrogen bonding. This clearly demonstrates that the stiffness and strength in these polyamides are a direct function of the extent of the hydrogen bonding in the system.

Influence of the strength of the hydrogen bonding on the mechanical properties of polyether and polyester based segmented polyurethanes and polyureas have also been demonstrated [2,3,12,13]. In polyether based systems there is a competition for hydrogen bonding between urethane–urethane in the hard segments and urethane–ether in the hard and soft segments. This leads to phase mixing in these systems and a reduction in the mechanical properties and performance of the copolymers. Segmented polyurethaneureas show much higher tensile strength and modulus values when compared with polyurethanes of similar compositions [2,12]. This is due to much stronger hydrogen bonding between urea groups when compared with urethanes.

It has also been shown that polydimethylsiloxane (PDMS) based segmented urethanes show much higher tensile strengths and tensile modulus values when compared

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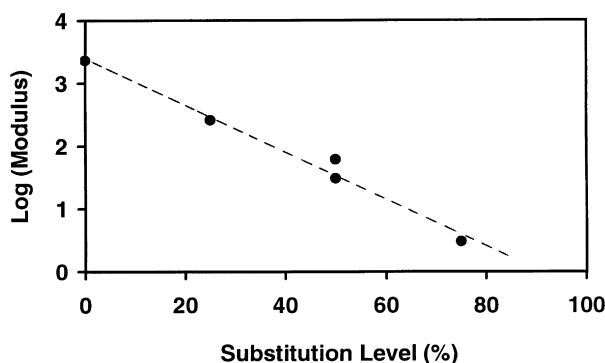
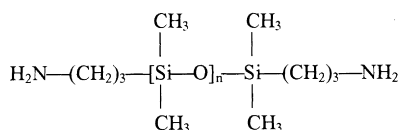
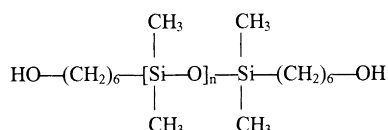


Fig. 1. Influence of level of N-substitution on the modulus of polyamide-6,10.

with polyether based polyurethanes of similar compositions [14]. This was attributed to the lack of any hydrogen bonding between PDMS and urethane segments, leading to better phase separation in these systems and stronger hydrogen bonding between the hard segments. Similarly, PDMS based segmented urea copolymers also show excellent tensile strength and elastomeric properties due to excellent phase separation and very strong hydrogen bonding in the urea hard segments. Very interestingly, in a series of



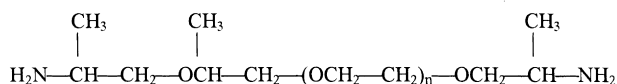
$\alpha,\omega$ -Aminopropyl terminated PDMS oligomer, (PDMS-NH<sub>2</sub>)



$\alpha,\omega$ -hydroxyhexyl terminated PDMS oligomer, (PDMS-OH)



Poly(ethylene oxide)glycol, (PEG)



$\alpha,\omega$ -Propylamine terminated poly(ethylene oxide) oligomers, (PEO)

Fig. 2. Chemical structures of polydimethylsiloxane and polyether oligomers used in the polymerization reactions.

PDMS–urea copolymers with increasing urea contents, when tensile strengths are plotted against the amount of hard segment in the system, a straight line is obtained, which goes through the origin [15]. This important observation very clearly demonstrates that the mechanical strength in PDMS–urea copolymers are only determined by the amount of urea hard segments and the hydrogen bonding between them.

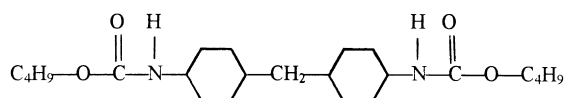
The presence and the extent of hydrogen bonding in polymeric systems, such as segmented polyurethanes can qualitatively and to some extent semi-quantitatively be determined by infrared spectroscopy [16–20]. Hydrogen-bonding components of the solubility parameter values of the hard and soft segments also provide some information about the probability and the extent of hydrogen bonding in these systems [12,21]. However, all of these methods provide a qualitative picture and usually cannot explain the major differences observed between the thermal and mechanical behavior of urethane and urea copolymers of similar compositions.

In this study, our aim was to provide a more quantitative explanation to hydrogen bonding in urethane and urea type segmented copolymers, through experiments and complementary quantum mechanical calculations. For this purpose model polymers based on PDMS and polyethers with uniform hard segments were prepared. In addition, model urethane and urea compounds were also prepared and characterized. Methods of characterization included FTIR spectroscopy and thermal analysis by differential scanning calorimetry. In addition to experimental studies, quantum mechanical calculations were also performed in determining the extent of intermolecular hydrogen bonding in model urea and urethane compounds. These were achieved by calculating the changes in the enthalpy of formation due to attractive interactions (mainly hydrogen bonding) along the minimum energy path between two similar molecules, such as urea or urethanes. Similar calculations were also carried out to determine the existence and the extent of the hydrogen bonding between urea and model siloxane or ether groups. Experimental data obtained was compared with the results of quantum mechanical calculations.

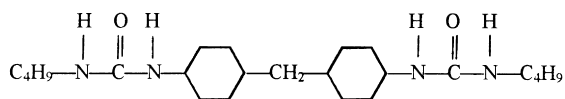
## 2. Experimental

### 2.1. Materials

$\alpha,\omega$ -Aminopropyl (PDMS-NH<sub>2</sub>), and  $\alpha,\omega$ -hydroxyhexyl (PDMS-OH) terminated PDMS oligomers were either obtained from Th. Goldschmidt AG, Essen, Germany, or prepared in our laboratories [22].  $\alpha,\omega$ -Propylamine terminated poly(ethylene oxide) (PEO) oligomers were obtained from Huntsman Corporation. Poly(ethylene oxide)glycol (PEG) oligomers were kindly supplied by BP Chemicals. The structures of these oligomers are given in Fig. 2. Molecular weights of amine terminated oligomers were



Bis(4-butylcarbamatecyclohexyl)methane



Bis(4-butylureacyclohexyl)methane

Fig. 3. Chemical structures of model URETHANE and UREA compounds.

determined by the titration of the end groups with standard hydrochloric acid. Number average molecular weights of hydroxyhexyl terminated PDMS oligomers were determined by  $^1\text{H-NMR}$  spectroscopy [23]. Bis(4-isocyanatohexyl)methane (HMDI) with a purity of greater than 99.5% was supplied by Bayer AG. *n*-Butanol, *n*-butylamine, urea, 1,3-dimethylurea and tetramethylurea with purities better than 99.5% were purchased from Aldrich and were used as received. Chromatographic grade reaction solvents, tetrahydrofuran (THF) and dimethylformamide (DMF) were obtained from Carlo Erba and used without further purification. Dibutyltin dilaurate (DBTDL) catalyst was obtained from Witco.

## 2.2. Preparation of model compounds

Model hard segments, bis(4-butylcarbamatecyclohexyl)-methane (URETHANE) and bis(4-butylureacyclohexyl)-methane (UREA) (Fig. 3) were synthesized in three neck, round bottom flasks fitted with an overhead stirrer, nitrogen inlet and an addition funnel. In the synthesis of the URETHANE compound, 0.1 mol of HMDI (26.24 g) and 0.6 mol of *n*-butanol (44.50 g) were introduced into the reaction vessel, dissolved in 100 ml of DMF and reacted at 80°C for 5 h, under the catalytic action of DBTDL. Completion of the reaction was determined by the disappearance of a strong isocyanate peak at 2260  $\text{cm}^{-1}$  in the FTIR spectrum. The product obtained was coagulated in *n*-hexane, washed several times with hexane/IPA (90/10)

mixture, filtered and dried in a vacuum oven at 50°C. For the preparation of the UREA compound 0.1 mol of HMDI (26.24 g) was introduced into the reactor and was dissolved in 50 ml of DMF. *n*-Butylamine (0.4 mol, 29.26 g) was separately dissolved in 50 ml of DMF and introduced into an addition funnel. The reaction was conducted by the dropwise addition of *n*-butylamine solution into the HMDI solution at room temperature. As the reaction proceeded the product started precipitating out of solution. To prevent this 50 ml of methanol was added as a co-solvent. Product obtained was coagulated in hexane, washed several times with *n*-hexane/IPA (80/20) mixture, filtered and dried in a vacuum oven at 50°C. All reactions were monitored by FTIR spectroscopy. Yields were quantitative. Products were characterized by  $^1\text{H-NMR}$  spectroscopy, elemental analysis and differential scanning calorimetry. Table 1 gives the results of elemental analysis and melting points of the model URETHANE and UREA compounds. The urea compound decomposes during melting as determined by thermogravimetric analysis.

## 2.3. Polymer syntheses

Siloxane–urea copolymers were prepared by the reaction of stoichiometric amounts of amine terminated PDMS oligomers and HMDI, in THF solution, under dry nitrogen atmosphere, as described before [24]. Polyether–urea copolymers were prepared in a three neck round bottom flask fitted with an overhead stirrer, nitrogen inlet and an addition funnel. Calculated amount of HMDI was introduced into the flask and dissolved in DMF. Stoichiometric amounts of PEO oligomers were separately dissolved in DMF in an Erlenmeyer flask and introduced into the addition funnel. Reactions were conducted at room temperature by the dropwise addition of HMDI solution into the reaction flask.

PDMS–urethane and PEO–urethane copolymers were prepared by the reaction of equimolar amounts of PDMS-OH or PEO and HMDI in toluene at 80°C under the catalytic action of dibutyltin dilaurate.

Completion of all polymerization reactions were followed by monitoring the disappearance of strong isocyanate peak at 2260  $\text{cm}^{-1}$  using FTIR spectroscopy.

Table 2 gives the compositions of copolymers synthesized. Polymer codes denote the following systems: PDMS–Urea (PSU), PDMS–Urethane (PSPU), PEO–Urea (PEOU) and PEO–Urethane (PEOPU).

Table 1  
Characteristics of model urethane and urea compounds

Compound	Composition	C (wt.%)		H (wt.%)		N (wt.%)		m.p. (°C)
		Calcd	Found	Calcd	Found	Calcd	Found	
Urethane	$\text{C}_{23}\text{H}_{42}\text{O}_4\text{N}_2$	67.28	66.83	10.31	10.47	6.82	6.48	120
Urea	$\text{C}_{23}\text{H}_{44}\text{O}_2\text{N}_4$	67.63	67.42	10.85	10.96	7.83	7.57	> 200

Table 2  
Chemical compositions of segmented PDMS and PEO copolymers

Polymer code	Mn (g/mol)	Oligomer wt. (g)	HMDI wt. (g)
PSU-1	890	77.3	22.7
PSU-2	1150	81.4	18.6
PSU-3	1675	86.5	13.5
PSU-4	2480	90.4	9.6
PSU-5	3750	93.5	6.5
PEOU-1	630	70.6	29.4
PEOU-2	900	77.5	22.5
PEOU-3	1990	88.4	11.6
PSPU-1	900	77.5	22.5
PSPU-2	2400	90.2	9.8
PEOPU-1	1040	79.8	20.2
PEOPU-2	1950	88.1	11.9

#### 2.4. Polymer characterization

Spectroscopic characterization of copolymers were obtained by using a Nicolet Impact 400D FTIR spectrometer. In these studies thin polymer films were cast on KBr disks from THF or THF/DMF solutions and dried in a 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, in THF, with a flow rate of 1 ml/min. DSC analyses of the products were obtained on a Rheometrics PL-DSC Plus instrument, under nitrogen atmosphere with a heating rate of 10°C per minute. Temperature and enthalpy calibration of DSC was obtained by using indium, lead and tin standards.

#### 2.5. Quantum mechanical calculations

To calculate the extent of the hydrogen bonding between various constituents of copolymers, we have carried out semi-empirical quantum mechanical calculations using the AM1 parametrization [25]. We have previously shown that the strength of hydrogen bonding in polymers can be studied with this formalism [26]. The minimum energy paths for the model pairs of urea–urea, urethane–urethane, urea–ether, and urea–siloxane were obtained by fully optimizing all geometrical parameters. As a result of the nature of the relatively weak interactions, a number of possible mechanisms were tried. For example, in urea–urea system one possible mode of interaction is the formation of a H-bond between the carbonyl oxygen and one of the hydrogens in the (–N–H) group. Another possibility is the symmetric approach of urea such that both (–N–H) hydrogens form H-bond with the carbonyl oxygen in a triatomic manner. Finally, another possibility is the intermolecular H-bond between (–N–H) groups. The change in the enthalpy of formation due to hydrogen-bonding, for all of these modes of interaction were determined for urea–urea system and also for all other systems described above.

### 3. Results and discussion

Hydrogen bonding plays very important roles in determining the overall properties and performance of various polymer systems, such as polyamides, polyurethanes and polyureas. In block copolymers, where the hard segment is urethane or urea, thermal and mechanical properties are usually strongly dependent on the extent of phase separation between the soft and hard segments. Improved phase separation in these copolymers leads to stronger hydrogen bonding in the hard segments and usually better physical properties. If there is strong electronic interaction between hard and soft segments, this usually leads to phase mixing and therefore, significantly reduces the hydrogen bonding in the hard segments. In fact we have already reported that [14,23] there are dramatic differences in the mechanical integrity and tensile strengths of siloxane–urea and polyether–urea copolymers of identical structures and compositions due to major differences in the strength of H-bonding between hard and soft segments. As will be discussed later in this manuscript, our quantum mechanical calculations also provide a very clear explanation to this observation.

In order to quantify the hydrogen bonding in polyurethane and polyurea copolymers, PDMS and polyether based model segmented copolymers with well defined hard segments consisting of mainly the diisocyanate backbone and the end groups of the respective oligomers were prepared. No chain extenders were used in order to eliminate the possibility of formation of crystallizable urethane or urea hard segments, which usually complicates the analyses. In addition to these copolymers, model urethane and urea compounds were prepared by the end capping reactions of HMDI with *n*-butanol and *n*-butylamine, respectively. Several techniques, which investigate the problem from very different angles, were used for characterization. These included FTIR spectroscopy, thermal analysis by DSC, stress strain tests and semi-empirical quantum mechanical calculations. As will be explained in detail in the following sections, we believe these techniques are complementary to each other and provide a clear, quantitative picture of various aspects of hydrogen bonding in these polymeric systems.

#### 3.1. DSC studies

A simple but very informative technique, which provides quantitative information about the strength of the hydrogen bonding in homologous series of crystalline compounds, is the determination of melting points and the enthalpy of fusion. This is because during the melting process all order in the system, and long and short range interactions between molecules are either eliminated or minimized. As a direct result of this, it is expected that as the hydrogen bonding in a homologous series of compounds gets stronger, the melting points also should show systematic increases. This can easily be seen when the melting points of

Table 3  
Characteristic IR absorption frequencies for polyurethanes and polyureas

Group	Mode	Frequency (cm <sup>-1</sup> )
N–H	Free	3445–3450
N–H	N–H···N–H	3315–3340
N–H	N–H···O (ether)	3260–3290
C=O (urethane)	Free	1730–1740
C=O (urethane)	C=O···H–N	1703–1710
C=O (urea)	Free	1690–1700
C=O (urea)	C=O···H–N	1660–1670 (disordered)
C=O (urea)	C=O···H–N	1630–1645 (ordered)
NH–C=O	Amide II	1540–1560

tetramethylurea (–1°C), 1,3-dimethylurea (106°C) and urea (133°C) are compared. Similar trend is also observed in the melting points of model URETHANE (120°C) and UREA (>200°C) compounds as determined by DSC or the values reported in the literature for similar model compounds [18].

More quantitative information on the strength of hydrogen bonding can be obtained from enthalpy of fusion ( $\Delta H_{\text{fus}}$ ) values. From DSC measurements  $\Delta H_{\text{fus}}$  values for 1,3-dimethylurea and urea were determined as 242.4 and 141.6 kJ/mol, respectively. For model URETHANE the value of  $\Delta H_{\text{fus}}$  was determined to be 87.0 kJ/mol. Since the model UREA compound showed degradation upon melting, we were not able to get reliable data for its enthalpy of fusion. However,  $\Delta H_{\text{fus}}$  values for urethane and urea compounds based on an aromatic isocyanate were reported [18] to be 131 and 169 kJ/mol, respectively. All these data clearly show that hydrogen bonding between urea groups is much stronger than that of urethanes.

### 3.2. FTIR studies

The extent of hydrogen bonding in polyurethanes or polyureas can qualitatively be studied by determining the frequency shifts in hydrogen bonded (–N–H) and (–C=O) peaks (–N–H···O=C) relative to the free (–N–H) and (–C=O) peaks. The shifts in these peaks to lower frequencies result from the weakening of the bonds between (N–H) and (C=O) due to hydrogen bonding. Table 3 gives a detailed list of absorption frequencies for various groups and their hydrogen bonded complexes. Comparative FTIR

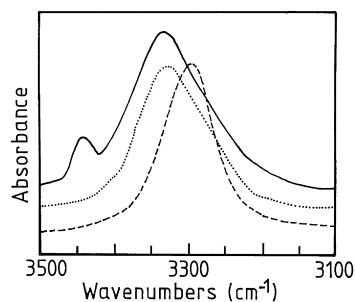


Fig. 4. (N–H) stretching region of FTIR spectra for model URETHANE (– – –), PSPU-1 (—) and PEOPU-1 (···).

spectra for (–N–H) and (–C=O) stretching regions of model URETHANE and UREA compounds and the copolymers, PSU-1, PSPU-1, PEOU-2 and PEOPU-1 are given in Figs. 4–7. Peak positions and stretching frequencies for these spectra are summarized in Table 3. When the spectra for (–N–H) stretching region are examined for models URETHANE, PSU-1 and PEOU-2 (Fig. 4) one observes a single broad peak for URETHANE with a maxima at 3295 cm<sup>-1</sup>. Compared to hydrogen bond free (–N–H) peak given in Table 2, there is a 150 cm<sup>-1</sup> shift in the peak position which indicates very strong hydrogen bonding in this compound, as expected. PEOPU-1 also shows one broad peak in this region with peak maximum at 3331 cm<sup>-1</sup> indicating complete hydrogen bonding of (–N–H) in this copolymer also. The shift is somewhat less than the model compound. This may be due to two different types of H-bonding in the system, with different H-bond energies, namely (–N–H···O=C) and (–N–H···O), where (O) is the ether oxygen in PEO. Silicone–urethane copolymer, PSPU-1, on the contrary shows two peaks in this region, a small peak with maxima at 3450 cm<sup>-1</sup>, due to H-bond free (–N–H) and another at 3333 cm<sup>-1</sup> due to H-bonded (–N–H). The small H-bond free (–N–H) peak in PSPU-1 is most probably due to slight interaction between PDMS and the urethane segments (as shown by quantum mechanical calculations), in which PDMS may have a shielding effect, preventing the H-bonding.

Fig. 5 gives the (–N–H) region of the FTIR spectra of the model UREA compounds, PSU-1 and PEOU-2. Since urea groups can form much stronger H-bonding than urethanes all of these compounds display single broad peaks in the region, with no H-bond free (–N–H) peaks. The peak maxima for model UREA compound, PSU-1 and PEOU-2 are at 3315, 3338 and 3338 cm<sup>-1</sup>, respectively.

When (–N–H) absorption frequencies of model URETHANE and UREA are compared, considering that the intermolecular hydrogen bonding between urea is stronger than that of urethane, it may be somewhat surprising to observe that the frequency shift in urethane (–N–H) is somewhat higher than that of urea (–N–H). This can easily be explained by the fact that in urethanes one (–N–H) group hydrogen bonds to the (C=O), which is shown in Fig. 10. On the contrary, as shown in Fig. 9(a), in urea two (–N–H) groups participate in a three-dimensional hydrogen bonding with (C=O), and as a result the frequency shift per (–N–H) is lower than that of urethane.

Carbonyl region of the FTIR spectra for model URETHANE, PSPU-1 and PEOPU-1 are reproduced in Fig. 6. Model URETHANE compound has a single, H-bonded carbonyl peak with a peak maximum at 1685 cm<sup>-1</sup>. This shows a fairly strong shift of 50 cm<sup>-1</sup> from H-bond free carbonyl stretching frequency given in Table 3. Silicone–urethane and polyether–urethane copolymers both show peaks with very substantial shoulders. PSPU-1 shows a well defined peak with maxima at 1706 cm<sup>-1</sup> and a shoulder at 1723 cm<sup>-1</sup>, whereas

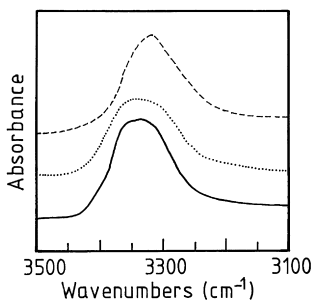


Fig. 5. (N–H) stretching region of FTIR spectra for model UREA (– – –), PSU-1 (—) and PEOU-2 (···).

PEOPU-1 shows a peak at  $1720\text{ cm}^{-1}$  and a shoulder at  $1707\text{ cm}^{-1}$ . When compared with Table 3, the peaks at  $1720$  and  $1723\text{ cm}^{-1}$  are attributed to H-bond free (C=O) stretchings and those at  $1706$  and  $1707\text{ cm}^{-1}$  are due to H-bonded (C=O) stretchings. These spectra indicate that there is more extensive H-bonding between (–N–H) and (C=O) in silicone–urethane when compared with that of polyether urethane. This can be explained by the fact that in polyether–urethanes (–N–H) groups form H-bonding with (C=O) of the urethane hard segments and the oxygen in the polyether soft segments. As we will see from the quantum mechanical calculations, H-bond energies for both of these interactions are fairly similar, meaning that there is a fairly strong competition between carbonyl and ether towards (–N–H). Since there are fairly large concentrations of ether groups in the system it can easily be seen that some of the carbonyl will not have a chance to H-bond. As for the silicone–urethane system, again from the quantum mechanical calculations, the competition for H-bonding with (–N–H) is substantially dominated by (C=O) when compared with that of siloxane oxygen. Therefore, in these systems most of the carbonyls are hydrogen bonded.

Fig. 7 gives the carbonyl stretching region of the FTIR spectra for model UREA compound and silicone and polyether urea type segmented copolymers. Model UREA compound and the silicone–urea copolymer, PSU-1, both give single sharp carbonyl peaks at  $1625$  and  $1628\text{ cm}^{-1}$ , respectively. Both of these indicate very strong H-bonded carbonyl groups in these systems, which is expected. In

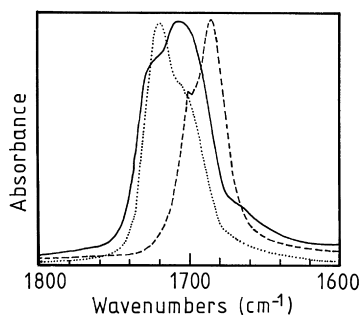


Fig. 6. (C=O) stretching region of FTIR spectra for model URETHANE (– – –), PPSU-1 (—) and PEOPU-1 (···).

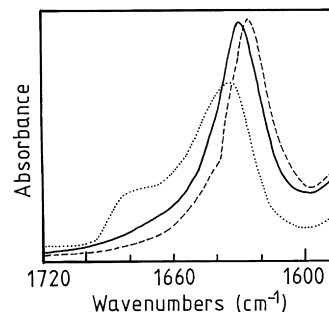


Fig. 7. (C=O) stretching region of FTIR spectra for model UREA (– – –), PSU-1 (—) and PEOU-2 (···).

polyether–urea copolymer, PEOU-2, however, there is a very broad absorption band in the carbonyl region, which shows a fairly strong peak at  $1635\text{ cm}^{-1}$  due to H-bonded (C=O) and a shoulder at  $1678\text{ cm}^{-1}$ , due to H-bond free (C=O) stretching. This again indicates that due to strong competition between (C=O) and (–O–) in polyether towards (–N–H), combined with limited (–N–H) concentration but high ether concentration in the system, some of the carbonyl groups cannot form H-bonding.

### 3.3. Quantum mechanical calculations

In order to better understand and provide a more quantitative explanation to the hydrogen bonding in urethane and urea containing copolymers we have also conducted extensive semi-empirical quantum mechanical calculations on model compounds using the AM1 parametrization [25]. Chemical structures of model compounds are given in Fig. 8. The minimum energy paths for the model pairs of urethane–urethane, urea–urea, urea–ether and urea–siloxane systems were obtained by fully optimizing all geometrical parameters. The results are summarized in Table 4. As explained before, in urea–urea system one possible mode of interaction is the formation of a H-bond between the carbonyl oxygen and one of the hydrogens in the (–N–H) group. Another possibility is the symmetric, perpendicular approach of one urea molecule to the other such that both (–N–H) hydrogens of one compound form H-bond with the carbonyl oxygen of the other compound in a triatomic manner. Finally, another possibility is the intermolecular H-bond between (–N–H) groups. Enthalpy changes during these different modes of interaction were determined.

Fig. 9(a) depicts the symmetric, perpendicular approach of a urea molecule to another such that both (–N–H) hydrogen atoms of one urea molecule form H-bonds with the carbonyl oxygen of the other. This provides the strongest H-bonding, with an interaction energy of  $21.8\text{ kJ/mol}$ . The (H···O) bond distance is around  $2.18\text{ Å}$  which is the accepted H-bond length. The asymmetrical approach shown in Fig. 9(b), also forms an H-bond which is  $6.3\text{ kJ/mol}$  less stable. These findings are in very good agreement with the X-ray results which also gave a symmetric structure with (H···O) distances varying from  $2.14$  to  $2.27\text{ Å}$  [18].

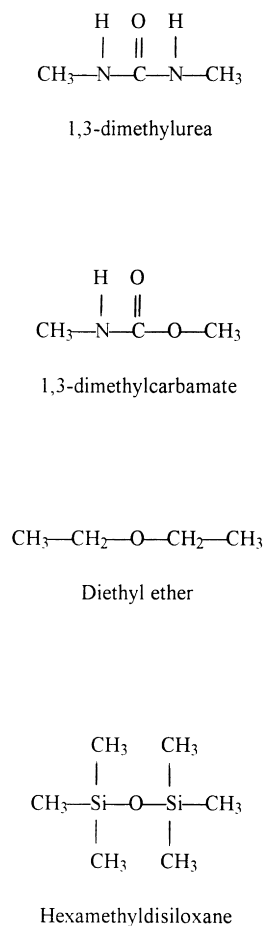


Fig. 8. Chemical structures of model compounds used in quantum mechanical calculations.

Similarly possible modes of intermolecular hydrogen bonding between model urethane compounds were also investigated. Fig. 10 gives optimum geometries for intermolecular interactions between urethane–urethane model systems. Fig. 11 gives the plots of interaction energy against intermolecular distance for urea–urea and urethane–urethane systems. From these curves H-bond energies for urea–urea and urethane–urethane systems are calculated to be 21.8 and 18.4 kJ/mol, respectively. It is clear that urea groups form much stronger intermolecular H-bonding than urethanes. According to our quantum mechanical calculations, in more quantitative terms, H-bond energy between urea is about 18% higher than that of urethane.

The strength of H-bonding interactions between urea–ether and urea–siloxane were also determined by following the same procedure. Fig. 12 shows molecular geometries for intermolecular interactions between urea–ether (Fig. 12(a)) and urea–siloxane (Fig. 12(b)) model systems where the strongest hydrogen bonding energies are observed. Interaction energy versus intermolecular distance plots for these systems are reproduced in Fig. 13. From these curves H-bond energies for urea–ether and urea–siloxane systems are calculated to be 19.2 and 7.5 kJ/mol, respectively. It is

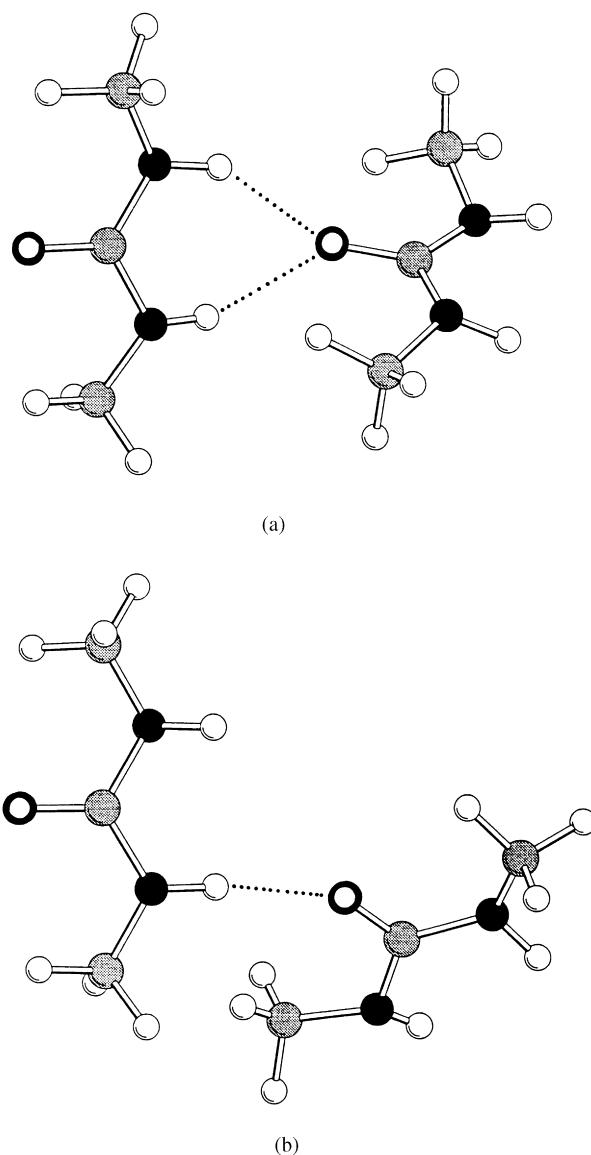


Fig. 9. Computer generated representation of two possible intermolecular geometries for hydrogen bonding between 1,3-dimethylurea: (a) symmetrical triatomic interaction; and (b) asymmetrical diatomic interaction.

clear that, as expected, the interaction between siloxane and urea is fairly small. In fact the interaction energy calculated is much smaller than typical H-bond energies. Therefore, the interaction between urea and siloxane is not H-bonding but most probably a dipole–dipole type interaction. On the contrary, the calculated H-bond energy between urea and ether is very high (19.2 kJ/mol), in fact surprisingly even higher than the intermolecular H-bond energy between urethanes (18.4 kJ/mol).

The results of quantum mechanical calculations correlate well with the shifts observed in the carbonyl region of FTIR spectra. Table 5 provides a summary of the frequency shifts observed in FTIR and H-bonding energies calculated by quantum mechanical calculations. Strongest interaction is between urea groups, as clearly indicated both by

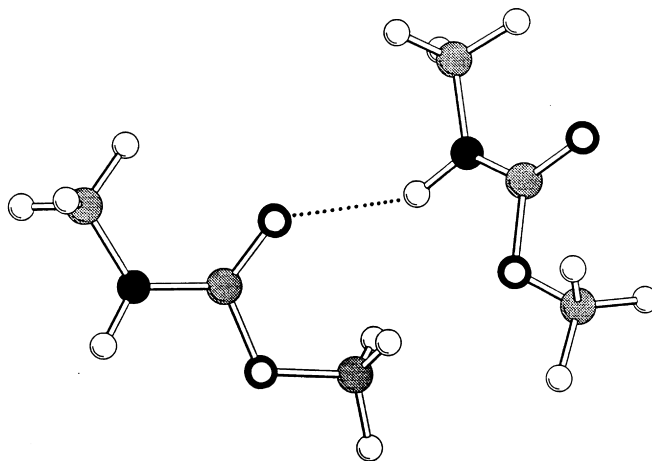


Fig. 10. Optimum geometry for intermolecular hydrogen bonding between 1,3-dimethylcarbamate molecules.

$\Delta H(\text{H-bond})$  and  $\Delta\nu$  values. Urethanes show weaker interactions thus smaller  $\Delta H(\text{H-bond})$  and  $\Delta\nu$  values, when compared with those of urea. A similar trend is also observed between the FTIR shifts when polyether and PDMS based urethane and urea copolymers are compared, urea copolymers showing larger frequency shifts than urethanes.

These results also clearly explain the two major reasoning behind the formation of siloxane–urea copolymers with excellent mechanical strength whereas polyether–urea copolymers of similar chemical structures and compositions show almost no mechanical strength at all at room temperature [14,15]. In siloxane–urea copolymers due to very weak interactions between siloxane and urea groups,

Table 4  
Hydrogen bonding energies and bond distances  $R(\text{H}\cdots\text{O})$  for various systems studied by quantum mechanical calculations

System	$\Delta H$ (kJ/mol)	$R(\text{H}\cdots\text{O})$ (Å)
Urea–urea	21.8	2.18
Urethane–urethane	18.4	2.13
Urea–ether	19.2	2.22
Urea–siloxane	7.5	2.78

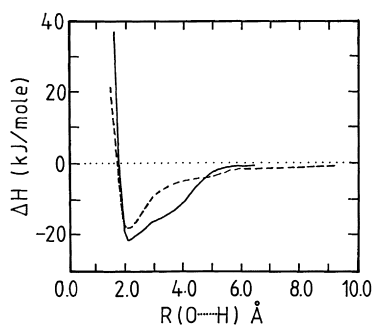
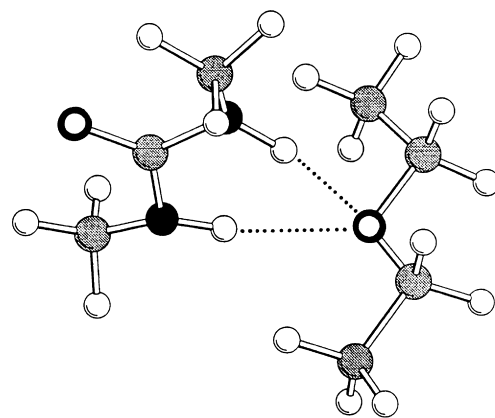
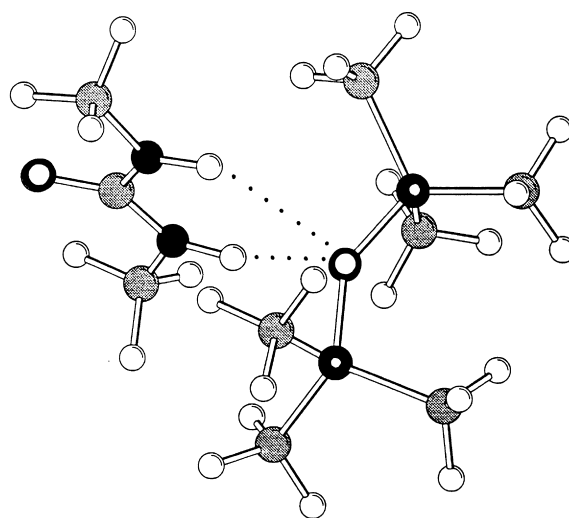


Fig. 11. Plots of interaction energies against  $(\text{O}\cdots\text{H})$  interatomic distances for 1,3-dimethylurea (---) and 1,3-dimethylcarbamate (—).



(a)



(b)

Fig. 12. Optimum geometries for intermolecular hydrogen bonding between (a) 1,3-dimethylurea/diethyl ether and (b) 1,3-dimethylurea/hexamethyldisiloxane.



Table 5

Comparison of the frequency shifts observed in the strongest (C=O) peaks in FTIR spectra and H-bond energies determined by semi-empirical quantum mechanical calculations

Compound/system	$\nu$ (C=O) (cm <sup>-1</sup> )	$\Delta\nu$ (cm <sup>-1</sup> )	$\Delta H$ (H-bond) (kJ/mol)
Model urethane	1685	50	18.4
PEOPU-1	1717	18	–
PSPU-1	1706	29	–
Model urea	1625	70	21.8
Model urea/ether	–	–	19.2
Model urea/siloxane	–	–	7.5
PEOU-2	1635	60	–
PSU-1	1628	67	–

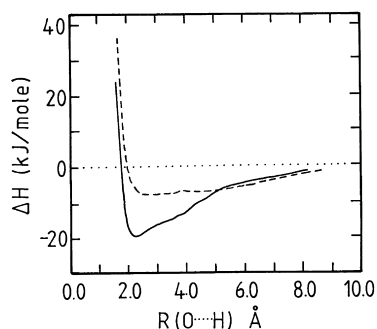


Fig. 13. Plots of interaction energies against (O...H) interatomic distances for 1,3-dimethylurea/diethyl ether (---) and 1,3-dimethylurea/hexamethylsiloxane (—).

there is very good microphase separation between PDMS and urea hard segments. Since there is no phase mixing, urea groups are also able to form very strong intermolecular hydrogen bonding. On the contrary, in polyether–urea systems, there is strong competition between urea carbonyl and ether oxygen to H-bond with (–N–H) in the urea hard segments. This leads to extensive phase mixing between urea and ether segments and as a result dramatic reduction in the intermolecular H-bonding between urea hard segments.

#### 4. Conclusions

Hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea type segmented copolymers were investigated by infrared spectroscopy and quantum mechanical calculations. Studies on model urea and urethane compounds by FTIR, DSC and quantum mechanical calculations clearly show the formation of strong intermolecular H-bonding in both of these systems, ureas displaying much stronger interactions than urethanes. Quantum mechanical calculations have clearly shown that, as expected, there is negligible interaction between urea and siloxane groups. However, surprisingly, H-bonding between

urea and ether is very strong, much stronger than the urethane–urethane interaction.

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