Morphology and mechanical properties of poly(dimethyl siloxane-b-styrene-b-dimethyl siloxane) block copolymers

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The films of poly(dimethyl siloxane-b-styrene-b-dimethyl siloxane) block copolymers cast from different solvents showed significant changes in both the phase morphology and the tensile behaviour. Methyl ethyl ketone and tetrahydrofuran gave hard films and appear to have a continuous polystyrene phase. Conversely cyclohexane, a good solvent for polydimethyl siloxane segment gave softer more elastic films. Intrinsic viscosity data of block copolymers of varying siloxane content showed highest value in toluene and least in cyclohexane which is a theta solvent for polystyrene segment. The tensile properties are also influenced by thermal ageing of films at 100 and 150°C.

INTRODUCTION

The advent of block copolymerization has given rise to a novel concept for the design and control of polymer properties. Some properties of the homopolymers can be maintained nearly unchanged in a block copolymer system. Furthermore, the added benefit of some new property due to the block copolymer morphology arises that belongs to neither of the homopolymers. The introduction of thermoplastic elastomers[1] particularly Kraton has stimulated considerable interest in this new family of polymers. The simplified processability of these polymers is a direct consequence of their unique morphology. Recently, poly(styrene-siloxane) block copolymers have been introduced due to their higher thermo-oxidative stability in comparison to styrene-butadiene block copolymers. The morphology of AB, $(AB)_x$, ABA and BAB type styrene–siloxane copolymers has been studied by Saam[2,3] *et al.* and Morton[4] by transmission electron microscopy. The morphological behaviour of block copolymers has also been studied by low angle X-ray and laser diffraction[5] and from sonic modulus[6] for finding out the domain size. The formation of micelles of styrene-b-butadiene copolymers in methyl ethyl ketone has been observed from light scattering studies[7]. Pochan *et al.*[8] have also reported the effect of solvents on the morphology of polydimethylsiloxane/poly(α-methyl styrene) block copolymers. The purpose of this paper is to present some data on dilute solution properties and the morphology of poly(dimethyl siloxane-b-styrene-b-dimethyl siloxane) copolymer films cast from different solvents and the effect of morphology on the stress-strain behaviour of the polymers. The effect of thermal ageing on mechanical properties has also been considered.

EXPERIMENTAL

Poly(dimethyl siloxane-b-styrene-b-dimethyl siloxane) copolymers (PDMS-St-PDMS)

HO$\leftarrow$PDMS–PS–PDMS$\rightarrow$OH copolymers were prepared by anionic polymerization using lithium biphenyl initiator in tetrahydrofuran-toluene mixture as described previously[9]. The reaction mixture was neutralized with 1 ml of acetic acid followed by 1.0 g of sodium bicarbonate solution to give a solution of the block polymer with a silanol end group. The solution was finally washed with water and precipitated with methanol.

The composition of these block polymers was determined by silicon analysis.

The intrinsic viscosity in solvents of varying solubility parameter was determined in an Ubbelohde viscometer at 30° ± 0.05°C. Number average molecular weight ($\bar{M}_n$) were measured using high speed Membrane (dynamic) osmometry at 25°C in THF. Copolymer films (0.1–0.15 mm thickness) were obtained from 20% solution made in different solvents. During casting 2% curing mixture (dibutyl tin dilaurate and tetraethoxysilane in 1:3 wt ratio) was added for room temperature vulcanization as reported previously[10].

For morphological studies the ultrathin films of about 400 Å were cast from 2% solution in different solvents. The high electron density of the polysiloxane segment, as compared to the polystyrene, led to sufficient contrast without the need for staining techniques. Electron transmission micrographs were taken on a AEI 802 transmission electron microscope. Stereoscan S4–10 (Cambridge) electron microscope was also used for studying the surface of block copolymer films prepared from 10% solution in different solvents.

Specimen for tensile experiments were cut from solution cast films. The stress–strain measurements on ASTM D638-68 dumb-bell tensile specimens were made on Instron tester at a cross head speed of 100 mm/min and the chart speed 200 mm/min on a full scale load of 1 kg. The tensile properties of the films were also determined after thermal ageing in the air oven at 100°C and 150°C for 1–3 h.

RESULTS AND DISCUSSION

Effect of solvents on intrinsic viscosity

Polydimethyl siloxane–polystyrene copolymers are much more incompatible as compared to styrene-butadiene block

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polymers due to the greater difference in the solubility parameter of each segment. This large difference in compatability may be reflected in increased segment A (PDMS) segment B (PS) interactions which will give rise to expanded coil configurations of the copolymers in solution. The influence of solvents on intrinsic viscosity is shown in *Figure 1*. The solvents used are, toluene, mutual solvent for both the segments and methyl ethyl ketone and cyclohexane which are theta solvents for PDMS and PS resepectively.

In toluene, higher $[\eta]$ values are observed in all the copolymers irrespective of the composition. These results suggest expansion of the polymer coils by polymer–solvent interactions and A–B interactions are minimum. In cyclohexane, however, agglomeration of polystyrene segment takes place which explains the lowest $[\eta]$ value for all the copolymers. Similarly, in methyl ethyl ketone, PDMS segment agglomerates and shows lower intrinisc viscosity values as compared to that observed in toluene. Moreover, as the solubility parameter of the solvent approaches that of the polymer, the intrinsic viscosity increases. This can be seen from the maximum $[\eta]$ value of polystyrene in tetrahydrofuran. However, the introduction of PDMS segment in the block polymer (PDMS–PS–PDMS) decreases the solubility parameter and shows the maximum intrinsic viscosity in toluene. Similar studies have been conducted on polystyrene[11], styrene–butadiene–styrene[12,13] and styrene–siloxane[14] block polymers.

It is possible to calculate A–B interactions between polydimethyl siloxane and polystyrene segments from the intrinsic viscosity date as reported by Davies and Jones[14]. By considering the copolymer as a binary mixture of homopolymers the empirical expression:

$$[\eta]^* = n_A\eta_A + n_B\eta_B \qquad (1)$$

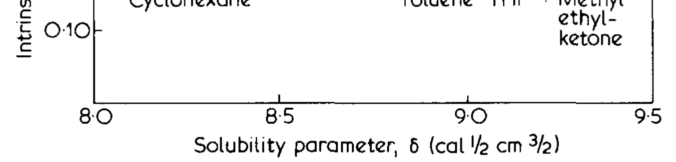


Figure 1 Effect of solvents on the intrinsic viscosity of poly(styrene–siloxane) block copolymers: A, $(\mathrm{Me_2SiO})_n$–53.3 wt%, $\bar{M}_n$–62 000; B, $(\mathrm{Me_2SiO})_n$–42.0 wt%, $\bar{M}_n$–37 000; C, $(\mathrm{Me_2SiO})_n$–34.65 wt%, $\bar{M}_n$–22 000; D, polystyrene, $\bar{M}_n$–15 000

This equation has been further expanded by using Mark–Houwink relationship to give:

$$[\eta]^* = n_A K_A M^{\alpha A} + n_B K_B M^{\alpha B} \qquad (2)$$

where $[\eta]^*$ is the calculated intrinsic viscosity, n_A and n_B are the mole fractions of A and B segment and M is the overall number average molecular weight for the copolymer. Using equation (2) a qualitative estimation of the chain configuration and A–B interaction was obtained. The results are listed in *Table 1*.

For all three solvents, higher $[\eta]$ values were observed than calculated $[\eta]^*$ value. This indicates expansion of the copolymer coils due to A–B interactions. In toluene the differences $\Delta[\eta]$ are small and vary between 4.6–14% of the calculated value depending on the composition of copolymers. In methyl ethyl ketone, however, the values of $\Delta[\eta]$ are up to 47% greater than the calculated and also proportional to the mole fraction of polystyrene. Cyclohexane also caused expansion of the coil configuration but to a smaller extent than methyl ethyl ketone. The difference in viscosity values, i.e. $\Delta[\eta]$ was found to be only 1.5% in the copolymer having 53.5% PDMS. This data shows the expansion of the predicted coil configuration due to A–B segment interactions. In good solvent like toluene, the coils are expanded by polymer-solvent interactions whereas, in theta solvents, i.e. MEK and cyclohexane, repulsive A–B interactions contribute towards coil expansion. Relevant Mark–Houwink data are given in *Table 2*.

Morphology and phase separation

Electron micrographs of PDMS–St–PDMS block copolymer films cast from different solvents show the formation of microphases. The darker regions in all the cases represent polydimethylsiloxane phase. Electron photomicrographs of very thin films cast from benzene, *Figure 2a*, show cell like spherical structure with black domains of PDMS embedded in polystyrene matrix. PDMS domain size is 338 Å ± 40 Å in diameter which corresponds to the calculated value of (315 Å)PDMS segment. Calculations were made by using Meier's treatment[16] ($R = 4/3\alpha M^{1/2}K$) where $K = 7.5 \times 10^{-9}$ and interfacial tension was assumed to be 5 dyne/cm. This uniform spacing is particularly evident because of the entrapment of polydimethylsiloxane within polystyrene phase. In

Table 2 Mark–Houwink data for polystyrene and polydimethylsiloxan

	Toluene at 25°C		MEK at 20°C		Cyclohexane at 34°C	
Polymer	K	α	K	α	K	α
PDMS	2.0×10^{-4}	0.66	8.1×10^{-4}	0.50	1.59×10^{-4}	0.70
Polystyrene	4.4×10^{-4}	0.65	7.03×10^{-5}	0.71	8.2×10^{-4}	0.50

Table 1 Comparison of $[\eta]^*$ with $[\eta]$ of Poly(DMS–St–DMS) block copolymers in different solvents

$\bar{M}_n \times 10^{-3}$ by osmometry	$[\mathrm{CH_3}]_2$ SiO units in copolymer, wt %	Mole fraction of polystyrene n_A	Toluene at 25°C		Methyl ethyl ketone at 20°C		Cyclohexane at 34°C	
			$[\eta]$ dl/g	$[\eta]^*$	$[\eta]$ dl/g	$[\eta]^*$	$[\eta]$ dl/g	$[\eta]^*$
22.0	34.65	0.5316	0.235	0.224	0.190	0.101	0.160	0.146
37.0	42.00	0.4326	0.330	0.295	0.255	0.143	0.225	0.210
62.0	53.5	0.2752	0.430	0.368	0.260	0.195	0.305	0.300

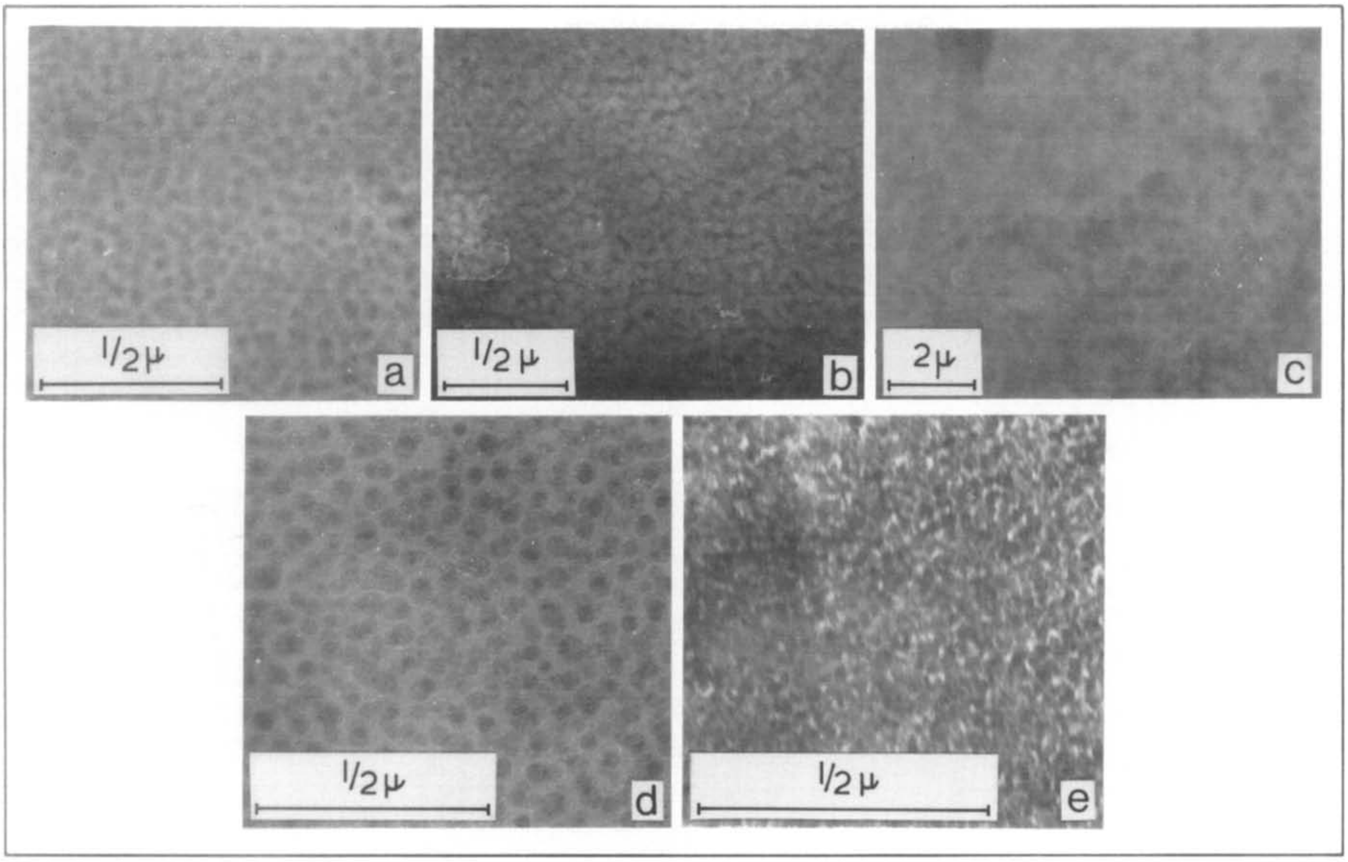


Figure 2 Electron photomicrographs of poly(styrene–siloxane) block copolymer films cast from different solvents. (a) film cast in benzene, $(Me_2SiO)_n$–50 wt %, $\bar{M}_n$–80 000; (b) film cast in benzene, $(Me_2SiO)_n$–34.65 wt %, $\bar{M}_n$–22 000; (c) block copolymer, $(Me_2SiO)_n$–50 wt % cast in tetrahydrofuran; (d) methyl ethyl ketone; (e) cyclohexane

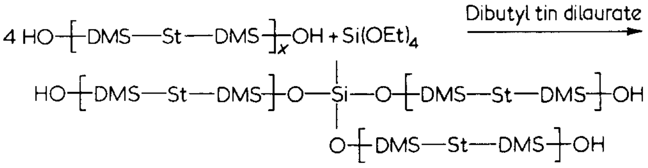
Figure 2b where polystyrene blocks are now present in the greater amount more of white polystyrene phase with a rod like structure shows.

A more discrete microphase separation is observed in a film cast from tetrahydrofuran (*Figure 2c*) which is a good solvent for polystyrene. This shows a continuous phase of polystyrene with black aggregated PDMS spheres. Cell like black PDMS domains have also been observed in block polymer film cast from methyl ethyl ketone. However, the size of the PDMS spheres is much bigger in comparison to that obtained in benzene. As methyl ethyl ketone is a preferential solvent for PS, bigger size of PDMS domains (*Figure 2d*) may be attributed to the aggregation of siloxane chains. A reversal in structure was observed when films were made from cyclohexane (*Figure 2e*) a selective solvent for PDMS. This formed a film composed of a PDMS matrix with small rod like structures of PS. However, phase separation is not very distinct as shown by SEM. Thus the film structure can be altered in a predictable manner by the addition of selective solvents. *Figure 3* is scanning electron microscopy (SEM) photographs which illustrate the surface texture of PDMS-St-PDMS block polymer cast from different solvents. The use of THF and cyclohexane which selectively solvate either the polystyrene segment or PDMS block gave films which show better separation of the microphases (*Figures 3a and b*). On the other hand, in toluene, a mutual solvent for both the segments produced lamellar type structure (*Figure 3c*). Kawai and his associates[15] have also reported lamellar structures for styrene/isoprene/styrene block polymers that contain almost equal amounts of styrene and isoprene.

This is further confirmed from SEM photograph of block polymers containing 34 wt % and 42 wt % polydimethyl siloxane segment (*Figure 4*), which shows cellular structure in toluene instead of lamellar structure (*Figure 3c*).

Mechanical properties.

The mechanical properties of the block polymer films cast from different solvents are tabulated in *Table 3*. The noticeable feature of these data is the markedly lower strength of these polymers compared to PS-PDMS-PS thermoplastic elastomers. In fact, in elastomeric block copolymers, for a continuous network to exist both ends of the elastomer segment must be immobilized in the non-elastomeric domains. PDMS–St–PDMS block copolymer is expected to be a weak material in comparison to St–PDMS–St block polymer. It was therefore, necessary to introduce some crosslinks through silonalate end groups while casting films at room temperature:



$$4\,HO{-}[DMS{-}St{-}DMS]_x{-}OH + Si(OEt)_4 \xrightarrow{\text{Dibutyl tin dilaurate}}$$
$$HO{-}[DMS{-}St{-}DMS]{-}O{-}\overset{|}{\underset{|}{Si}}{-}O{-}[DMS{-}St{-}DMS]{-}OH$$
$$O{-}[DMS{-}St{-}DMS]{-}OH$$

However, the extent of crosslinking was not high due to the limited number of available hydroxyl end groups. Holden *et al.*[17] have also reported butadiene-styrene-butadiene block polymers as weak materials unless vuncanized.

It is interesting to note that methyl ethyl ketone and tetrahydrofuran which are selective solvents of polystyrene segment produced films with high initial modulus characte-

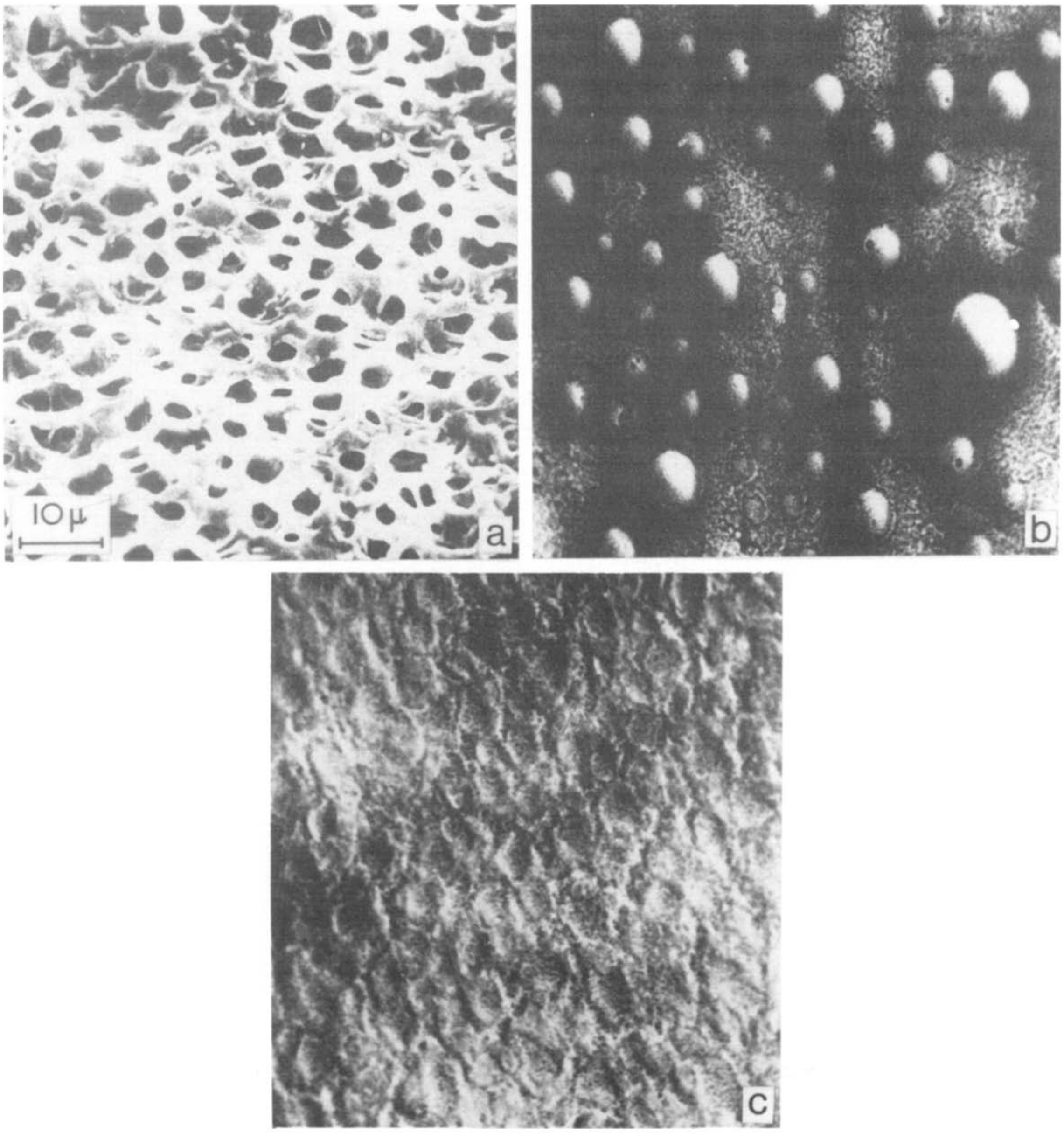


Figure 3 Scanning electron micrographs of poly(styrene–siloxane) block copolymer, [$(Me_2SiO)_n$–50 wt%, $\bar{M}_n$–80 000] film cast from different solvents. (a) Tetrahydrofuran, (b) cyclohexane, (c) toluene

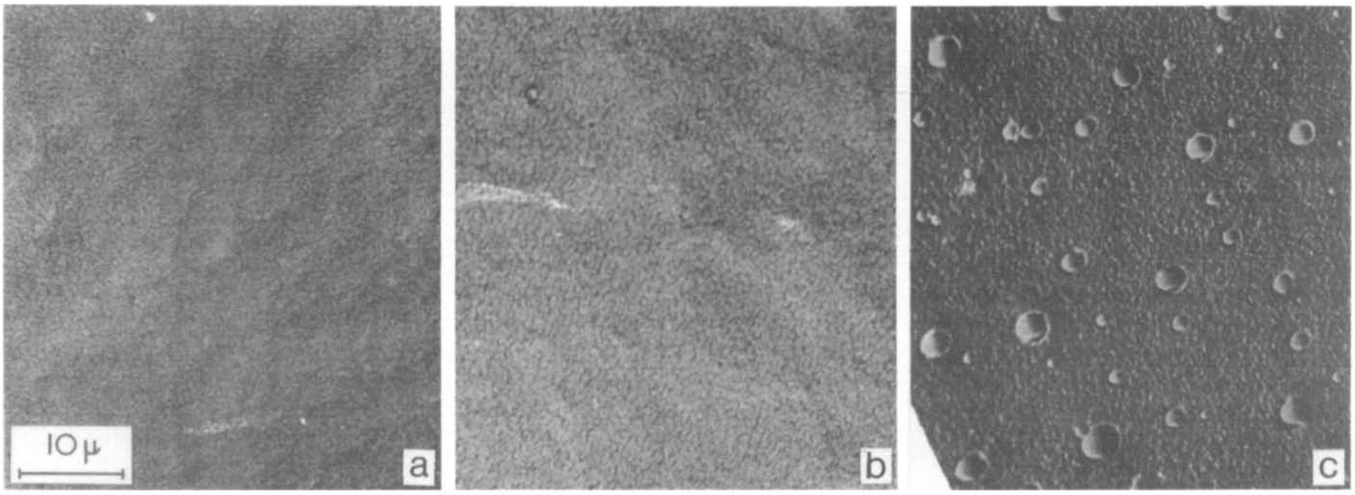


Figure 4 Scanning electron micrograph of (PDMS–St–PDMS) block polymers. (a) Block polymer having 34.65 wt% PDMS, cast in toluene; (b) block polymer having 42.0 wt% PDMS, cast in toluene; (c) block polymer having 42.0 wt% PDMS, cast in cyclohexane

ristics of a plastic rather than of a rubber. However, the tensile strength was found to be maximum in toluene cast films which show lamellar structure in scanning electron microscopy. The high strength may be attributed to the homogeneous dispersion of the ductile glassy polystyrene domains in toluene (*Table 3*). Films cast from cyclohexane have both lower modulus and poorer tensile strength than specimens prepared from the other solvents. This may be related to the weak continuous elastomeric polydimethylsiloxane matrix in which polystyrene segments are agglomerated.

Composition of the block polymer also influences the tensile behaviour. Initial modulus, yield point and tensile strength increases with increase in the polystyrene domains. Overall, significant changes in stress–strain behaviour of the block copolymer films have been observed which are related with the morphology and phase boundaries of the PDMS and PS segments. In this connection it is noteworthy to mention that Morton *et al.*[18] have shown the linear relation between strength and degree of adhesion in rubber vulcanizates. Poor tensile properties of styrene–siloxane block polymers are related to the low surface free energy of PDMS (24 dyne cm^{-1}) compared to carbon polymers (32–33 dyne cm^{-1}) which leads to poor adhesion.

Effect of thermal ageing on tensile properties

A comparison of the effect of temperature on the tensile strength of PDMS–St–PDMS block copolymers is provided in *Table 4*. Initially, heating the films at 100°C for 1 h (around T_g of polystyrene) showed decrease in tensile strength as well as elongation except the film cast from toluene. A further decrease in strength was noticed in films heated at 100°C for 3 h. Further heating at 150°C for 3 h showed an improvement in strength in a film cast from methyl ethyl ketone, but marginal decrease in strength in films prepared from THF, toluene and cyclohexane in comparison to the original value. Improvement in tensile strength or reduction in the tensile losses in films heated at 150°C for 3 h may presumably be due to the introduction of cross-links through methyl silicon by thermal aging:

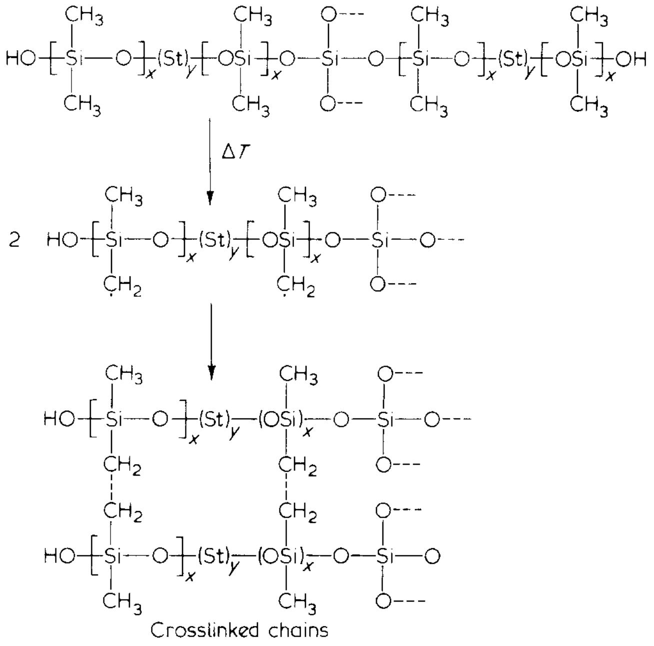


Table 3 Mechanical properties of Poly(DMS–St–DMS) block copolymer(a), films cast from different solvents

Solvent	Tensile strength psi	Elongation %	Initial modulus psi	Stress yield psi	Strain yield %
Cyclohexane	822	120	3260	425	25.0
Methyl ethyl ketone	885	85	6502	605	16.0
Tetrahydro-furan	942	85	5778	560	12.0
Toluene	978	117.6	4038	480	32.0
Cyclohexane[b]	1128	97.5	4718	750	26

[a] $[\eta]_{30°}$ in toluene = 0.26, $(Me_2SiO)_n$ wt % = 49.0
[b] $[\eta]_{30°}$ in toluene = 0.21, $(Me_2SiO)_n$ wt % = 33.4

Introduction of crosslinks in the elastomeric segment can be further supported from the significant drop in elongation of the heated films. Thermogravimetric analysis of vulcanized film also shows the higher threshold degradation temperature after thermal ageing at 150°C (*Figure 5*). Thus drop in the elongation and higher initial decomposition temperature of thermal aged films confirm the introduction of crosslinks during thermal ageing.

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Table 4 Mechanical properties of (PDMS–St–PDMS) block copolymers* [a] film cast from different solvents

	Before thermal ageing		Film heated at 100°C for 1 h in air oven		Film heated at 100°C for 3 h in air oven		Film heated at 150°C for 1 h in air oven		Film heated at 150°C for 3 h in air oven	
Solvent	Tensile (σ) strength (psi)	Elongation %	(σ) psi	Elongation %	(σ) psi	Elongation %	(σ) psi	Elongation %	σ psi	Elongation %
Cyclohexane	822	120	800	117	751	117	751	86	793	78
Methyl ethyl ketone	885	85	861	72.5	892	67.3	894	67.0	921	56.0
Tetrahydrofuran	942	85	892	85	884	65	923	62.5	928	53
Toluene	978	117.6	977	113	932	108	935	105.5	949	100
Cyclohexane (b)	1128	97.5	859	85	786	40	807	38.0	821	36

[a] $[\eta]_{30°}$ in toluene of the (PDMS–St–PDMS) block copolymer = 0.26, $(Me_2SiO)_n$ = 49 wt %
[b] $[\eta]_{30°}$ in toluene = 0.21, $(Me_2SiO)_n$ = 33.4 wt %

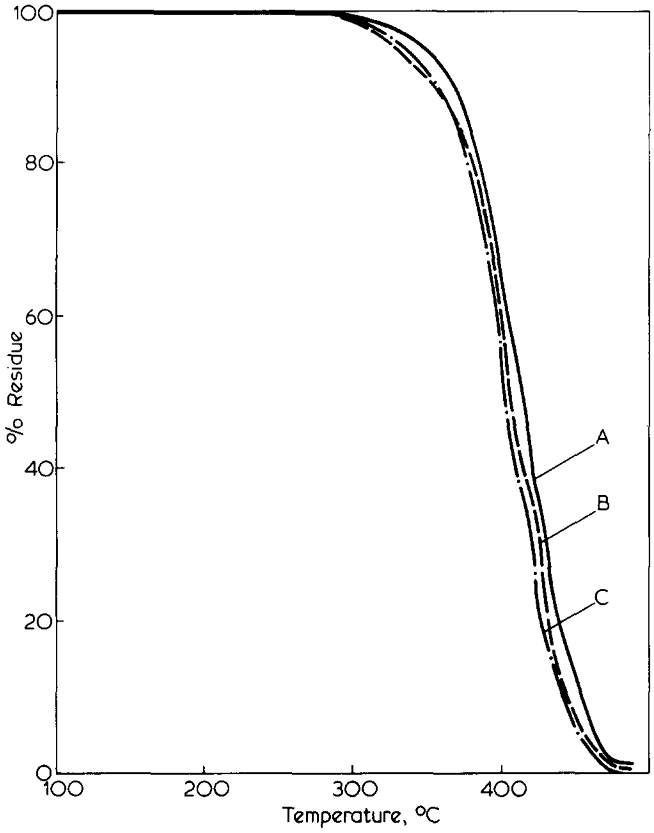

Figure 5 Effect of crosslinking on thermal behaviour. A, vulcanized film heated at 150°C for 1 h; B, after vulcanization; C, block polymer, [$(Me_2SiO)_n$ – 49 wt %], before vulcanization

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