Segmented organosiloxane copolymers: 2 Thermal and mechanical properties of siloxane–urea copolymers

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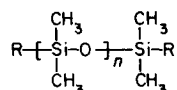*(Received 12 January 1984)*

The structure–property behaviour of new siloxane–urea containing segmented copolymers has been investigated. Amino-propyl terminated poly(dimethylsiloxane) oligomers of from 900–3660 $\langle M_n \rangle$ were reacted with various diisocynates to form segmented copolymers with urea linkages. The length of the hard segments in these copolymers corresponds approximately to the length of the diisocynate unit employed. A number of mechanical and thermal properties were investigated for these phase separated materials. It was found that the performance of these copolymers was effected by varying the hard segment type and/or content and that high strength necessitates a microphase texture. The two phase nature of these copolymers was verified by dynamic mechanical, thermal and SAXS studies. The phase separation was found to occur in these copolymers even with 6% hard segment by weight. In conclusion, these materials displayed a behaviour similar to the segmented polyurethanes and were found to be superior to the unfilled silicone elastomers.

(Keywords: siloxane; segmented; copolymers; polyurea; mechanical properties; thermal properties)

INTRODUCTION

Silicone elastomers have received widespread attention since they were introduced commercially. Several review articles have appeared in the literature dealing with the current and developing technology of silicone elastomers[1–7]. Over 15 000 publications throughout the world have appeared on elastomeric siloxane materials[1,5]. Special interest exists in these systems, since many engineering needs are fulfilled by their unique properties.

The most common and widely used silicone elastomers are principally based on poly(dimethylsiloxane) (PDMS) whose chemical formula can be given as:

$$R \text{--} \left[\begin{array}{c} CH_3 \\ | \\ Si\text{--}O \\ | \\ CH_3 \end{array} \right]_n \begin{array}{c} CH_3 \\ | \\ Si\text{--}R \\ | \\ CH_3 \end{array}$$

The interesting and useful properties of silicone elastomers are a result of somewhat unusual molecular structure of the polymer chains which consists of alternating silicone and oxygen atoms[8]. These backbone chains are sometimes considered to have an 'organic–inorganic' nature as compared to typical organic elastomers. The repeat unit is characterized by very low intermolecular forces, ease of rotation and the relatively long Si–O bond length. These characteristics enable the polymer molecules to be unusually flexible and to display properties which are fairly constant over a wide temperature range.

Elastomers based on the siloxane linkages are observed to be quite thermally stable which may be at least partially due to the fairly strong silicon–oxygen bond[9–11]. This bond has an energy of dissociation of 108 kcal mol^{-1} as compared to 85.5 kcal mol^{-1} for a C–C bond. In addition to high bond strength, the siloxane bonds are unique in terms of their partial ionic character and the availability of silicon's d-orbitals for chemical bonding[2]. Nevertheless, the siloxane linkages may degrade by lower energy dissociation routes which involve exchange with other siloxane units or impurities[12–14]. These reactions are reversible which has encouraged numerous studies of the effect of impurities and imperfections on thermal stability. One important method here has been the use of chemorheological studies[15]. The strong Si–O bond also results in chemical inertness and incompatibility with most organic materials. Silicone elastomers resist sunlight, weathering, ozone and in general, conditions which would degrade most organic elastomers[5].

As a result of low intermolecular forces and flexibility, siloxane polymers possess elastomeric capabilities even at extremely low temperatures $(T_g = -123°C)$[16–18]. This is especially true if a low percentage of such comonomers such as diphenyl or methyl phenyl units are incorporated to prevent low temperature crystallization. The importance of low T_g elastomers for impact resistance both at low and ambient temperatures have been well documented[19,20]. Siloxane elastomers have also been of considerable interest in theoretical studies due to their nearly ideal behaviour in experimental elastomeric investigations[21,22].

Silicone elastomers have been used as insulation on wires and cables because of their excellent electrical properties at elevated temperatures[23]. Even when the insulation is exposed to direct flame, properly controlled systems burn to a non-conducting ash. That is, the degraded material may continue to function as insulation

in a suitably designed cable[6]. These elastomers have also found widespread utility as biomaterials and have been used with success in external prosthesis for encapsulation and some usage as blood-compatible surface coatings[24,25]. For delicate assemblies and other applications, moulds can be made conveniently and economically using liquid silicone rubber, as they flow readily and can thus reproduce the finest details of the pattern with almost no shrinkage[26]. In addition, siloxane containing materials are noted for their high permeability to gases, high surface activity and hydrophobic character. However, because of poor mechanical properties, many potential applications have not been fully realized.

It has been well accepted that the mechanical response of an elastomeric material depends greatly on the test temperature relative to the glass temperature. In addition, the density of permanent and transient crosslinks as well as the presence and type of filler greatly affect the mechanical behaviour[27]. Organosiloxane elastomers are about 150°C above their glass transition temperature at room temperature. These facts can generally be related to the relatively poor mechanical properties (e.g. tear and toughness) displayed by silicone vulcanizates.

In linear form, PDMS behaves as a viscous liquid above T_g unless it is of an extremely high molecular weight and/or is crosslinked whereby some degree of solid like character exists[28].

A silicone elastomer network is weak because flaws or microcracks encounter little resistance to growth due to the high mobility of chains at room temperature[29]. As a consequence of their poor mechanical properties, organic siloxane elastomers are seldom used as pure 'gums'. In order to achieve desirable mechanical properties, it is imperative that a structural modification be introduced, which not only acts as stiffener, but also impedes the growth of these microcracks. The modification of the basic PDMS backbone, however, can be improved through particulate reinforcement or by the incorporation of rigid plastic domains.

Certain finely divided solids have been incorporated within the siloxane matrix to improve the mechanical behaviour or these siloxane elastomers, while maintaining many of their other desirable characteristic properties[30-35]. Reinforcement is important to silicones because the unfilled methyl gumstock is too weak to be of much use (0.35 MPa tensile strength at ambient temperature). The highest degree of reinforcement is achieved in silicone elastomers by compounding with fused silica[36]. The elastic modulus and tensile strength are two of the parameters that are profoundly influenced by such fillers. This reinforcement of elastomers by finely divided solids is often attributed to[37]:

(1) additional crosslinks;
(2) polymer/filler interaction of a chemical nature;
(3) a physical-mechanical interference of filler particles with the stress distribution and deformation of elastomer molecules; and
(4) filler/filler interaction which gives rise to a coherent filler network.

However, there is no complete agreement on the exact nature and mechanism of polymer–filler interfacial bonding and the presence of crepe hardening and bound rubber formation has only tended to confuse the issue[38,39]. Moreover, the utilization of these reinforced siloxane elastomers requires one to first overcome the usual problem encountered in processing filled and cross-linkable systems.

Segmented copolymers composed of hard and soft segments are well recognized to provide a very useful concept for the design and control of polymer properties[40,41]. They are $[AB]_n$ type alternating block copolymers in which the blocks are relatively short and numerous. Such resultant copolymers can range from thermoplastics to thermoplastic elastomers depending upon the nature of blocks, composition ratio and/or the average segment length. Thermoplastic elastomers are obtained in systems where intersegmental and intrasegmental secondary binding forces are different[42]. This generally results in a two phase solid state structure for the segmented copolymers due to the thermodynamic incompatibility of the two dissimilar segment types. In these systems, junction points are provided by the hard segments without requiring chemical crosslinking and, at the same time, the hard domain serve as reinforcing filler in the rubbery phase[43]. For elastomeric behaviour at the service temperature, one component is viscous or rubbery while the other is either a high temperature melting crystalline structure or high temperature softening glass.

These segmented copolymers thereby form a reversible elastomeric system since the hard domains soften at their glass or melting transition temperatures. Hence, they can be, in favourable cases, fabricated either from the melt or from solution[44]. However, in general, melt processibility can be limited by the excessively high viscosities exhibited by two phase melts[45]. Utilizing the unique properties of siloxane, segmented copolymers containing PDMS as the soft segment and oligomers of various thermoplastics such as polystyrene[46], poly(α-methylstyrene)[47], polysulphone[48] and bisphenol-A polycarbonate[49] have been synthesized and studied.

In the present work, structure property relationships of segmented copolymers based on soft siloxane segments having urea linkages have been investigated. Since the mechanical response in these materials is dictated by the morphology, it is desirable to characterize the morphology and determine what factors influence it. It has been well accepted that the morphology in segmented copolymers is affected by hard and soft segment type, respective volume fractions of the two segments, intermolecular bonding, molecular weight distribution and the length of the segments.

Segmented copolymers of the $[AB]_n$ form are usually obtained via step growth (condensation) polymerization reactions. The reaction components consist of a difunctional soft segment, difunctional hard segment component and perhaps a chain extender. For this work the hard segments were principally obtained via stoichiometric reaction of the hard component (e.g. diisocyanates) with amino functional siloxane oligomers. More details on the synthesis reaction have been reported by Yilgor *et al.* in the preceding paper[54].

One of our goals was to utilize the chemical composition as a means to control or vary the desired molecular structure. Specifically the final molecular properties such as polarity, hydrogen bonding capability and crystallizability of the blocks is affected by the chemical composition. *In many of these copolymers there is no length distribution of the small hard segment since a chain extender is not used.* This suggests that if a two phase morphology is noted, there is a likelihood of only a relatively small

amount of interfacial region between the hard and the soft segments. In this paper, we discuss structure–property behaviour of segmented copolymers that contain urea linked hard segments. The mechanical and thermal properties obtained can be controlled by changing the hard segment type and content. These segmented copolymers also serve somewhat as models, since network imperfections such as dangling chain ends, which are believed to contribute to premature rupture[50], are minimal. Moreover, the plastic domain should serve as an effective mechanism for imparting toughness[29].

EXPERIMENTAL

Aminopropyl terminated poly(dimethylsiloxane) oligomers (PSX)
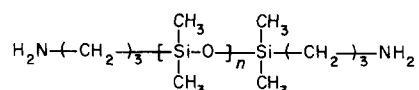
were synthesized by the equilibration of cyclic octamethyltetrasiloxane (D_4) with bis (γ-aminopropyl) tetramethyldisiloxane in bulk at approximately 80°C using alkaline catalysts as discussed elsewhere[51,53]. The oligomers were characterized by *F*Ti.r. and n.m.r. spectroscopy, h.p.l.c. end-group titration and by thermal analysis (d.s.c.). The diisocyanates (MDI, TDI and H-MDI) used were generously supplied by Mobay Chemical Corporation. All starting materials were carefully purified by either fractional distillation under vacuum or by recrystallization. Reaction solvents included tetrahydrofuran (THF), 2-ethoxyethyl ether (EEE) and *N*-methylpyrolidone (*N*MP) and were dried over sodium or calcium hydride by refluxing and then fractionally distilled under vacuum before use.

Siloxane–urea copolymers were synthesized in solution, under dry N_2 atmosphere using EEE or THF as the solvents. A solution of PSX (and chain extenders, if desired) was slowly added through a dropping funnel into the isocyanate solution (MDI, TDI or H-MDI) in the reaction flask at room temperature while the system was stirred continuously. After reacting for 2 h, the system was heated to 50°C and maintained at that temperature for another 2 to 3 h. The products were recovered by coagulation in methanol or isopropanol. This was followed by filtration and drying under vacuum at 50°C.

Various amino terminated poly(dimethylsiloxane) oligomers, with the molecular weight $\langle M_n \rangle$ ranging from 900 to approximately 3600 were reacted with MDI, TDI or hydrogenated MDI (H-MDI) to provide the necessary urea linkages. The stoichiometric ratio of [–NCO] to [–NH₂] for all samples was 1.0. Thus three series of polymers with varying soft segment size were obtained. Additional synthesis details are provided in the preceding paper[54]. The segmented copolymers obtained with the 1770 molecular weight PSX and MDI is refered to as PSX-1770-MDI-88, where 88 represents the weight percent of siloxane blocks including the propyl groups. Similar nomenclature is employed for other samples.

Structural characterization of the polymers was obtained by *F*Ti.r. spectroscopy (Nicolet MX-1). The intrinsic viscosities were determined at 25°C using THF as the solvent.

Films of the siloxane containing segmented copolymers were prepared by compression moulding the dried material for 10 minutes at 180°C and 10 000 psi. The required moulding temperature could be estimated from the TMA response (discussed later). For chain extended systems, the required temperature would, of course, be higher than for the stoichiometrically extended materials with the same hard segment. After removal from the press, all samples were immediately quenched to room temperature and placed under vacuum in a dessicator until further testing.

'Dog-bone' specimens were cut from the films for the mechanical testing of the segmented copolymers. Mechanical measurements included stress–strain, stress relaxation, tensile hysteresis and permanent set behaviour. All these tests were performed on an Instron Model 1122 at room temperature. All stress–strain and hysteresis measurements were carried out at a strain rate of 200% per minute based on the initial sample length. Stress relaxation experiments were performed by stretching the samples to different elongations at an initial elongation rate of $10\,000\%\ \text{min}^{-1}$ to the desired elongation.

Tensile hysteresis experiments were performed by deforming and unloading the dog-bone specimen to increasing strain levels for each successive cycle. The end of each cycle was concluded when the Instron showed a zero stress level. Strain levels ranged from 25% to 900% in incremental steps of 50% strain. The per cent hysteresis for a given cycle was calculated by the ratio of the area bounded by the loading and unloading curve to the area under the loading curve; the areas were determined using a digital planimeter.

Permanent-Set measurements were carried out in a similar manner as employed for tensile hysteresis. The sample length for a given cycle was measured prior to starting the next cycle. Instantaneous values of permanent set were obtained when the end of one cycle and the beginning of the next one were marked by the sample showing zero stress. The kinetics of further recovery were also studied by lengthening the time between the loading and the unloading steps. The intervals varied from 10 min to 24 h at room temperature (25°C).

For the purpose of investigating the two phase nature and low temperature properties of these copolymers, dynamic mechanical spectra were obtained. These experiments were conducted with a Rheovibron Model DDV II-C at 110 Hz and the Dynamic Mechanical Thermal Analyser manufactured by Polymer Laboratories, England. The heating rate for the sample was maintained at 5°C min⁻¹. The formation of domain structure (microphase separation) was further verified by using the small angle X-ray analysis. An automated Kratky small angle X-ray camera was utilized for the SAXS experiments. The X-ray source was a Siemens AG Cu 40/2 tube, operated at 40 kV and 20 mA by a GE XRD-6 generator. A CuKα-radiation of wavelength 1.542 Å was obtained by Ni-foil filtering.

Thermal analysis (d.s.c., t.g.a., t.m.a.) of the block copolymers was performed on a Perkin–Elmer System 2. Experiments were carried out under helium or nitrogen atmosphere using a heating rate of 10°C min⁻¹. The d.s.c. and t.m.a. scans were started at − 140°C, whereas thermal degradation studies (t.g.) began at 50°C. During t.m.a. measurements, a constant load of 10 g was employed.

RESULTS AND DISCUSSION

Our work to date[51,53] and herein has demonstrated that it is possible to synthesize novel segmented elastomers based on aminopropyl terminated poly(dimethylsiloxane) oligomers. By using MDI, TDI or hydrogenated MDI (H-MDI), we are able to produce segmented copolymers containing urea linkages. As will be discussed later, all of the materials display very interesting behaviour. Through the choice of different molecular weight of the polysiloxane segments, various siloxane–urea segmented copolymers were obtained in high yields by solution polymerization.

Intrinsic viscosities of the copolymers were reasonably high[54]. Spectroscopic (*FT*i.r. and ^{1}H-n.m.r.) characterization of the products also showed the formation of urea linkages in these systems as expected. As will be demonstrated, the thermal and mechanical characterization clearly indicate the dependence of the overall properties of the copolymers on the type and amount of 'hard' segments present in the system.

Although the experiments were carried out on fresh as well as well aged (e.g. one week after moulding) samples, no appreciable 'ageing' effect was observed on the microphase separation character of these materials. This is mainly because of the fact that the siloxane chains are about 150°C above their glass transition temperature at ambient conditions. Thus, these already flexible and mobile chains can attain their 'pseudo equilibrium' conformations almost immediately. The term pseudo equilibrium is used here since it must be remembered that in block copolymers a true equilibrium morphological texture is seldom attained.

The engineering stress–strain curves for samples with urea linkages obtained with H-MDI and different PSX molecular weights (and hence variable urea segment content) are shown in *Figure 1*. This system compares very well with the siloxane–urea copolymers obtained with MDI[55]. All curves are shown up to the fracture stress of the sample. For the purpose of comparison, curves are also included for two filled silicone elastomers as well as an unfilled system as reported earlier in the literature[56,57]. The moduli are also reported in *Figure 1*. As expected, the value of the initial modulus is directly related to hard segment content. At the higher content of H-MDI segment, a yield point is observed, due possibly to some continuity of the hard phase or perhaps the presence of short soft segments may influence this behaviour for the lower molecular weight oligomers. The molecular weight distribution of the oligomer was found by g.p.c. to be similar in all our samples and implies therefore that the high molecular weight PSX oligomers have a relatively smaller number of short chains.

It is noted from *Figure 1* that the average ultimate elongation varies from 400%–1000% depending on the molecular weight of PSX. Also, the strength of the elastomer depends greatly on the concentration of the polar urea linkages. If this is the case, then by preparing PSX oligomers of even higher molecular weight and using chain extenders to increase the urea linkages, it should be possible to obtain reasonably strong elastomeric materials. Some work has already been done based on this premise and will be reported at a later time. Interestingly, the preliminary work done on these high molecular weight chain extended materials did not show the presence of any yield point. Since the higher molecular weight
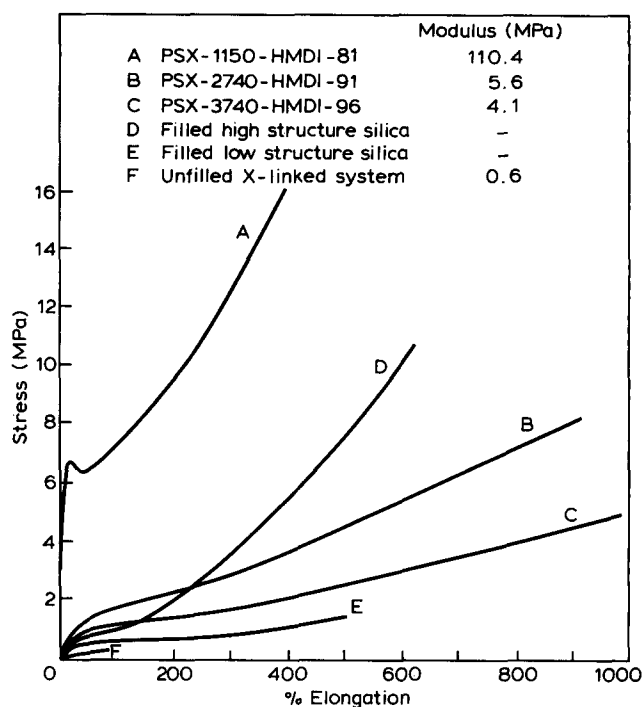

Figure 1 Stress vs % elongation behaviour for siloxane–urea segmented copolymers from H-MDI as a function of molecular weight of oligomer used and the hard segment content at 25°C. Curves D and E are from ref. 56 and curve F from ref. 57

PSX materials have fewer number of short chains, the results indicate that the yield point observed in lower molecular weight material is therefore possibly due to the presence of short PSX chains as mentioned earlier.

The tensile strength of 16 MPa was obtained for PSX-1140-HMDI-82 with an ultimate elongation of 600%. A value of 13.0 MPa has been reported by Polmanteer *et al.*[56] for a silicone system filled with about 40% of high structure Me_3SiO_4 treated silica particles after 4 h of heat treatment. The ultimate elongation for this filled system was 640%, although the values reported by Boonstra *et al.*[38] for the same system are considerably lower. For an unfilled but crosslinked system, a value of about 0.30 MPa has been reported by Levin *et al.*[57] with a maximum elongation of only 75%. Considering that PDMS with a molecular weight between 1000 and 4000 is essentially a free flowing viscous liquid at room temperature, the segmented copolymer structure has dramatically changed the mechanical response and properties of PDMS. Not only are many good elastomeric characteristics obtained, these segmented systems are actually better than the filled and crosslinked systems in many ways and can be prepared in a very systematic and controlled fashion. More importantly, these materials are easily thermally processable by conventional techniques, since the junction points are provided by the domain structure and these domains can be disrupted at elevated temperatures. A summary of the stress strain results is given in *Table 1* for the siloxane–urea systems obtained with MDI, TDI and H-MDI. As expected, the ultimate elongation and tensile strength and modulus are seen to be governed by the hard segment content and the molecular weight of the siloxane chains.

It is worthwhile to notice that even with as little as 6 wt% of the H-MDI hard component, a 'siloxane liquid' has been modified to show elastomeric behaviour. This

Table 1

M.W. of PSX	Isocyanate	%Wt PSX	Modulus (MPa)	% Elongation	σ_B (MPa)
900	MDI	78	81.3	430	16.6
1140	MDI	82	33.7	570	11.7
1150	TDI	87	39.5	520	10.0
1150	HMDI	81	110.4	400	16.6
1770	MDI	88	19.1	730	10.0
1770	TDI	91	7.3	800	3.6
2420	MDI	91	7.0	940	8.8
2740	HMDI	91	5.6	950	9.0
3660	MDI	94	5.1	1000	4.0
3740	HMDI	94	4.9	1000	4.8
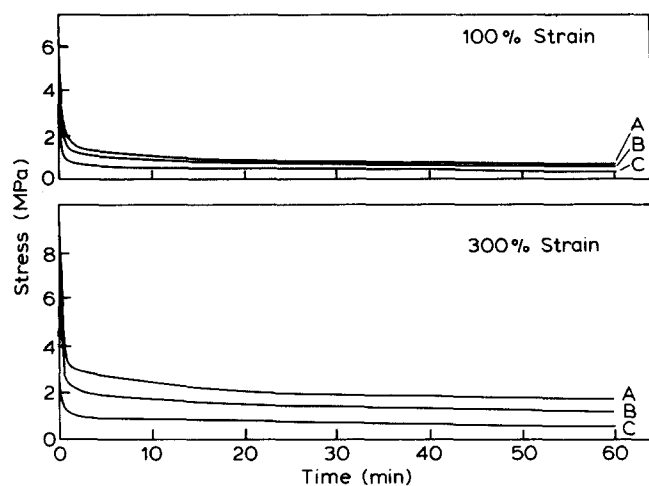
Figure 2 Stress–relaxation behaviour for (A) PSX-1150-HMDI-81, (B) PSX-2740-HMDI-91, and (C) PSX-3740-HMDI-94 for 100 and 300% elongations at ambient conditions

Figure 3 Percent hysteresis vs. percent elongation behaviour for siloxane–urea segmented copolymer system obtained from H-MDI. Curve (A) PSX-1150-HMDI-81, (B) PSX-2740-HMDI-91 and (C) PSX-3740-HMDI-94

implies the formation of small hard segment domains with equal length, which would be, in fact, the length of an H-MDI unit. This certainly suggests that little, if any, interfacial regions can exist for these domains given the differences in molecular structure between the siloxane and polar hard urea segments. One point of interest is the presence of propyl units at the end of the siloxane chains. Because of their intermediate cohesive energy density, we have not been able to clearly decide whether the propyl units should be considered part of the hard or the soft segments. They may even serve as an 'interfacial region' between the two segments.

As mentioned by Yilgor et al.[54], a tin octate catalyst had to be used with TDI systems as the reaction of the second isocyanate group is slow due to resonance and steric reasons. Also, for the H-MDI system the solvent used was THF instead of EEE which was used in the preparation of the MDI system. The chain extenders are difficult to incorporate in MDI system due to the large solubility differences and the inability of the solvent to uniformly dissolve the reactants as discussed in detail in the preceding paper.

The stress relaxation curves for the H-MDI system (shown in *Figure 2*) illustrate that for these copolymers the stress rapidly decays to a near equilibrium value. For all samples this equilibrium character was reached within 2 h, dropping to about 25% of the initial stress level. This again confirms the fact that we are dealing with a pseudo crosslinked system, for the material would have continued flowing rapidly after stretching if this had not been the case.
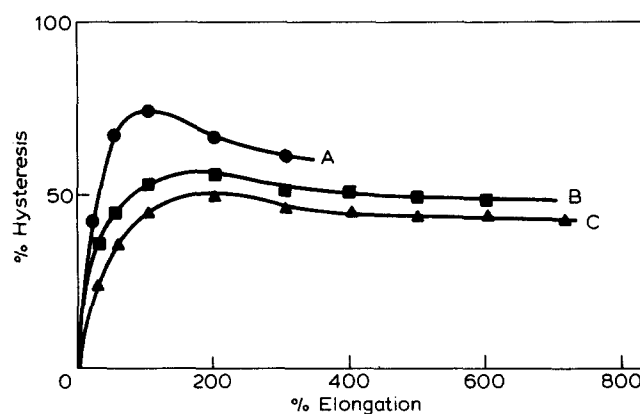
In *Figure 3*, the hysteresis behaviour is shown as a function of elongation. With an increase in molecular weight of PSX, the per cent hysteresis decreases. Although the segmented system prepared with 3600 molecular weight PSX has less than 6 wt% hard segments, they show only 50% hysteresis at 100% elongation. These hysteresis properties are somewhat poorer when compared with some conventional polyether-MDI-BD based polyurethanes containing 35% hard segment content[58] which show 30% and 40% hysteresis at 100% and 500% elongations respectively under the same loading conditions. As seen from the Figure, the tensile hysteresis goes through a maxima with elongation. This behaviour, which is also seen in many block and segmented copolymers, is primarily attributed to the breaking up of the continuity in the hard segment phase. Hence, there is an excessive amount of energy lost in these processes which is irreversible at short times and this appears as the maxima at short elongations. However, there is an experimental factor which would also contribute to this behaviour, and therefore should be kept in mind. Specifically, the hysteresis experiment is carried out at constant cross-head speed of the Instron and hence there is an increasingly larger time interval available for the unloading part of the cycle at high elongations. This would result in the soft siloxane chains having more time to relieve the stress by conformational rearrangement. This is especially true for these soft segments for they are about 150°C above their glass transition temperature at ambient conditions and therefore are highly mobile and have short relaxation times.
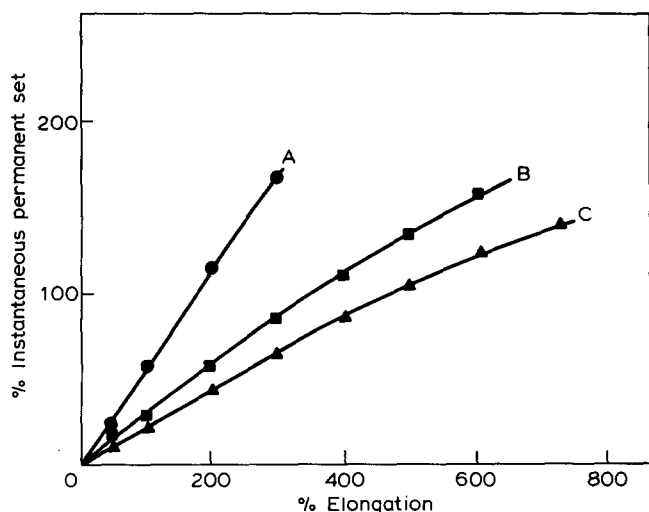
Figure 4 Percent 'Instantaneous' permanent set at different elongations for siloxane–urea segmented copolymer system from H-MDI
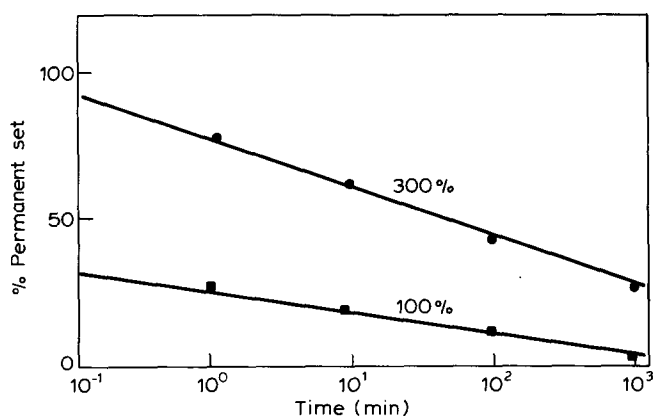

Figure 5 Semi-logrithmic plot of permanent set as a function of time different elongations for siloxane–urea segmented system obtained from MDI and siloxane oligomer of molecular weight 1140

Figure 4 shows the instantaneous permanent set behaviour again as a function of elongation. Although the instantaneous permanent set values are large, especially at higher hard segment content, these systems show reasonably good recoverability in the copolymer, which is also dependent on the physical network structure. When compared with typical thermoplastic elastomer segmented urethanes of comparable hard segment content, the values obtained for stress relaxation and instantaneous permanent set are somewhat higher for the siloxane systems. This comparison may not be completely valid since in most of the reported data on permanent set a 10 min relaxation time is generally allowed in between the loading and the unloading cycles. Hence, it is difficult to directly compare the permanent set data unless the same time interval is used for the materials to be compared. This is of significance as shown by the kinetic study of the permanent set on these copolymers. The kinetics of permanent set in *Figure 5* shows dramatic differences for longer time intervals following unloading. The data has been presented on a semi-logrithmic scale because of the large time intervals considered and also to bring out the exponential nature of the permanent set recovery. For example, the permanent set for a high hard segment

content MDI system at 100% elongation had an instantaneous value of 60%. This value dropped to 13% after 10 min and was only 5% after 24 h.

The engineering stress–strain curves for siloxane–urea segmented copolymers obtained from either MDI, TDI or hydrogenated MDI are shown in *Figure 6*. Only one molecular weight of oligomer is shown for each system. In these stoichiometrically linked systems, it is found that the mechanical behaviour is almost the same, especially for the MDI and TDI systems. This is expected since the cohesive energy density of the hard domains is about the same, although hard–soft segment compatibility is somewhat affected. This similarity in behaviour between MDI and TDI containing copolymers indirectly suggests that the number density of the hard segments may be a more critical parameter in determining the performance of these systems rather than their volume or weight fraction. In other words, since the size of the hard segment is very small, the hydrogen bonding and polarity of the linkages dictate the mechanical performance. The symmetry consideration and hard–soft segment compatibility may also be important although we have not yet systematically addressed this issue.

Turning now to the thermal response of these materials, the d.s.c. thermograms of the starting polysiloxane oligomers display a sharp transition around $-120°C$ as expected for the siloxane backbone. The value of T_g increases slightly as the oligomeric molecular weight decreases, which can be attributed to the restrictions imposed on the soft siloxane segments by the n-propyl capping groups which would be expected to display a higher 'T_g'. For molecular weights greater than 4000 for the polysiloxane oligomers, crystallization and melting peaks are also observed around $-90°C$ and $-50°C$ respectively for the PDMS backbone. The transition temperatures together with the molecular weights of the oligomers have already been reported[59]. However, the d.s.c. results from the copolymers differ significantly from those on the oligomers. Although the d.s.c. thermograms for all siloxane–urea copolymers (based on either MDI,
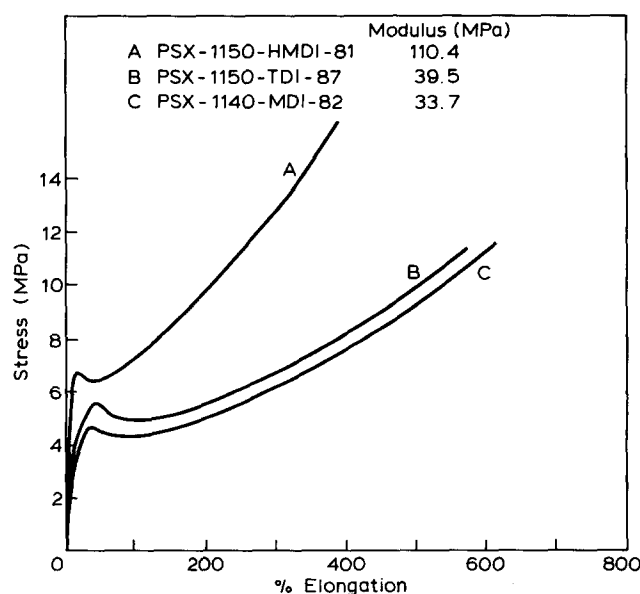

Figure 6 Stress vs. percent elongation behaviour for various siloxane–urea segmented copolymers containing about the same molecular weight of the siloxane oligomer
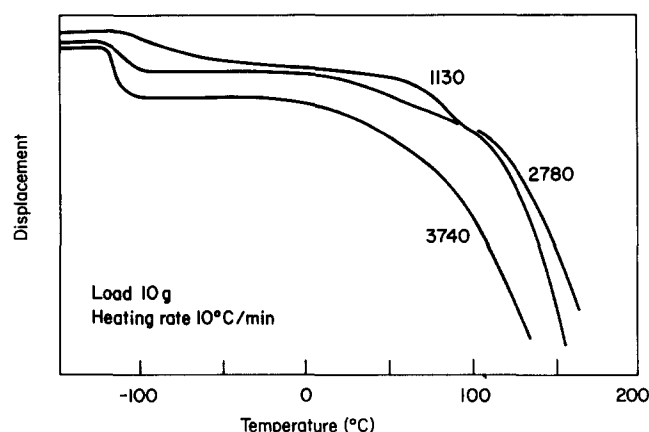
Figure 7 T.m.a. penetration curves for siloxane–urea copolymers from H-MDI containing different molecular weight of the siloxane oligomer as indicated next to the curves

TDI or H-MDI) exhibit a siloxane T_g which is dependent on the molecular weight of the siloxane oligomer used, the d.s.c. analysis on most of these segmented copolymers surprisingly show no distinct signs of siloxane crystallinity. Also, any distinct transition attributable to the hard segments was not observed. Regarding the lack of crystallinity, this is mainly because of the very small lengths of the soft siloxane chains ($\langle M_n \rangle$ 600–4000). As noted by many other workers as well[60,61], the siloxane crystallinity is either not present at low molecular weights or it is at too low a level to allow its detection. As for the T_g of the hard segment not being observed, this may not be surprising since, the hard segment content is quite small. Yet, due to the large difference in the solubility and polarity, the thermodynamic forces exist to promote microphase separation of the hard and the soft segments. Hence it is conceivable that the hard segment domains may possible inhibit the crystallization process by imposing non-equilibrium chain conformations on the soft siloxane segments.

A softening transition for hard segments was indicated by t.m.a. measurements for all of the copolymers. *Figure 7* compares the thermomechanical spectrum of the three representative copolymers obtained from H-MDI. In each representative plot, there are clearly two softening transitions in the region of $-120°$ and $+180°C$ which indicate the formation of phase separated segmented copolymers. The lower temperature penetration around $-120°C$ is clearly due to the glass transition of the siloxane segments. The extent of rubbery plateau is not strongly dependent on the type of hard segment utilized and hence the curves for MDI and TDI are not shown as they overlap those obtained for H-MDI. This behaviour can be explained by the similar polarity and hydrogen bonding capabilities of all the hard segments. All the urea linked copolymers are characterized by a large rubbery plateau and small penetration over the temperature range studied. Although they contain nearly 90% dimethyl siloxane in their structure, these copolymers retain their integrity against penetration up to 160°C, where they then begin to soften and flow. The shape of the t.m.a. penetration curve within these siloxane–urea systems is, however, dependent on the molecular weight of the PSX and, more importantly, on the amount and type of chain extender incorporated. This dependence, however, is decreased as the molecular weight of the siloxane segments is increased.

Thermogravimetric analysis on these siloxane containing copolymers gives strong evidence of their excellent thermal stability. T.g.a. curves for these materials are given in *Figure 8*. These segmented systems are very stable at temperatures around 200°C but have lost 50% of their weight near 400°C. Copolymers based on either MDI, TDI or H-MDI show nearly the same behaviour. The degradation of these copolymers above 200°C is believed to be due to the instability of the hard segment itself. We have been able to show this by introducing different linkages and hard segments and observing the changes in thermal stability. For example, siloxane–imides were found to be stable up to 400°C with only 15% weight loss observed at 500°C[59]. These imide copolymers were prepared by reacting benzophenone tetracarboxylic dianhydride (BTDA) with the PSX oligomers[62].

The dynamic mechanical behaviour for the urea linkages containing systems obtained with H-MDI also serves as an example to illustrate the two phase nature of these materials. As shown in *Figure 9*, all of the samples show a transition around $-110°C$ corresponding to the T_g of the siloxane segment. The transition in E' from glassy to the rubbery region is more gradual for the low oligomeric molecular weight PSX material as compared to the higher oligomeric molecular weight samples. These results suggest a higher degree of mixing between the two components for the low molecular weight siloxane materials. The transition temperature observed from this analysis also shows that the T_g increases with decreasing molecular weight of the PSX oligomer. The transitions observed from the Rheovibron are 8–9°C higher than those obtained from the d.s.c. because of frequency dependence. Hence, the transition at $-123°C$ for high molecular weight copolymer by d.s.c. is observed at 115°C by the dynamic mechanical technique. The results of transition temperature from the Rheovibron also show a reciprocal behaviour with the molecular weight. The 'end' restrictions due to hard segment coupling are believed principally responsible for this rise in the T_g of low molecular weight copolymers, although some of this behaviour also likely comes from the argument given earlier regarding the influence of the higher content of the n-propyl capping group for low molecular oligomers. From the dynamic mechanical results it can be seen that as the hard segment content is increased, the value of modulus corresponding to the rubbery plateau is increased. On the other hand the height of the tan δ peak
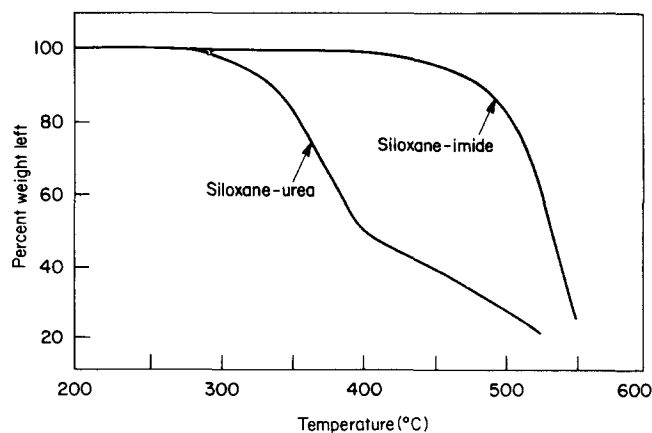

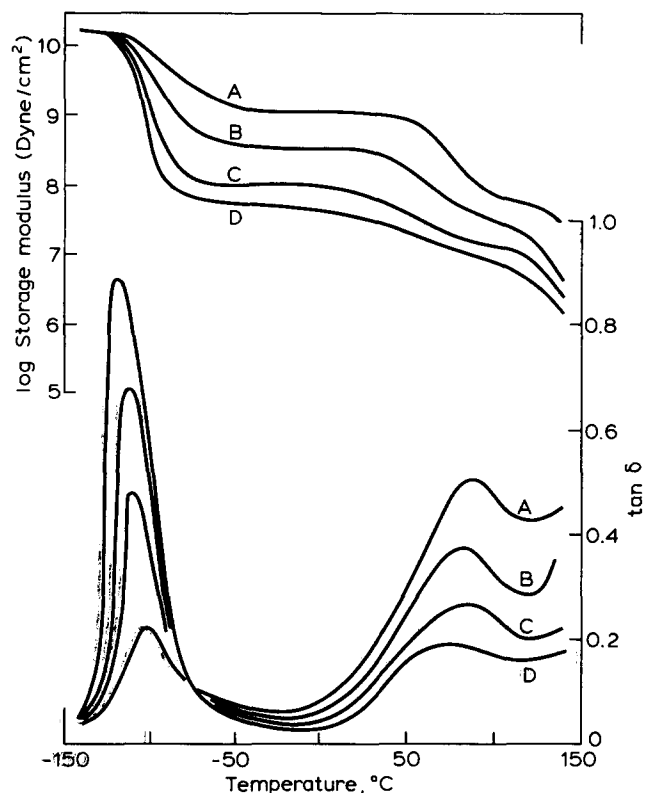**Figure 8** Comparison of thermal degradation for various siloxane copolymers by t.g.

Figure 9 Dynamic mechanical behaviour of siloxane—urea copolymers prepared from H-MDI. Curve (A): PSX-1150-HMDI-81; curve (B): PSX-1770-HMDI-87; curve (C): PSX-2770-HMDI-91; curve (D): PSX-3680-HMDI-94

appears to be quantitatively associated with the siloxane content. The second $\tan\delta$ peak, associated with the transition for the hard segments also shows the same behaviour.

The presence of the two phase nature has been strongly implied above from the results of t.m.a. and dynamical mechanical analysis. In order to more directly confirm the presence and character of the domain structure, small angle X-ray analysis was applied to these copolymers. In *Figure 10*, scattered intensity is plotted against κ, where κ is given by:

$$\kappa = \frac{4\pi}{\lambda}\sin\theta \qquad (1)$$

The curves have been moved in vertical direction, in order to clearly show the effect of hard segment content. From the smeared SAXS data in *Figure 10*, a shoulder or '*d*' spacing of 40 Å was obtained for sample PSX-900-MDI-88 and 60 Å for PSX-3660-MDI-94. In addition, the physical size of the hard segment (MDI unit) in these systems was also calculated. By taking into consideration the bond angles between various atoms, the interatomic distances and the planar nature of the aromatic rings, the end-to-end distance was found to be less than 12 Å. This value would increase to about 17 Å if the n-propyl units are included in the hard segments. Thus, the SAXS spacing obtained is too large to be directly correlated to the domain size. The fact that the spacing is increased by an increase in the molecular weight of PSX, suggests that we are dealing with the average interdomain spacing as might be expected. Based on the above results and other work to be reported, a possible simplified domain model

of these segmented siloxane block copolymers is depicted in *Figure 11*. As shown in the Figure, the molecular weight distribution can affect the conformational aspects of the soft siloxane chains. This is to be expected since the intermolecular forces between siloxane chains is small whereas, the interaction between the polar hard segments is quite large. The model shows that most likely only a few hard segments combine together through H-bonding to form the pseudo crosslinks. This is not surprising since the siloxane backbone chain has a relatively large cross-section and hence not many chains can combine without promoting high strain at the interface of junction points between hard and soft units.

Utilizing this proposed model, it may be shown that the presence of short soft segments may give rise to the yield
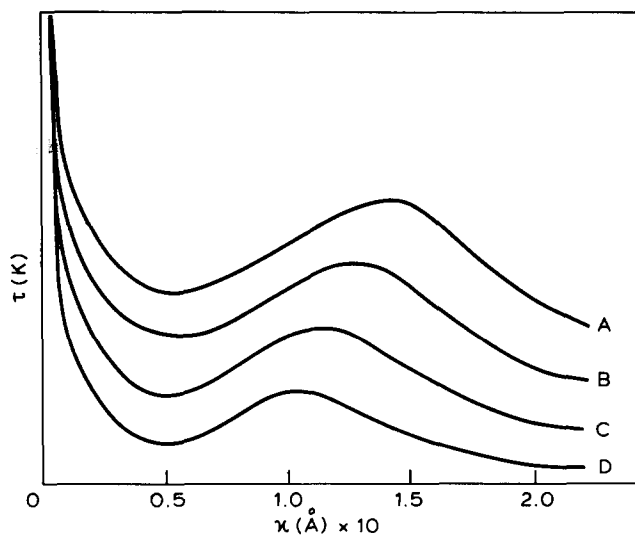

Figure 10 Small angle X-ray scattering curves for various copolymers obtained by varying the molecular weight of the oligomer. Curve (A) PSX-1150-HMDI-81, (B) PSX-1770-HMDI-88, (C) PSX-2740-HMDI-91, and (D) PSX-3740-HMDI-94
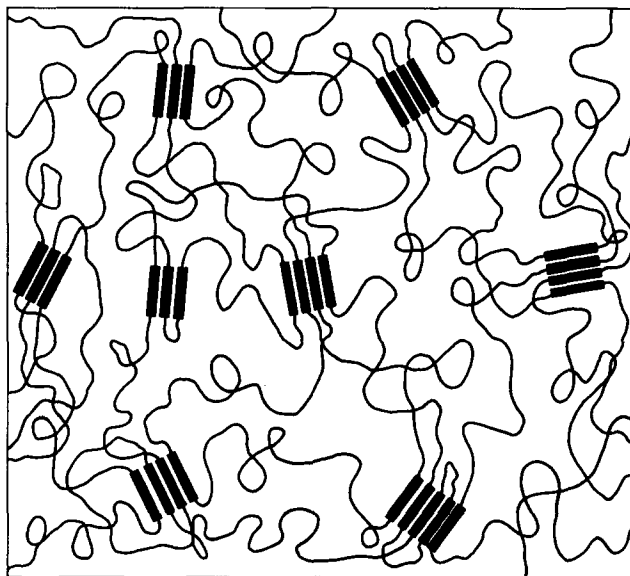

Figure 11 Simplified schematic domain model for the copolymers of low hard segment content. Notice that no attempt has been made to distinguish the end capping propyl units from the hard or the soft segments

Table 2

Sample: PSX-3660-MDI-94

% Elongation	M_c	Approx. no. of units
50	8036	2
100	12646	3
300	19960	5
500	23776	6
700	26700	6.5

behaviour as observed for low molecular weight PSX materials. This model is also supported by the calculation of M_c (molecular weight between junction points) from the theory of rubber elasticity. By using the relation:

$$\sigma_0 = \frac{\rho R T}{M_c}[\lambda - 1/\lambda^2] \qquad (2)$$

where:

ρ = density
λ = extension ratio
σ_0 = equilibrium stress
T = temperature
R = molar gas constant
M_c = average molecular weight between junction points

M_c values were determined from the equilibrium stress values for different elongations. As shown in *Table 2*, the M_c increases with increasing elongations. This is expected since upon deformation some hard segments will be pulled away from the domains to relieve the imposed strain and thus a rearrangement of hard domains would take place. The consequence of this action would be seen by a corresponding increase in the value of M_c. When this imposed strain is removed from the sample, all the hard units will not instantaneously return to their original domains. As a result of this, after the release of loading, some of the siloxane chains would be under considerable stress and will pull the hard segments towards the positions occupied by them prior to earlier deformation. This interpretation would in turn also help explain the time dependence of the permanent set behaviour discussed earlier.

To determine some indication of the potential processibility character of these segmented copolymers, their melt viscosities were measured. The results for the dynamic melt viscosities at 180°C are presented in *Figure 12* for the MDI containing siloxane urea systems. The viscosities at low shear rates lie approximately around 10^5 poise. For PSX-3660-MDI-94 the zero shear viscosity is 1.1×10^5 poise, while for PSX-1140-MDI-88 this value lies at 3.5×10^4 poise. It can be seen from this Figure that the onset of the non-Newtonian shear thinning behaviour occurs at a lower shear rate as molecular weight of the oligomer increases. In other words, the Deborah number increases when oligomeric siloxane molecular weight is increased. This should be expected when the same degree of polymerization is assumed. In that case the copolymer chains are necessarily going to be longer when higher molecular weight of the oligomer is used. These longer chains are then likely to be more entangled and would therefore increase the relaxation time and consequently

the Deborah number. The Deborah number can be defined as the ratio of the response time of the material to the experimentation or observation time.

Regarding the future work, efforts are being made to systematically study the effect of changing the urea linkage of the hard segments to either that of amide or imide linkages. This would result in a different H-bonding capabilities of the hard segments due to their extreme differences in the cohesive energy densities. As a consequence of this, the thermal and mechanical response of the siloxane–urea copolymers would be vastly different from that of siloxane–amide or siloxane–imide copolymers. As indicated within this paper, some preliminary data obtained on these newer systems has been obtained and the results are in line with the anticipated behaviour. Also, additional work is being done to study the solid state properties of these copolymers which have been chain extended. Finally, some initial studies have already been completed where the backbone of the siloxane oligomer has been modified to include some fraction of either diphenyl of tri-flouro propyl methyl units. These studies will be also continued and reported at a later time.

CONCLUSIONS

Segmented poly(dimethylsiloxane)–urea linked copolymers, synthesized by solution polymerization can display good thermoplastic elastomeric behaviour. The urea linkages were obtained by reacting either MDI, TDI or H-MDI and PSX oligomers with amine end groups. By varying the hard segment type and/or content, a wide range of mechanical and thermal properties were obtained. It was found that the modulus and ultimate tensile strength decreased when the molecular weight of poly-(dimethylsiloxane) (PSX) oligomer was increased. This was expected and may be explained by the fact that any increase in PSX molecular weight decreases the hard segment content. The data presented demonstrates that the properties depend on the molecular weight of the PSX segment and that high strength necessitates a dispersed phase or microphase texture. For the same molecular weight of the PSX oligomer, the siloxane–urea copolymers obtained from MDI, TDI and H-MDI showed
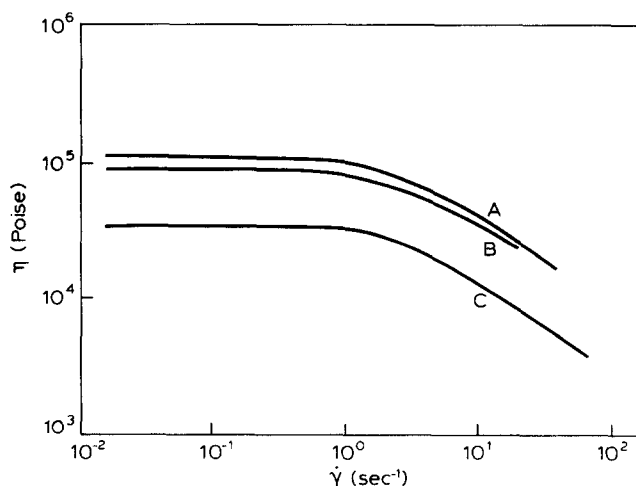

Figure 12 Viscosity as a function of shear rate for siloxane–urea segmented copolymers from MDI as a function of molecular weight at 180°C. Curve (A) PSX-3660-MDI-94, (B) PSX-1770-MDI-88, and (C) PSX-1140-MDI-82

similar mechanical responses. This implies that the number density of the hard segments may be a more critical parameter for the control of mechanical behaviour as compared to volume or weight fractions. The stress-at-break does increase rapidly with the concentration of hard segments. This increase can be attributed primarily to the presence of a second rigid microphase (broadening of the relaxation spectrum), which gives an increased capability for energy dissipation. However, the ultimate elongation decreases with increasing hard segment content since the siloxane segments become smaller.

The segmented siloxane–urea copolymers show interesting recovery behaviour. Even with a very small amount of hard segment content, these copolymers display hysteresis behaviour which is comparable to other segmented copolymer systems of higher hard segment content.

The two phase domain formation was supported by thermal, dynamic mechanical, as well as the SAXS studies. From these investigations it was evident that these hard segment domains act as physical crosslinks in the rubbery phase and prevent it from flowing. The hard segment domains also seem to be serving as a reinforcing filler as is typical of other microphase separated segmented copolymers. The thermomechanical spectrum showed that the nature and extent of rubbery plateau was affected by varying the molecular weight involved on the soft segments. At high temperatures these siloxane containing copolymers showed sufficient thermoxidative stability to be easily moulded at temperatures up to 200°C.

ACKNOWLEDGEMENTS

REFERENCES

1 Warrick, E. L., Pierce, O. R., Polmanteer, K. E. and Saam, J. C. *Rubber Chem. Technol.* 1979, **52**, 437
2 Polmanteer, K. E. *Rubber Chem. Technol.* 1981, **54**, 1051
3 Lewis, F. M. *Rubber Chem. Technol.* 1962, **35**, 1222
4 Hunter, M. J. *Kautsch. Gummi* 1964, **17**, 498
5 Lewis, F. M. in 'High Polymers, Volume XXIII, Part 2', (Eds. J. P. Kennedy and E. G. M. Tornquist), Interscience, 1969, p. 767
6 Bobear, W. J. in 'Rubber Technology', (Ed. M. Morton), Van Nostrand Reinhold, 1973, p. 368
7 Polmanteer, K. E. *J. Elastoplastics* 1970, **2**, 165
8 Eaborn, C. in 'Organosilicon Compounds', Butterworth Scientific Publication, London, 1960
9 Johnson, D. H., McLoughlin, J. R. and Tobolsky, A. V. *J. Phys. Chem.* 1954, **58**, 1073
10 Thomas, D. K. *Polymer* 1966, **7**, 99
11 Osthoff, R. C., Bueche, A. M. and Grubb, W. T. *J. Am. Chem. Soc.* 1954, **76**, 4659
12 Lee, T. C. P., Sperling, L. H. and Tobolsky, A. V. *J. Appl. Polym. Sci.* 1966, **10**, 1831
13 Schroeder, H., Schaffling, O. G., Larchar, T. B., Frulla, F. F. and Heying, T. L. *Rubber Chem. Technol.* 1966, **39**, 1184
14 Nikitina, T. S., Khodzhemirova, L. K., Alexsandrova, Yu. A. and Pravednikov, A. N. *J. Polymer Sci. U.S.S.R.* 1969, **11**, 3228
15 Shaw, M. T. and Tobolsky, A. V. *Polym. Eng. Sci.* 1070, **10**, 225
16 Konkle, G. M., Selfridge, R. and Servais, P. C. *Ind. Eng. Chem.* 1947, **39**, 1410
17 Ohlberg, S. M., Alexander, L. E. and Warrick, E. L. *J. Polym. Sci.* 1958, **27**, 1
18 Polmanteer, K. E. and Hunter, M. J. *J. Appl. Polym. Sci.* 1959, **1**, 3
19 Hagerman, E. M. *J. Appl. Polym. Sci.* 1969, **13**, 1873
20 Matsuo, M., Ueda, A. and Kondo, Y. *Polym. Eng. Sci.* 1970, **10**, 253
21 Mark, J. E. and Andredy, A. L. *Rubber Chem. Technol.* 1981, **54**, 809
22 Erman, B. and Flory, P. J. *Rubber Chem. Technol.* 1979, **52**, 127
23 Koksharov, A. M. *Kauch. Rezina* 1971, **30**, 18
24 Noll, W. in 'Chemistry and Technology of Silicones', Academic Press, New York, 1968
25 Braley, S. *Plast. Reconstr. Surg.* 1973, **51**, 3
26 Lynch, W. in 'Handbook of Silicone Rubber Fabrication', Van Nostrand-Reinhold, New York, 1978
27 Eirich, F. R. Mechanical Behaviour of Materials, Proc. 1st Intrnal. Conf. 1975, **3**, 405
28 Warrick, E. L., Piccoli, W. A. and Stark, F. O. *J. Am. Chem.* 1955, **77**, 5017
29 Smith, T. L. *Rubber Chem. Technol.* 1978, **51**, 225
30 Voet, A., Marwski, J. C. and Donnet, J. B. *Rubber Chem. Technol.* 1977, **50**, 342
31 Baker, D., Charlesby, A. and Morris, J. *Polymer* 1968, **9**, 437
32 Berrod, G., Vidal, A., Papirer, E. and Donnet, J. B. *J. Appl. Polym. Sci.* 1979, **23**, 2579
33 Chahal, R. S. and Saint Pierre, L. E. *Macromolecules* 1968, 1(2), 152
34 Cekada, J. (to Dow Corning Corp.), US Patent 3,355,406 (28 November 1967)
35 Pocknell, D., Thomas, D. R. and Kendrick, T. C. 4th Intrnal. Syn. Rubber Symp., Lect. 1, 1969, 5
36 Maxson, M. T. and Lee, C. L. *Rubber Chem. Technol.* 1982, **55**, 233
37 Charlesby, A., Morris, J. and Montague, P. *J. Polym. Sci.* 1969, **C16**, 4505
38 Boonstra, B. B., Cochrane, H. and Dannenberg, E. M. *Rubber Chem. Technol.* 1975, **48**, 558
39 Ashmead, B. V. and Owen, M. J. *J. Polym. Sci.* 1971, **A2**(9), 331
40 Noshay, A. and McGrath, J. E. in 'Block Copolymers: Overview and Critical Survey', Academic Press, New York, 1977
41 Allport, D. C. and Janes, W. H. (Editors), 'Block Copolymers', Halstead Press, New York, 1972
42 Gibson, P. E., Vallence, M. A. and Cooper, S. L. in 'Developments in Block Copolymers—I', (Ed. I. Goodman), Applied Science Publishing Ltd., Essex, UK, 1982
43 Trelor, L. R. G. *Rubber Chem. Technol.* 1974, **47**, 625
44 Matzner, M., Noshay, A. and McGrath, J. E. *Tran. Soc. Rheo.* 1977, **21**, 273
45 Matzner, M., McGrath, J. E. *et al. Appl. Polym. Symp.* 1973, **22**, 143
46 Saam, J. C. and Fearon, F. W. G. *Ind. Eng. Chem. Prod. Res. Dev.* 1971, **10**, 10
47 Morton, M., Kesten, Y. and Fetters, L. J. *Polym. Prepr.* 1974, **15**(2), 175; ACS Symp. Series, (Ed. N. Platzer), 1975
48 Noshay, A., Matzner, M. and Merriam, C. N. *J. Polym. Sci.* 1971, **A1**(9), 3147
49 Vaughn, H. A. *J. Polym. Sci.* 1969, **B7**, 569
50 Andrady, A. L., Llorente, M. A., Sharaf, M. A., Rahalkar, R. R., Mark, J. E., Sullivan, J. L. and Yu, C. U. *J. Appl. Polym. Sci.* 1981, **26**, 1829
51 Yilgor, I., Eberle, J., Johnson, B. C., Yilgor, E., Stecle, W. P., Jr., Tyagi, D., Wilkes, G. L., McGrath, J. E. *Polym. Prepr.* 1983, **24**(1), 170
52 Yilgor, I., Riffle, J. S., Wilkes, G. L. and McGrath, J. E. *Polym. Bull.* 1982, **8**, 535
53 Tang, S. H., Meinecke, E. A., Riffle, J. S., McGrath, J. E. *Rubber Chem. Technol.* 1980, **50**, 1160 ACS Rubber Div. Meeting, Toronto, May 10, 1983
54 Yilgor, I. *et al. Polymer* 1984, **25**, 1800
55 Tyagi, D., Wilkes, G. L., Yilgor, I., McGrath, J. E. *Polym. Bull.* 1983, **8**, 543
56 Polmanteer, K. E. and Lentz, C. W. *Rubber Chem. Technol.* 1975, **48**, 795
57 Levin, V. Y., Andrinov, K. A., Slonimskii, G. L., Zhdanov, A. A., Lyubavskaya, Y. A. and Malykhin, A. P. *J. Polym. Sci. U.S.S.R.* 1974, **A16**, 2257
58 Abouzahr, S. Ph.D. Dissertation, VPI & SU, 1981
59 Tyagi, D., Yilgor, I., Yilgor, E., Wilkes, G. L. and McGrath, J. E., paper presented at Thermal Analysis Meeting at Wiiliamsburg, VA, Sept. 1983
60 Andrady, A. L., Llorente, M. A. and Mark, J. E. *Polym. Prepr.* 1980, **21**(1), 159
61 Allan, J. F. C., Shaver, A. and Eisenberg, A. *Polym. Prepr.* 1980, **21**(1), 74