Structural Modifications in Hydroxy Ether–Dimethyldiphenylsiloxane Copolymers

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ABSTRACT: Segmented hydroxy ether–siloxane copolymers that are chemically cross-linked and have microphase-separated morphologies were prepared. In this series of copolymers, the dimethylsiloxane or soft block was modified by the incorporation of various compositions of diphenylsiloxane. The incorporation of the more polar diphenylsiloxane decreased the solubility parameter difference between the siloxane and hydroxy ether segment, allowing bulk copolymerization. Bulk copolymerizations were realized with soft segments containing 50 wt % or more diphenylsiloxane. Calorimetric, dynamic mechanical, and small-angle X-ray scattering measurements showed that microphase-separated morphologies were achieved at diphenylsiloxane compositions of 50 wt % and less in the siloxane soft segment or block. The mechanical behavior of these copolymers was influenced by the compositional and subsequent morphological changes.

Introduction

The incorporation of a filler is the most common way to reinforce or toughen many elastomers. The influence of a filler on the mechanical properties depends on the volume fraction and dispersion of filler, hydrodynamic effects or the increase in "internal" friction,[1] and the nature of the stress concentration at the interface between the particle and matrix.[2] The increase in "internal" viscosity serves to distribute the stresses more evenly, relieving stress concentrations. The triaxial stress field produced by the moduli mismatch between the filler and matrix in a stressed specimen may induce cavitation, which often has a stabilizing effect by relieving stress in local areas. Gent and Tompkins[3] have shown that small voids are considerably more stable than large cavities due to surface energy effects. Finally, the dispersed phase may also blunt or deflect the growing crack.

The microphase-separated morphology of block copolymers can, also, improve the strength of elastomeric materials. Thermoplastic elastomers are block copolymers generally comprised of two incompatible segments or blocks: one hard and one soft component with T_g's above and below the use temperature, respectively. The hard blocks associate into microdomains (~50–500 Å) and serve as reinforcing sites (fillers) or pseudo-cross-linking junctions. Factors that influence the morphology and, consequently, the mechanical properties include the volume fraction of hard segment, hydrogen bonding,[4] molecular weight,[5,6] molecular weight distribution of the blocks,[7] casting solvent,[8] and thermal history.[9]

Recently, we have published the synthesis, morphology, and properties of both segmented and block copoly(hydroxy ether–siloxane) networks.[10-12] These networks were synthesized by the reaction of diglycidyl ether of Bisphenol A (DGEBA) or epoxy-terminated hydroxy ether oligomers with α,ω-bis(aminopropyl)-terminated dimethylsiloxane oligomers. In this monomer–oligomer or oligomer–oligomer synthetic approach, a hydroxy ether linkage was formed between the siloxane blocks. Initially, DGEBA was employed as both a chain extender and a cross-linking agent. The large solubility parameter difference between the siloxane and hydroxy ether components (7.3 and 9.5) together with the strong intermolecular interactions within the hard segment produced a microphase-separated morphology. The mechanical properties of these networks varied depending on the molecular weight of the oligomers used and which phase was continuous. The moduli ranged from 1 to 650 MPa, and the ultimate elongations ranged from 40 to 200%.

In the synthesis of epoxy networks, it is desirable to have a two-component system that is miscible at ambient temperatures and may then be cured for an appropriate time and temperature to allow network formation. In this article, a modification of the siloxane oligomers that decreases the solubility parameter difference between the two components will be discussed. The synthetic approach utilized was the coequilibrium of cyclic diphenylsiloxane tetramer and cyclic dimethylsiloxane tetramer with α,ω-bis(aminopropyl)tetramethyldisiloxane, which produced random copolymers. The solubility parameter of the diphenylsiloxane has been estimated to be around 9.5, which is similar to that of the hydroxy ether hard block used in this study.

Experimental Section

Octamethylcyclotetrasiloxane (D_4), octaphenylcyclotetrasiloxane (D''_4), and 1,3-bis(aminopropyl)tetramethyldisiloxane (end blocker) were purchased from Petrarch. The tetramethylammonium hydroxide pentahydrate purchased from Aldrich was used without further purification. The DGEBA was supplied by Dow Chemical Co. The number-average molecular weight was 340 g/mol as determined by a potentiometric titration[11] of the epoxide end groups using 0.1 N HBr in glacial acetic acid and a melting point of 40 °C.

The α,ω-bis(aminopropyl)dimethyldiphenylsiloxane oligomers of various molecular weights were synthesized by base (tetramethylammonium hydroxide pentahydrate) catalyzed-bulk anionic equilibrium reaction of D_4 and D''_4 with 1,3-bis(aminopropyl)-tetramethyl disiloxane end blocker. The D''_4 is a crystalline solid and is not soluble in the mixture of D_4 and end-blocking agent. However, the D''_4 is soluble in oligomers of dimethylsiloxane. Therefore, these coequilibrations had to be performed sequentially. First, the D_4, end-blocking agent, and catalyst were charged and heated to 80 °C, yielding oligomers of dimethylsiloxane after about 2 h. The cyclic tetramer of diphenylsiloxane was then charged and allowed to coequilibrate. The oligomers containing the higher siloxane content had to be heated to 150 °C to form a homogeneous reaction mixture and then cooled to 80 °C. The reaction temperature was maintained at 80 °C for 48 h and then increased to 150 °C for 5 h to decompose the catalyst. The oligomers were heated (150 °C) under (0.05–0.10 mmHg) vacuum to remove the equilibrium cyclics.

The aminopropyl-terminated dimethylsiloxane oligomers and the dimethyldiphenylsiloxane oligomers containing the lower weight percents of diphenylsiloxane compositions were allowed to react with DGEBA at 50 °C for 36 h in chloroform (35 wt % solids) as previously described.[10-12] The solutions were cast into films on cellophane and the solvent or solvent mixture was allowed to evaporate slowly (24 h). The solid films were then cured at 100 °C (1 h) and post cured at 120 °C (1 h). The oligomers with the higher diphenylsiloxane compositions were mixed with DGEBA at 80 °C and poured into a hot mold and cured as described above.

The number-average molecular weights of the aminopropyl-terminated siloxane oligomers were determined by titration using a Fisher computer aided titrimeter. The siloxane oligomers were

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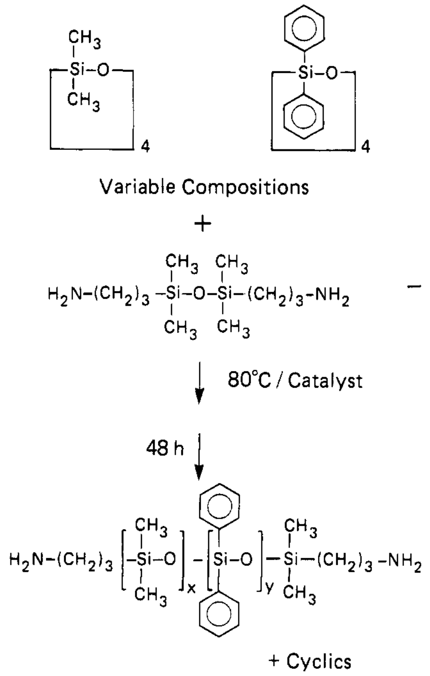
Scheme I



dissolved in isopropyl alcohol and titrated with 0.1 N HCl. The DGEBA was dissolved in a 2:1 mixture of chlorobenzene and acetic acid and titrated with 0.01 N HBr in acetic acid.

Calorimetric measurements were performed on a Du Pont DSC 910 at a 10 °C/min heating rate. Stress–strain measurements were made on an Instron tensile testing machine at a strain rate of 10 mm/min (22 °C). The dynamic mechanical measurements were performed by using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) at 10 Hz and a heating rate of 3 °C/min.

Small-angle X-ray scattering measurements were obtained with a Kratky slit collimated camera using Ni-filtered Cu Kα radiation. A standard focus, sealed X-ray tube operated at 40 kV and 20 mA served as the source. Scattered radiation, collected with a TEC-205 detector, was discriminated electronically prior to storage on a Tracor Northern 1705 multichannel analyzer. The scattering profiles were corrected for electronic noise, parasitic scattering, and detector homogeneity in the standard manner. All data were desmeared using the method of Vonk.[13]

Chemorheology tests were performed by stretching the samples in an environmental chamber attached to the Instron. The chamber was preheated to 100 °C, and a small strain of 5% was applied to the sample and then held constant throughout the test. The load was recorded as a function of time, producing data of the continuous stress relaxation. In another set of experiments, a series of short strain (5%) pulses were applied to the specimen (100 °C). The load readings for this series of pulses provided the data of the intermittent stress relaxation.[14]

Results and Discussion

Bis(aminopropyl)-terminated dimethylsiloxane and dimethyldiphenylsiloxane oligomers were synthesized by a base-catalyzed anionic equilibration reaction.[15] α,ω-Bis(aminopropyl)tetramethyldisiloxane (end-blocking agent) was reacted at 80 °C with either the cyclic tetramer of dimethylsiloxane (D_4) or a mixture of the cyclic tetramer of dimethylsiloxane and diphenylsiloxane (D''_4) using tetramethylammonium hydroxide pentahydrate as the catalyst[15,16] (Scheme I). The dimethylsiloxane oligomers generally required less than 24 h to complete the equilibration. However, the oligomers based on the more reactive cyclic tetramer of diphenylsiloxane required longer reaction times (48 h) so as to avoid blocky structures.[17] The equilibrations were performed in bulk to minimize the equilibrium cyclics generated upon completion of the reaction.[17] The crystalline cyclic tetramer of diphenylsiloxane was only partially soluble in the cyclic tetramer of dimethylsiloxane; however, the D''_4 was soluble in oligomers of dimethylsiloxane at elevated temperatures. Therefore, the dimethyldiphenylsiloxane equilibrations were performed sequentially, where the end-blocking agent, catalyst, and D_4 were initially charged and allowed to react, generating oligomers followed by the addition of D''_4. Upon completion of the equilibration, the oligomers were heated to 150 °C for 4–5 h to decompose the transient tetramethylammonium siloxanolate catalyst.[15,17] Finally, the cyclics remaining from the equilibration, usually 10–15 wt %, were removed by vacuum distillation at 150 °C.

Table I
Characteristics of
α,ω-Bis(aminopropyl)dimethyldiphenylsiloxane Oligomers
Containing Various Diphenylsiloxane Compositions

sample	diphenylsiloxane, wt%	$\langle M_n \rangle$, g/mol[a]	T_g, °C[b]
1	0	5400	-121, -42[c]
2	25	4800	-109
3	50	5400	-71
4	75	5700	-26

[a] Titration with standard HCl. [b] DSC 10 °C/min heating rate. [c] Melting point.

Table II
Characteristics of a
α,ω-Bis(aminopropyl)dimethyldiphenylsiloxane Oligomers
Containing 50 wt % Diphenylsiloxane

sample	diphenylsiloxane, wt %	$\langle M_n \rangle$, (g/mol)[a]	T_g, °C[b]
1	50	1950	-76
2	50	2300	-75
3	50	2800	-75
4	50	3700	-69
5	50	5400	-70
6	50	6600	-65
7	50	12500	-62

[a] Titration with standard HCl. [b] DSC, 10 °C/min heating rate.

The molecular weights of the bis(aminopropyl)-terminated dimethylsiloxane and dimethyldiphenylsiloxane oligomers were controlled by the ratio of the end blocker to the cyclic tetramer(s). Table I contains characteristics of the oligomers synthesized with diphenylsiloxane compositions ranging from 0 to 75 wt %. The molecular weights, determined by potentiometric titrations of the aminopropyl end group with 0.1 N HCl,[15,18] were maintained in the 5000 g/mol range to facilitate comparison. The glass transition temperatures ranged from −123 °C for the poly(dimethylsiloxane) to −26 °C for the poly(dimethyldiphenylsiloxane) containing 75 wt % diphenylsiloxane.

A second series of oligomers were prepared where the diphenylsiloxane composition was held at 50 wt % and the number-average molecular weights were varied. Table II contains the number-average molecular weights of the aminopropyl-terminated oligomers along with their thermal characteristics. The T_g's range from −62 to −76 °C and decrease with decreasing oligomer molecular weight. It is interesting to note that the aminopropyl end groups lowered the T_g in these dimethyldiphenylsiloxane oligomers.

The bis(aminopropyl)-terminated dimethyldiphenylsiloxane oligomers of various molecular weights and diphenylsiloxane compositions were reacted with the diglycidyl ether of Bisphenol A (DGEBA) as shown in Scheme II. The tetrafunctional siloxane oligomers, together with the difunctional DGEBA, produce a network structure. Since each of the components contain mutually reactive end groups, perfectly alternating sequence dis-

Scheme II

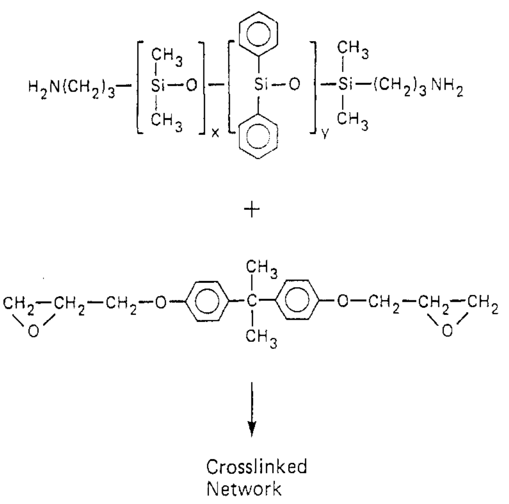


Table III
Characteristics of Hydroxy Ether–Siloxane Networks Containing Various Diphenylsiloxane Compositions

diphenylsiloxane, wt %	$\langle M_n \rangle$, g/mol[a]	thermal anal. of networks[b]	
		T_g, °C[c]	T_g, °C[d]
0	5400	-120	10
25	4800	-102	20
50	5400	-55	17
75	5700	-5	

[a] Of siloxane oligomer. [b] DSC, 10 °C/min heating rate. [c] Soft segment. [d] Hard segment.

tributions are obtained. Ring opening of the epoxide by the amine forms a hydroxy ether linkage between the siloxane blocks. We have previously described[10,11] the copolymerization and network formation of bis(aminopropyl)-terminated dimethylsiloxane oligomers with DGEBA. The large difference in solubility parameters between the two components prevented network formation by a bulk or neat copolymerization. Chloroform was required to facilitate both the mixing and the initial polymerization. A similar synthetic approach was used for the siloxane oligomers containing the lower diphenylsiloxane compositions. The bis(aminopropyl)-terminated siloxane oligomers containing 25 wt % diphenylsiloxane and a stoichiometric amount of DGEBA were reacted in chloroform at reflux temperatures (~35 wt % solids). Films were then cast and cured for 1 h at 100 °C and then for 1 h at 120 °C, as previously described.[10,11]

In contrast, the bis(aminopropyl)-terminated siloxane oligomers containing 50 wt % and various diphenylsiloxane compositions may be copolymerized with DGEBA in the bulk. The addition of the more dipolar diphenylsiloxane decreases the solubility parameter difference between the two components, affording a homogeneous mixture at approximately 80 °C. The DGEBA and siloxane oligomers were mixed at temperatures between 80 and 100 °C and poured into a hot mold (100 °C) and cured for 1 h at 100 °C and an additional 1 h at 120 °C.

Table III contains the characteristics of the networks synthesized by this monomer–oligomer approach with varying diphenylsiloxane compositions. The number-average molecular weights of the siloxane or soft segment blocks were approximately 5000 g/mol and the diphenylsiloxane content was varied from 0 to 75 wt %. Two glass transition temperatures were observed for those networks containing up to 75 wt % diphenylsiloxane in the siloxane block, indicating a microphase-separated morphology. The T_g of the network containing the poly(dimethylsiloxane) soft block has a T_g nearly identical with that of the oligomer used. In contrast, the networks containing the various diphenylsiloxane compositions (25–50 wt %) have soft segment transitions somewhat higher than that of the oligomer used in the synthesis. The incorporation of the more polar diphenylsiloxane decreases the solubility parameter difference between the siloxane and hydroxy ether components and provides at least partial mixing in the siloxane phase. Finally, the siloxane oligomer containing the 75 wt % diphenylsiloxane shows a single T_g between that of the two components (-10 °C), indicative of a single-phase morphology.

Table IV
Characteristics of Hydroxy Ether–Siloxane Networks Containing 50 wt % Diphenylsiloxane

diphenylsiloxane, wt %	$\langle M_n \rangle$, g/mol[a]	thermal anal. of networks[b]	
		T_g, °C[c]	T_g, °C[d]
50	1950	-42	2
50	2300	-50	8
50	2800	-50	5
50	3700	-58	-2
50	5400	-58	5
50	6600	-60	e
50	12500	-61	e

[a] Of siloxane oligomer. [b] DSC, 10 °C/min heating rate. [c] Soft segment. [d] Hard segment. [e] Too weak to detect.

A second series of poly(hydroxy ether–dimethyldiphenylsiloxane) networks were prepared where the diphenylsiloxane composition was maintained at 50 wt % and the molecular weight of the siloxane oligomer was varied from 1950 to 12 500 g/mol. These networks were interesting in that bulk copolymerizations were possible while retaining the microphase-separated morphology. Table IV contains the number-average molecular weights of the oligomers used in the copolymerization and the thermal analysis of the networks synthesized. Those networks containing the lower molecular weight siloxane oligomers show two T_g's, indicative of a microphase-separated morphology. The T_g of the soft segment in the networks is significantly higher (~10–~30 °C) than that of the siloxane oligomers. The extent of phase separation or more precisely the phase purity is somewhat limited in these networks, containing the lower molecular weight siloxane oligomers. In contrast, the copolymers containing the 6600 and 12 500 g/mol poly(dimethyldiphenylsiloxane) oligomers show a soft segment T_g similar to those of the siloxane oligomers used in the network formation. These networks show only a soft segment T_g. The hard segment content in these cases is very small and may not be detectable calorimetrically.

These results are consistent with those reported earlier on poly(hydroxy ether–siloxane) networks with poly(dimethylsiloxane) as the soft segment. In these networks, the hard segment was believed to be composed of the DGEBA monomer unit and the aminopropyl end groups of the siloxane oligomer[10–12] as reported for similar siloxane-containing copolymers.[19–22] The hydroxy ether linkage produced by the ring opening of the epoxide moiety is polar and capable of hydrogen bonding, which enables interactions within the hard segment. The solubility parameter difference between the hydroxy ether and siloxane segments, the strong intermolecular interactions within the hard segment, and the molecular weight of the siloxane blocks contribute to the development of a separated morphology.

The dynamic mechanical results, consistent with the DSC results, are shown in Figure 1, for each of the networks containing the various diphenylsiloxane composi-

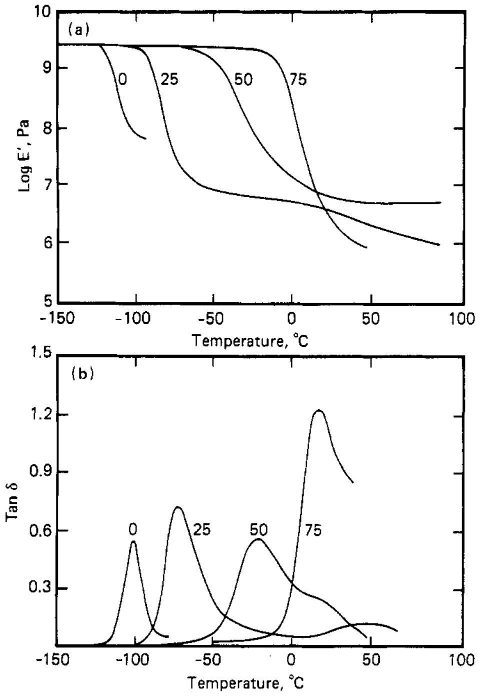


Figure 1. (a) Storage tensile modulus versus temperature. (b) tan δ versus temperature for the networks containing the various diphenylsiloxane compositions in the soft segment.

tions. The modulus and tan δ for the networks are shown as a function of temperature. The two-phase morphology for the networks containing up to 75 wt % diphenylsiloxane observed by the DSC thermogram is confirmed. The T_g of the soft segment in those networks containing the lower compositions of diphenylsiloxanes is somewhat higher than that of the initial oligomers, indicating at least a partial phase mixing. The network containing 75 wt % diphenylsiloxane in the soft block shows a single transition, indicative of a single-phase morphology.

The dynamic mechanical behavior for the networks that contain 50 wt % diphenylsiloxane and various molecular weight siloxane block lengths are shown in Figure 2. Both the modulus and tan δ for the networks are plotted as a function of temperature. In each case, two transitions were observed, indicating a microphase-separated morphology. The soft segment T_g decreases with increasing block length and, in the case of the network containing the 6600 g/mol block length, the T_g occurs at the same temperature as the initial oligomer. In contrast, the T_g of the network containing the 1950 g/mol siloxane block is significantly higher (~30 °C) than that of the siloxane oligomer. This indicates a significant amount of phase mixing in the siloxane phase in those networks containing the lower block lengths as previously indicated with the DSC.

The hard segment T_g becomes more pronounced with lower siloxane block lengths due to the increase in the molar ratio of each of the respective components. Since the hard segment is composed of the DGEBA monomer unit and the aminopropyl end groups of the siloxane oligomer, an increase in the molar ratio of the components will produce networks with a higher hard segment compositions. However, the tan δ is more diffuse at these block lengths indicative of phase mixing. The hard segment T_g for the networks containing the higher siloxane block lengths are much less pronounced but are shifted to higher temperatures, reflecting a morphology with greater demixing.

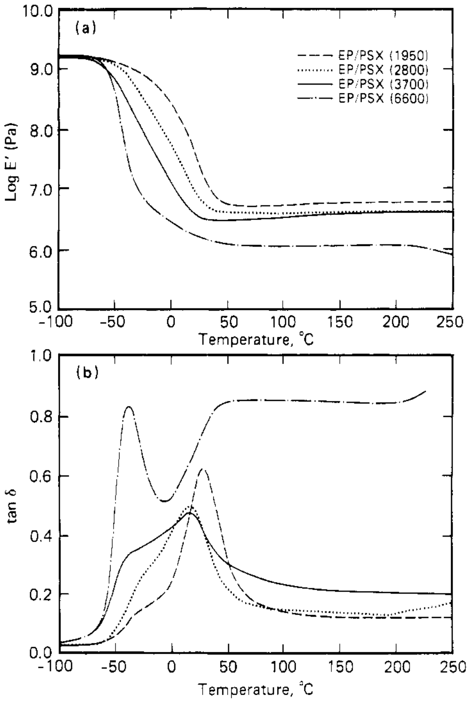


Figure 2. (a) Storage tensile modulus versus temperature. (b) tan δ versus temperature for the networks containing 50 wt % diphenylsiloxane with varying siloxane molecular weights.

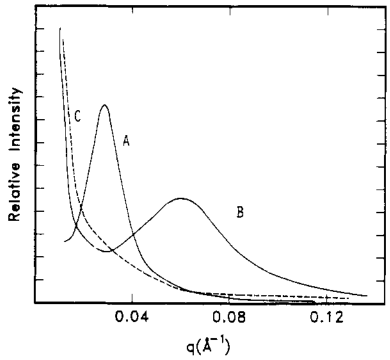


Figure 3. Small-angle X-ray scattering profiles for the hydroxy ether–siloxane copolymers containing varying amounts of diphenylsiloxane: 0% (A), 25% (B), and 50% (C).

The modulus at temperatures just above the hydroxy ether transition for the poly(hydroxy ether–dimethyldiphenylsiloxane) networks containing 50 wt % compositions varies directly with hard segment content. Furthermore, the modulus increases with temperature for each of the networks as would be predicted from rubber elasticity theory.[23] However, at temperatures above 210–220 °C, the modulus begins to decrease owing to degradation.

Small-angle X-ray scattering profiles for these copolymers are shown in Figure 3, where the diphenylsiloxane composition varies from 0 to 50% as a function of the scattering vector $q = (4\pi/\lambda) \sin (\epsilon/2)$. The addition of the diphenylsiloxane results in dramatic changes in the morphology. For the pure dimethylsiloxane-containing copolymer a well-defined maximum in the scattering profile is seen at q = 0.029 Å^{-1}, corresponding to a long period of ca. 220 Å. Increasing the diphenylsiloxane content to 25 wt % results in a shift of the maximum to q = 0.060 Å, corresponding to an average long period of ca. 104 Å, a substantial broadening of the reflection and a reduction in the scattering intensity. At a diphenylsiloxane weight content of 50% there is no evidence of a maximum and only a monotonically, decreasing scattering profile was observed. Similar results were also found for the higher diphenylsiloxane content copolymers.

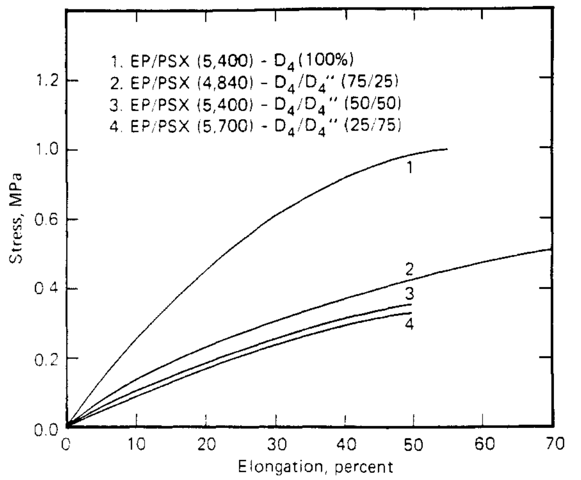


Figure 4. Stress versus percent elongation for the hydroxy ether–siloxane copolymers with the various diphenylsiloxane compositions in the soft segment.

The reduction in the long period can be explained partly by the number of segments in the siloxane block. For the pure dimethylsiloxane copolymer the degree of polymerization, DP, of the siloxane block is ca. 73 whereas for the 50 wt % diphenylsiloxane copolymer the DP is ca. 55. This results from the increase in the molecular weight of the diphenylsiloxane due to the two phenyl rings. Similar reductions are found for the 75% diphenylsiloxane content copolymer. If the extent of phase separation is unchanged, however, this reduced DP would account for only a 13% reduction in the long period as opposed to the nearly 54% reduction observed.

It is evident that the incorporation of diphenylsiloxane has produced a fundamental change in the morphology. The pronounced reduction in the scattering intensity shows that the electron density difference between the siloxane and epoxy domains has decreased. This can only be attributed to a partial mixing of the phases. Since the distribution of diphenylsiloxane in the soft block is random, it is difficult to assess the extent to which the epoxy chains are mixed into the siloxane phase and vice versa. However, it is clear that the addition of the diphenylsiloxane has reduced the unfavorable interactions between the hard and soft segments and has led to some intermixing of the components. By comparison of the results in Table III, it is apparent that the amount of siloxane in the hydroxy ether phase is much smaller than the amount of hydroxy ether moieties in the siloxane phase.

The partial mixing of the components is also reflected in the broadening of the SAXS reflection. For the pure dimethylsiloxane copolymer the microphase separation is such that the size and size distributions of the epoxy and siloxane phases are well defined. With the random addition of the diphenylsiloxane and size and size distribution of the phases is less well defined due to the penetration of the epoxy moieties into the siloxane phase. In view of the DSC results, this intermixing must be such that a core of the hard segment epoxy phase remained unchanged. This, coupled with the reduced DP of the siloxane phase may be giving rise to the reduced long period.

The networks behave as thermoplastic elastomers with mechanical properties varying with the relative composition of both diphenylsiloxane and the hard segment content of the copolymers. Stress versus percent elongation for the poly(hydroxy ether–siloxane) networks synthesized by the monomer–oligomer route with various diphenylsiloxane compositions is shown in Figure 4. The ultimate elongations vary from 50 to 70% and moduli vary from 1.2 to 2.5 MPa, depending on the diphenylsiloxane composition. These data are also included in Table V. The difference in mechanical properties is believed to result from the phase mixing associated with the polar diphenylsiloxane. In principle, the incorporation of diphenylsiloxane having a higher T_g should reduce both chain mobility and crack propagation. However, phase purity appears to have a more pronounced effect on the internal viscosity and mechanical properties than the increase in internal viscosity.

The stress versus elongation plots for segmented poly(hydroxy ether–siloxane) networks containing 50% diphenylsiloxane compositions are shown in Figure 5. These data are also summarized in Table VI. The moduli range from 0.58 to 3.5 MPa with elongations ranging from 25 to 72%. The tensile strength and moduli appear to be strongly dependent on the volume fractions and T_g's of the hard segments in the networks irrespective of the phase purity. The networks containing the shorter siloxane block lengths show only marginal improvements in mechanical properties. This is not surprising since the siloxane phase is the continuous phase in all cases.

Tables V and VI also contain the modulus and ultimate properties of a poly(dimethylsiloxane) (PDMS) network, which is used as a standard for comparison to the poly-

Table V
Mechanical Properties of Hydroxy Ether–Siloxanes Copolymers with Various Diphenylsiloxane Compositions

sample	diphenylsiloxane comp, %	modulus, MPa	tensile strength, MPa	elongation, %
PDMS network	0	0.5	0.4	70
EP/PSX (5400)	0	2.5	1.0	55
EP/PSX (5400)	25	1.7	0.5	70
EP/PSX (4850)	50	1.4	0.4	50
EP/PSX (5700)	75	1.2	0.3	48

Table VI
Mechanical Properties of Hydroxy Ether–Siloxane Copolymers Containing 50 wt % Diphenylsiloxane with Various Siloxane Molecular Weights

siloxane block length $\langle M_n \rangle$, g/mol	modulus, MPa	tensile strength, MPa	elongation, %
PDMS network	0.5	0.4	70
1950	3.5	1.6	72
2300	3.3	1.0	60
2800	2.4	0.44	25
3700	1.9	0.42	39
5400	2.5	1.00	55
6600	0.56	0.20	50
11300	0.53	0.22	75

[a] PDMS network.

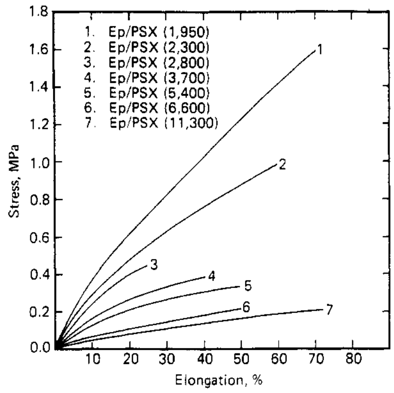


Figure 5. Stress versus percent elongation for the hydroxy ether–siloxane copolymers with 50 wt % diphenylsiloxane in the soft segment and varying siloxane block lengths.

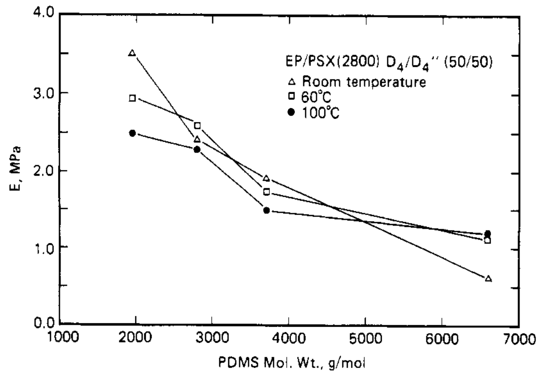


Figure 6. tensile modulus versus siloxane molecular weight for the copolymers containing 50 wt % diphenylsiloxane in the soft segment at various temperatures.

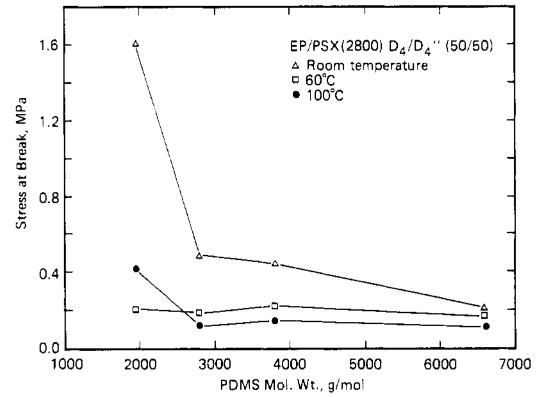


Figure 7. Tensile stress versus siloxane molecular weight for the copolymers containing 50 wt % diphenylsiloxane in the soft segment at various temperatures.

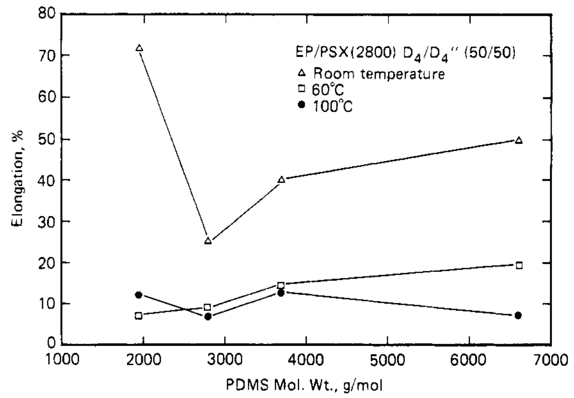


Figure 8. Elongation versus siloxane molecular weight for the copolymers containing 50 wt % diphenylsiloxane in the soft segment at various temperatures.

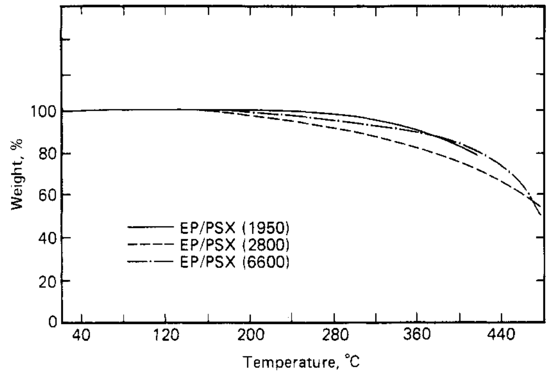


Figure 9. TGA thermograms (weight loss versus temperature) for networks with 50 wt % diphenylsiloxane composition and varying soft segment molecular weight (nitrogen atmosphere).

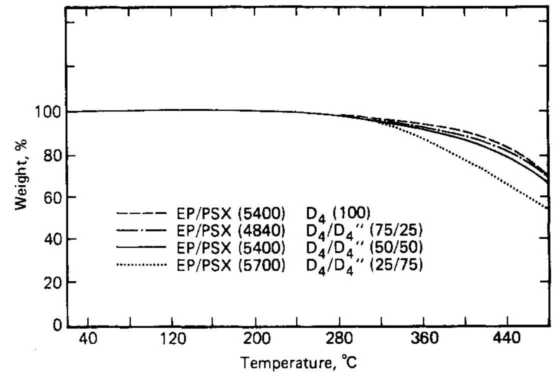


Figure 10. TGA thermograms (weight loss versus temperature) for networks with varying diphenylsiloxane compositions in the soft segment (nitrogen atmosphere).

(hydroxy ether–siloxane) networks. The heterogeneous morphology of the networks has a large influence on the mechanical properties particularly for those cases that contain the higher hard segment contents. The incorporation of the dispersed hydroxy ether phase is believed to act as a filler, increasing the internal viscosity of the PDMS network in a manner similar to that of the hard segment domains in segmented polyurethanes. This has been reported to reduce chain mobility, which retards both crack initiation and propagation.[1]

Tensile tests were also performed at various temperatures to assess the mechanical properties for the network containing 50 wt % diphenylsiloxane compositions with a molecular weight of 2800 g/mol. The moduli, tensile strength, and elongation to break were measured at 25, 60, and 100 °C (Figure 6–8). For low temperatures, there are significant differences in the moduli and tensile strengths (Figures 6, 7) since the hard segments are below their T_g's at ambient temperature. At higher temperatures, the effects of the hard segment at these low compositions are reduced, minimizing the modulus and tensile strength differences for the different temperatures. In contrast, as shown in Figure 8, the elongation to break or toughness is significantly reduced at elevated temperatures where a rubbery–rubbery rather than a rubbery–glassy copolymer system exists. It is apparent that the toughening mechanisms or the increased internal viscosity characteristic of the networks at room temperature is no longer available, minimizing reinforcement, which leads to reduced elongations.

The thermal stability of the networks was investigated in both air and nitrogen atmospheres. Figures 9 and 10 contain the thermogravimetric analysis (TGA) results for the networks containing a 50 wt % diphenylsiloxane composition with varying molecular weights and diphenylsiloxane composition, respectively, under a nitrogen atmosphere. Interestingly, all the networks appear to be thermally stable up to temperatures in excess of 400 °C. However, the networks containing higher diphenylsiloxane compositions (50 and 75 wt %) show weight loss prior to the decomposition. This may result from the mixed dimethyldiphenylsiloxane cyclics, which are much less volatile than the cyclic tetramer of dimethylsiloxane and are not as effectively removed by the vacuum distillation of the oligomeric precursor.

The TGA results for the networks tested in air demonstrated markedly different behavior. Thermal decomposition occurs at a much lower temperature in an apparent sequential or two-step process (Figure 11). The decomposition begins at approximately 240 °C for each of the networks and appears to level off prior to polymer de-

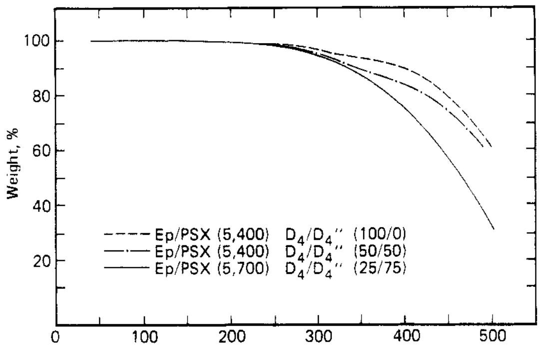


Figure 11. TGA thermograms (weight loss versus temperature) for networks with varying diphenylsiloxane compositions in the soft segment (air atmosphere).

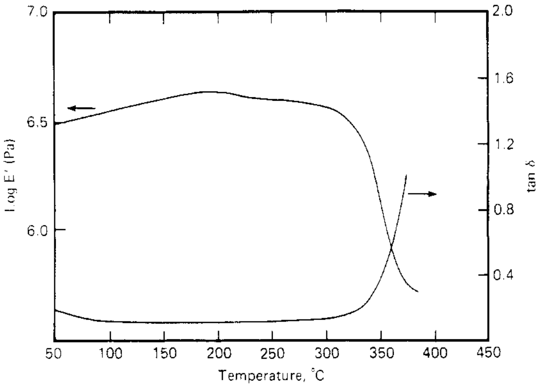


Figure 12. Tensile modulus and tan δ versus temperature for the network containing 50 wt % diphenylsiloxane with a soft segment molecular weight of 2800 g/mol (air atmosphere).

composition, particularly for those networks with the higher dimethylsiloxane compositions. These structures are much more susceptible to thermooxidative degradation than the networks with the high diphenylsiloxane compositions, which usually lead to cross-linking, minimizing the weight loss. In contrast, the network containing 75 wt % diphenylsiloxane shows continuous weight loss, suggesting chain session and the evolution of cyclics as the primary modes of degradation.

Variable-temperature and isothermal DMTA was used to assess the mechanical response as a function of temperature for the copolymer containing 50 wt % diphenylsiloxane with a block length of 3800 g/mol. The results in Figure 12 clearly show a modulus decrease and level off prior to 250 °C, which is consistent with the observed weight loss in the same temperature range as the TGA experiments. This further suggests chain scission with simultaneous thermoxidative cross-linking which maintains the modulus prior to the polymer decomposition just above 300 °C. Temperatures of 150 and 200 °C were used for the isothermal aging (Figure 13), and at 150 °C the network appears to be thermally stable as determined by the modulus invariance with time. In contrast, the sample aged at 200 °C showed an initial drop in modulus followed by a plateau as expected from the variable-temperature DMTA and TGA results.

The chemorheology results for the copolymer containing 50 wt % diphenylsiloxane with a siloxane block length of 2800 g/mol together with polydimethylsiloxane network control (Dow Corning Sylgard 182) are shown in Figure 14. The normalized load is plotted as a function of log (time) for both a static and a dynamic extension (constant 5% strain) generating both a continuous and intermittent stress relaxation test. The continuous stress relaxation data give the chain scission as a function of time. The

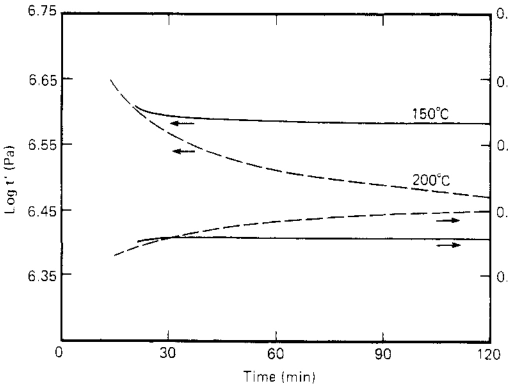


Figure 13. Tensile modulus and tan δ versus time at various temperatures for the network containing 50 wt % diphenylsiloxane with a soft segment molecular weight of 2800 g/mol (air atmosphere).

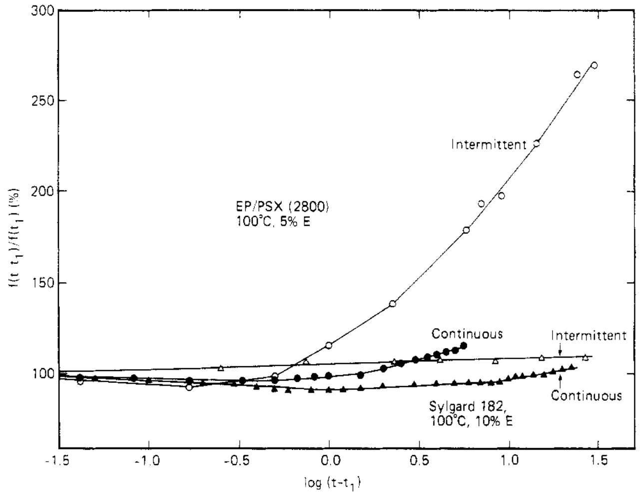


Figure 14. Chemorheology results, normalized load versus log time for both static and dynamic extension, for the network containing 50 wt % diphenylsiloxane with a soft segment molecular weight of 2800 g/mol and a dimethylsiloxane-based elastomer, Sylgard 182 (air atmosphere).

intermittent stress relaxation data give the total network density of the polymer, and the difference between the two is the contribution from cross-linking upon thermal degradation. For the block copolymer, both the continuous and intermittent curves demonstrate a small decrease of the cross-linking density at the beginning of the aging, indicative of chain scission. However, as the aging time increases, the total cross-linking density starts to increase dramatically after 0.5 h of aging and, after 26 h, is 2.6 times the initial value. In addition, continuous relaxation data show an unusual upswinging trend at longer aging times, which also indicates extensive cross-linking after extended aging. The early chain scission followed by extensive cross-linking observed by chemorheology experiments is consistent with the TGA and DMTA results discussed earlier. In contrast to this prominent degradation of the block copolymer, the dimethylsiloxane based network control (Sylgard 182) shows virtually no change in network density during aging at the same temperature.

Summary

Segmented hydroxy ether–siloxane copolymers were prepared by the reaction of DGEBA with bis(aminopropyl)-terminated poly(dimethyldiphenylsiloxane) oligomers of various molecular weights and diphenylsiloxane compositions. Perfectly alternating sequence distributions were obtained from the monomer and oligomers bearing mutually reactive end groups, and the hydroxy ether linkage is formed simultaneously with the growth of the second block. Bulk copolymerizations were realized when the diphenylsiloxane compositions in the soft segment were greater than 50 wt %, while lower diphenylsiloxane compositions required a solvent to facilitate both the mixing and initial polymerization. DSC, DMTA, and SAXS results demonstrate that microphase-separated morphologies were achieved when diphenylsiloxane compositions in the soft segment were 50 wt % or less. The mechanical properties of the networks varied with the compositional changes in the soft segment.

Registry No. $(D_4)(D_4'')$(DGEBA) (block copolymer), 123380-81-4.

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Synthesis and Characterization of the *tert*-Butyl Ester of the Oxydianiline/Pyromellitic Dianhydride Polyamic Acid

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ABSTRACT: Novel *tert*-butyl esters of oxydianiline/pyromellitic dianhydride polyamic acid were prepared in good yield. The polymers were prepared with either meta or para repeating units. The cure behavior of these *tert*-butyl esters was studied by IR, MS, and TG analysis and was compared to that of both the parent polyamic acid and its methyl ester. It was found that a rapid deprotection of the *tert*-butyl group occurs at around 200 °C with liberation of free polyamic acid. Consequently, the cure behavior at 200 °C of the *tert*-butyl ester approaches that of the parent polyamic acid. Furthermore, the isomerism of the repeating units does not appear to have any detectable effect on the cure behavior of the polymer, although meta isomerism appears to enhance solubility of the polymer in organic solvents.

Introduction

The lack of stability of polyamic acid solutions toward hydrolysis has been attributed to a catalytic effect engendered by the presence of an ortho carboxylic acid group.[1] Linear alkyl esters of polyamic acids[2-9] are much more hydrolytically stable in solution than the parent polyamic acids[3-8] and consequently show little change in molecular weight with time. This enhanced stability has been attributed to the blocking of the ortho carboxylic acid group by an ester group.[2] Unfortunately, the curing rates of linear alkyl esters are much slower than those of the corresponding free acids (up to 60 times slower for the *n*-butyl ester).[5] In our work we sought to avoid this difficulty by synthesizing a polyamic ester capable of thermally liberating the free polyamic acid. Moreover, it was hoped that this type of approach would yield novel polyimide precursors with thermally removable, bulky solubilizing groups. This could enable us to take advantage of the solubilizing effect of such groups during processing, giving access to low boiling point, film-casting solvents, while ensuring that the final cured polyimide retains valuable physical properties. This work reports the synthesis of the *tert*-butyl esters of the ODA/PMDA polyamic acids and describes some preliminary physical properties of these materials. The *tert*-butyl group (carbonate or ester) has been reported to thermally deprotect the hydroxyl group in styrene- and polycarbonate-based polymer systems.[10,11] This precedent encouraged us to choose this type of protecting group for our application. We chose to first study the *tert*-butyl ester of the polyamic acid derived from oxydianiline (ODA) and pyromellitic dianhydride (PMDA), because the simple alkyl esters (methyl, ethyl, propyl, butyl) of this polyamic acid have been prepared[5,6] and give a good basis for comparison.

Experimental Section

1. Materials and Characterization. Elemental analyses were obtained from Galbraith Laboratories, Inc. Polymer molecular weights were determined using a Waters Model 590 gel permeation chromatograph equipped with a Zorbax column, a Waters 410 differential refractometer, and a Waters Lambda-Max LC spectrophotometer. Molecular weights are given relative to polystyrene standards. NMR spectra were obtained on a JEOL