THERMAL STABILITY OF SEALANTS FOR MILITARY AIRCRAFT: MODIFICATION OF POLYSULFIDE SEALANTS WITH ETHER AND THIOETHER MONOMERS

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PJ HANHELA AND W MAZURUK

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Thermal Stability of Sealants for Military Aircraft: Modification of Polysulfide Prepolymers with Ether and Thioether Monomers

P.J. Hanhela and W. Mazurek

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Abstract

The effect of modifying Thiokol polysulfide prepolymers with dimercapto diethyl ether and dimercapto diethyl sulfide, on the resistance to heat ageing has been examined together with a commercially modified (PR-1770 B-2) and an unmodified equivalent sealant (PR-1750 B-2). Mechanical tests performed on specimens, after heat ageing at 182°C, indicated that the modifications did not improve the heat resistance of polysulfide sealants.

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Cordite Avenue, Maribyrnong
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Telephone: (03) 246 8111
Fax: (03) 246 8999

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Authors

P.J. Hanhela

Peter J. Hanhela is a Senior Professional Officer Class B, in the Protective Chemistry Division. He joined MRL in 1970 and has worked in areas of organic chemistry, including chemiluminescence and aircraft sealants. He is currently engaged in studies in Submarine Atmospheres Research, including monitoring and carbon dioxide removal.

W. Mazurek

Dr Waldemar Mazurek is a Principal Research Scientist in the Protective Chemistry Division. He joined MRL in 1967, moving to the Sealants section in 1982, where he became Task Manager of the section. He has been active in the areas of chemical degradation of sealants, structure/property relationships and the curing mechanisms of polysulfide sealants. He is currently managing the Submarine Atmospheres Research Task, with research activities in areas including the monitoring and the purification of submarine atmospheres.

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Thermal Stability of Sealants for Military Aircraft: Modification of Polysulfide Prepolymers with Ether and Thioether Monomers

1. Introduction

Since the introduction of polysulfide elastomers in the 1940s [1], polysulfide based sealants have found extensive application in the sealing of aircraft integral fuel tanks [2, 3] where there is a requirement for fuel resistance and flexibility at low and high temperatures. The polysulfide sealants can be used over the temperature range − 50°C to + 180°C although they have only a limited capacity to withstand the maximum temperature. Above this temperature, fluorosilicones are the materials most commonly used [4]. For example, in high performance military aircraft such as the F-111, a fluorosilicone sealant is used in the leading edge of the wing tank where the aerodynamic heating may exceed the temperature tolerance of a polysulfide based sealant. The fluorosilicones are considerably more expensive and cannot readily be applied to the required thickness in a single application [5] as the curing process requires diffusion of moisture from the air into the polymer.

Recently, it has been claimed that modification of existing commercial polysulfide prepolymers has resulted in polysulfide sealants with improved thermal resistance [6]. The modification involved insertion of ethers and thioethers into the polymer backbone of Thiokol prepolymers using the thiol-dilsulfide interchange reaction (eq 1).

$$H[S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S]_nH + mHS\text{-}R\text{-}SH \longleftrightarrow$$

$$H[S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S\text{-}(S\text{-}R\text{-}S)_m\text{-}S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S]_pH$$

$$+ H[S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S]_qH \qquad \text{eq 1.}$$

Of the ethers tested, the incorporation of dimercapto diethyl ether (DMDE) and dimercapto diethyl sulfide (DMDS) resulted in the best improvement of thermal stability with Thiokol LP-12 polysulfide prepolymer. A molar ratio of 1:1 and 1:2 of prepolymer to dithiol gave optimum physical properties.

In order to verify the assertion that the incorporation of these ethers into the prepolymer could significantly improve the thermal properties of the cured polymer, the abovementioned ethers were inserted into three Thiokol polysulfide prepolymers, LP-2, LP-12 and LP-32. This report describes the effect of these manipulations upon the physical properties (weight loss, hardness, elongation and tensile strength) of the sealants obtained after curing the modified prepolymers with manganese dioxide and exposing the resultant elastomers at 182°C for various periods.

2. *Experimental*

Dimercapto diethyl ether and dimercapto diethyl sulfide were obtained from Aldrich Chemical Co. and the polysulfide prepolymers were supplied by Morton Thiokol. All reagents were used without further purification. Literature methods were used for the preparation of dibutyl trisulfide [7] and 1,2,5 trithiepane [8].

2.1 *Oxidation of Dimercapto Diethyl Sulfide and Dimercapto Diethyl Ether*

Hydrogen peroxide (20 ml, 0.06 mol) was added dropwise to a stirred mixture of dimercapto diethyl sulfide (6.1 g, 0.04 mol) and aqueous NaOH (50 ml, 0.08 mol). After 1 h the reaction mixture was filtered and the white residue washed with water (2 × 50 ml) and dried in an oven at 60°C (1.9 g). The filtrate was extracted with $CHCl_3$ (3 × 50 ml) and the combined extracts were washed with water (3 × 50 ml) and dried over $MgSO_4$, filtered and the solvent was removed to give a viscous colorless liquid (2.0 g).

Dimercapto diethyl ether was treated in a similar manner and gave a viscous colorless liquid (3.5 g) without the formation of a solid.

2.2 *Preparation of Modified Prepolymers*

The dimercapto ethers were incorporated into the prepolymers at two concentrations, 4.0 g and 8.0 g per 100 g of prepolymer for dimercapto diethyl sulfide and 3.6 g and 7.2 g per 100 g of prepolymer for dimercapto diethyl ether. Triethylamine (three drops) was added to each mixture and one week was allowed for equilibration of the reaction mixtures prior to use.

2.3 *Specimen Preparation*

The polysulfide prepolymers and curing agent were either mixed manually using a spatula or with a mechanically driven spindle. The resultant mixture was poured onto a steel frame (150 × 150 × 2 mm) resting on a smooth sheet of Teflon coated glass mesh. When the mixture began to harden (approximately 15 min at 40°C) it was pressed between two rigid steel plates, separated by Teflon sheets, with a load of 3.36 MPa at 100°C, released four times (to allow air to be eliminated) and then finally pressed for 1 h. The sheets were post cured for five days at 50°C. Specimens (50 × 75 mm) were cut from the sheets and exposed in an oven for the required time after which dumb-bell shaped specimens were cut out for subsequent mechanical testing.

2.4 *Exposure at Elevated Temperatures*

Sealant specimens were subjected to heat ageing in a laboratory oven containing an air circulating fan, operated at 182°C and controlled with a Philips Plastomatic II temperature controller to within ± 2°C. This temperature represents the upper operating limit for polysulfide sealants [2].

2.5 *Hardness Measurements*

Hardness measurements were conducted with a Shore Convcloader Durometer type 2A.

2.6 *Tensile, Elongation and Modulus Measurements*

Tensile strength, elongation at break and modulus (100%) were determined in accordance with a standard test method [9] using an Amsler Tensile Tester. Unexposed specimens were 2 mm thick while the thickness of the heat aged specimens was measured prior to testing.

2.7 *^{13}C NMR*

NMR measurements were carried out using a Bruker model AM 300 spectrometer. Inverse-gated decoupled spectra were recorded for approximately 40% (w/w) solutions in $CDCl_3$ using a 90° pulse, a recovery delay of 3 s, and a spectral bandwidth of 15 kHz with the accumulation of 16 000 data points. Between 80 000 and 100 000 scans were used to obtain spectra. No line broadening was used. In all cases the free induction decays were zero filled to 32 k. Chemical shifts, in ppm, were referenced to TMS.

2.8 *Isolation of PR-1770 B-2 and PR-1750 B-2 Prepolymers*

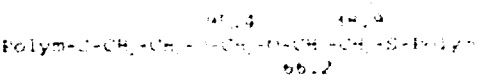
The sealant is supplied in two packs: cure paste and compounded prepolymer. The latter, for PR-1770 B-2 (422.7 g), was dispersed in methyl ethyl ketone to a total volume of 750 ml. The fillers were removed by centrifuging, the prepolymer solution was decanted and the solvent was removed on a rotary evaporator to give a viscous liquid (226.1 g, 53.5% of the formulation). Similar manipulations with PR-1750 B-2 (394 g) also yielded a viscous liquid (235 g, 59.6% of the formulation).

2.9 *Formulation of Sealant Specimens*

With the exception of PR-1750 B-2 prepolymer, all prepolymers were cured with the manganese dioxide cure paste supplied with and used to cure PR-1770 B-2 Permapol P-5 sealant (Product Research Corp., USA) [10]. The amount used was based on the ratio of thiol content (measured by infrared spectroscopy [11]) to cure paste formulated for this sealant.

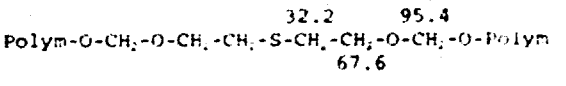
3. *Results and Discussion*

The ^{13}C NMR spectrum of the polysulfide prepolymer extracted from the PR-1770 B-2 sealant (Fig. 1) is typical of a polysulfide polymer with the dominant peaks arising from the idealized structure (1) [12].



1

Other components include small quantities of thioether (2) and thiol (3).



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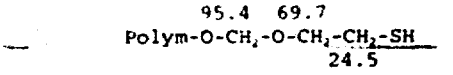

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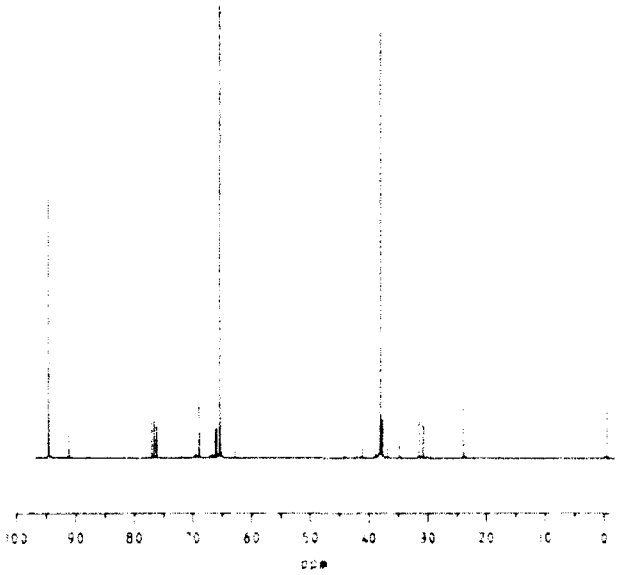
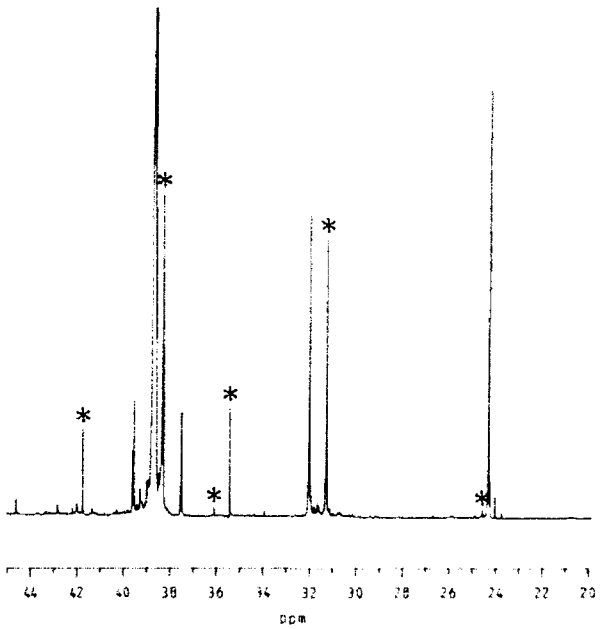




(b)

Figure 1: *^{13}C NMR of the polysulfide prepolymer extracted from sealed PR-1776 B-2 sealant, (*) denotes peaks arising from the addition of DMDS*

The spectrum of PR-1770 B-2 differs from that of PR-1750 B-2 (Fig. 2) and other polysulfide prepolymers because it contains six additional peaks (31.4, 38.6, 35.5, 41.8, and 24.7, 36.2 ppm).

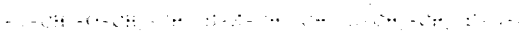
Addition of DMDS to LP-12 prepolymer (Fig. 3) resulted in a spectrum very similar to that of the PR-1770 B-2 prepolymer (Fig. 1). Comparison of the two spectra with that of DMDS (4) and LP-12 (Fig. 4) led to the identification of small quantities of unreacted dithiol in the spectrum of the modified LP-12 and PR-1770 B-2 prepolymers.

4

Similarly the spectrum of the corresponding disulfide polymer (5), prepared by the oxidation of the dithiol, resulted in the assignment of this component in the spectra of the DMDS modified LP-12 and the PR-1770 B-2 prepolymers.

5

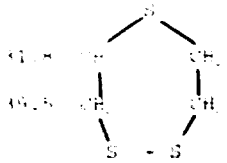
However the ^{13}C NMR cannot be expected to distinguish the difference between the homopolymer of this disulfide and the copolymer (6) formed from the disulfide and prepolymer (1) due to the relative similarity of the repeating units and the distance of the prepolymer ether oxygen from DMDS unit.



6

The identity of the remaining two peaks (31.4, 38.4 ppm) could not be determined. However, since these represent the most intense of the six peaks their identity is important.

A number of possibilities were considered. The possible formation of a cyclic disulfide (7) was eliminated since this compound had similar chemical shifts to the homopolymer.



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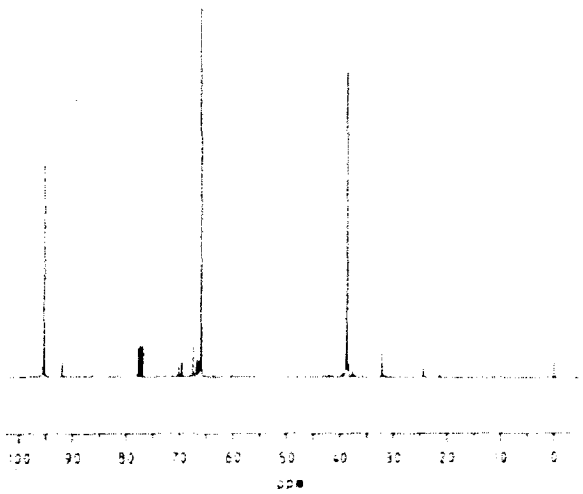


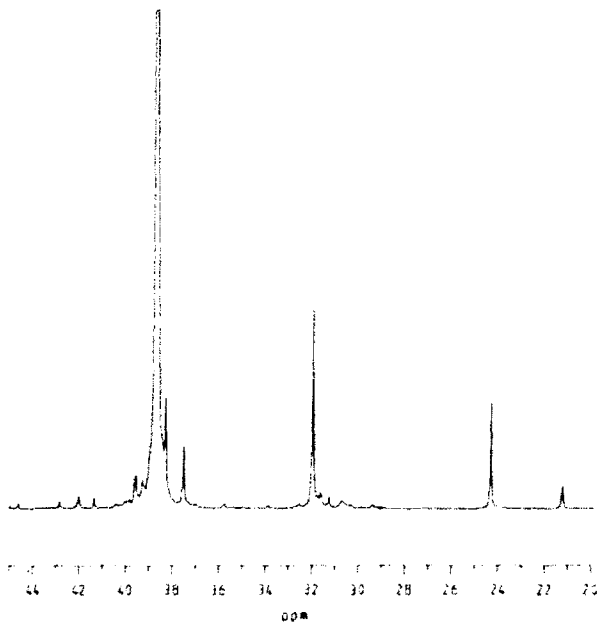


Figure 2: [illegible] *B-2 solution*

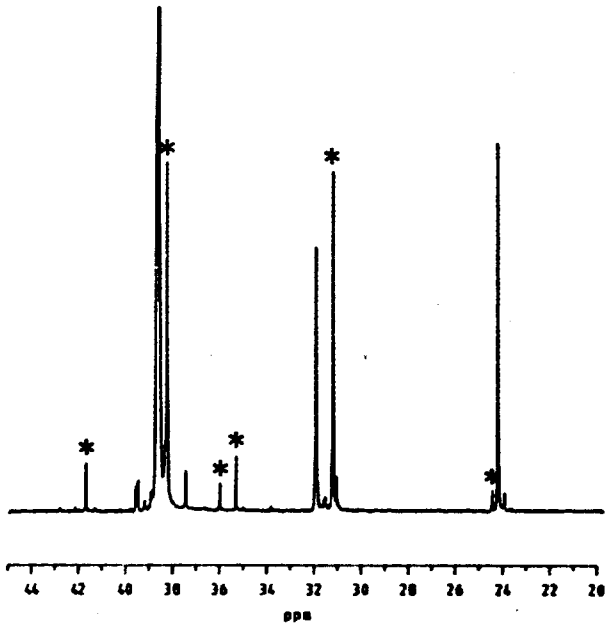


Figure 3: ^{13}C *NMR of LP-12 polysulfide prepolymer containing DMDS (8 phr). (*) denotes peaks arising from DMDS.*

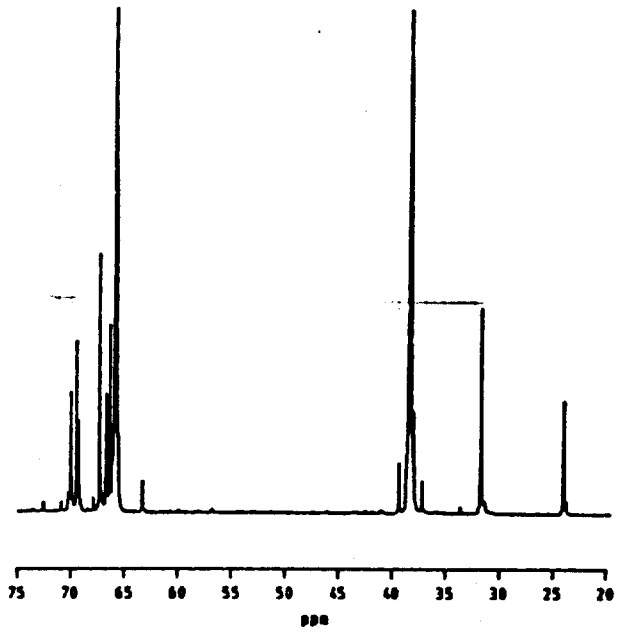
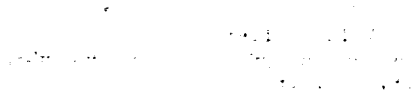


Figure 4: ^{13}C *NMR of LP-12 polysulfide prepolymer.*

The possibility of these peaks being due to the formation of a trisulfide was discarded when it was found that the trisulfide carbons (8) gave rise to resonances slightly down field from those of the disulfides (9).



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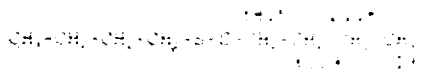

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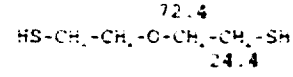
Despite not being able to unambiguously assign the two peaks at 31.4 and 38.4 ppm, the results clearly indicate that PR-1770 B-2 sealant is modified when interacted with DMDS. The data also indicate that the dithiol has been largely incorporated into the prepolymer with only a small portion of the free thiol being present as shown by the low intensities of the peaks at 24.7 and 36.1 ppm. The amount of DMDS incorporated into LP-12 appears to be approximately 95% at 8 parts per hundred rubber (phr) based on the free dithiol peak at 36.1 ppm and the combination of the disulfide peak at 35.5 ppm and the unassigned peak at 31.4 ppm. This corresponds to 20% more than in PR-1770 B-2 based on the relative intensities of the peaks at 32.1 ppm compared with the sum of the intensities at 31.4 and 35.5 ppm which suggests a DMDS content of 6.8 phr

Unlike with DMDS, the addition of DMDE to LP-12 prepolymer resulted in the appearance of only three additional peaks in the ^{13}C NMR spectrum (38.4, 69.2 and 72.4 ppm, Fig.-5) compared with the LP-12. ~~These peaks~~ corresponded with those in the spectra of unreacted (10) and oxidized DMDE (11). While free DMDE could barely be detected at 3.7 phr, at 7.2 phr it was estimated that approximately 90% of the dithiol was incorporated into the prepolymer based on the ratios of the peak heights at 72.4 and 69.2 ppm.



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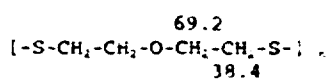

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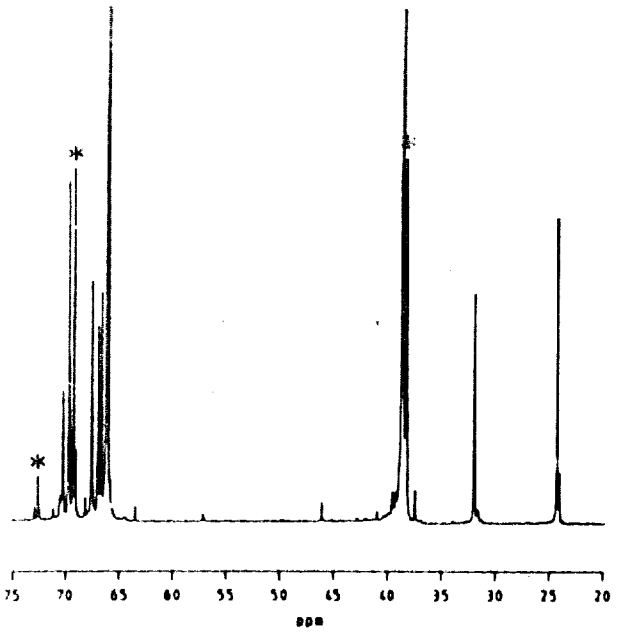

Figure 5: ^{13}C NMR of LP-12 polysulfide prepolymer containing DMDP (10 phr)
(*) denotes peaks arising from DMDP

There are various factors affecting the thermal stability of the cured prepolymers and sealants, but the chemical composition of the polymer chain is fundamental. Other factors include the nature of the curing agents and fillers present. It is necessary to eliminate these contributions before conclusions can be drawn about the effects of polysulfide prepolymer composition on the thermal stability of cured prepolymer or compounded sealant.

In order to compare the thermal stability of the Permapol PR-1770 B-2 sealant with that of the unmodified equivalent, PR-1750 B-2, samples of the two sealants were heat aged at 182°C for various periods and the physical properties evaluated. Similarly, samples of PR-1770 B-2 prepolymer, cured with PR-1770 B-2 cure paste, were exposed under the same conditions in order to determine the effects of fillers on the thermal stability of the sealants. Comparisons were made with PR-1750 B-2 prepolymer cured with the cure paste supplied with the sealant and with the PR-1770 B-2 cure paste (Table 1) to determine the contribution of the cure paste to the thermal stability of the cured polysulfide. Details of the polysulfide formulations are given in Table 1.

Table 1: Formulation of Polysulfide Samples

Prepolymer	Modification[a]	Thiol Content[b] (%)	Cure Paste[c] (phr)	Viscosity[d] (Poise)
PR-1750 B-2	-	1.5	15.0[e]	440
			18.7	
PR-1770 B-2	-	2.8	18.7	277
LP-32	-	1.6	10.7	690
	DMDE 3.6	3.2	21.0	130
	DMDE 7.2	4.7	30.9	45
	DMDS 4.0	3.2	20.8	130
	DMDS 8.0	4.6	30.5	47
LP-2	-	1.8	14.6	690
	DMDE 3.6	3.9	22.6	112
	DMDE 7.2	6.2	32.5	40
	DMDS 4.0	4.0	22.5	123
	DMDS 8.0	6.3	32.2	45
LP-12	-	1.5	9.6	715
	DMDE 3.6	3.1	20.3	189
	DMDE 7.2	4.6	30.2	40
	DMDS 4.0	3.1	20.1	107
	DMDS 8.0	4.5	29.8	44

a Additive in phr (w/w), dimercapto diethyl ether (DMDE), dimercapto diethyl sulfide (DMDS)

b Determined by IR [8].

c Cure paste from PR-1770 B-2 was used maintaining the same ratio of cure paste to thiol content as in PR-1770 B-2.

d Measured at 25°C using a Brookfield RVF viscometer, spindle 6 at 10 r/min

e PR-1750 B-2 cure paste was used as supplied by the manufacturer using the recommended ratio but allowing for the absence of fillers.

Weight loss determinations indicate little difference between PR-1770 B-2 and PR-1750 B-2 sealants (~ 11% after 10 h) with the latter showing slightly lower weight losses than the former (Fig. 6a). However, the PR-1770 B-2 cured prepolymer shows substantially higher weight losses than the PR-1750 B-2 cured prepolymers. There is little difference between the PR-1750 B-2

prepolymer cured with PR-1750 B-2 and PR-1770 B-2 cure pastes indicating that there is no significant contribution of the cure pastes to the thermal stability of the polysulfides. The prepolymer content of PR-1770 B-2 (54%) is similar to that of PR-1750 B-2 (60%) and on the basis of the weight losses shown by the sealants the maximum weight losses of these prepolymers should be approximately 22% as in the case of the PR-1770 B-2 prepolymer. However, the PR-1750 B-2 cured prepolymers have unexpectedly low maximum weight losses (~ 15%), suggesting the presence of volatile or less thermally stable components in the PR-1770 B-2 prepolymer compared with that of PR-1750 B-2.

Hardness measurements show an initial softening within 3 h of heat ageing of all specimens except PR-1770 B-2 sealant, followed by a gradual increase (Fig. 6b). As expected both compounded sealants are significantly harder than the cured prepolymers. The cured PR-1770 B-2 prepolymer appears to be softer than the cured PR-1750 B-2 prepolymers and this relationship is evident for approximately the first 5 hours of heat ageing after which the hardness increases to the level of the cured PR-1750 B-2 prepolymer. This behaviour is consistent with the high weight loss of the cured PR-1770 B-2 prepolymer (Fig. 6a).

The modulus at 100% elongation is highest for both the compounded sealants as expected (Fig. 6c). After 5 h of heat ageing the specimens become brittle and break before reaching 100% elongation. The cured prepolymers have a modulus approximately 10 times lower than the sealants, with that of the PR-1770 B-2 prepolymer slightly lower than the PR-1750 B-2 analogue. After 6.5 h the cured prepolymers become too brittle to reach an elongation of 100%.

The greatest elongation at breaking point is shown by the cured PR-1770 B-2 prepolymer (Fig. 6d). The PR-1750 B-2 prepolymer cured with PR-1770 B-2 cure paste has slightly greater elongation properties than both the compounded sealants and the PR-1750 B-2 prepolymer cured with PR-1750 B-2 cure paste which show very similar properties. All samples show diminished elongation properties after 1 h of heat ageing.

The tensile strength of the compounded sealants was found to be approximately five times greater than that of the cured prepolymers (Fig. 6e). While the tensile strength of the cured prepolymers is largely unaffected by heat ageing up to a period of 10 hours, the compounded sealants suffer a slight reduction in tensile strength after heat ageing.

The general trend appears to be a gradual hardening of the elastomers on heat ageing with the thiol modified elastomers showing no significant resistance to this process compared with the unmodified analogues.

Modifications of LP-2, LP-32 and LP-12 polysulfide prepolymers have also been reported [6]. All three prepolymers have similar chemical compositions with the major difference being the extent of crosslinking (2.0, 0.5 and 0.2%, respectively [13]). In order to evaluate the effect of these modifications both DMDS and DMDE were incorporated, in similar molar concentrations, into these prepolymers and the amount of curing agent (PR-1770 B-2 cure paste) required was based on the thiol content of the modified prepolymer using the same ratio of cure paste to thiol content as in PR-1770 B-2 (Table 1).

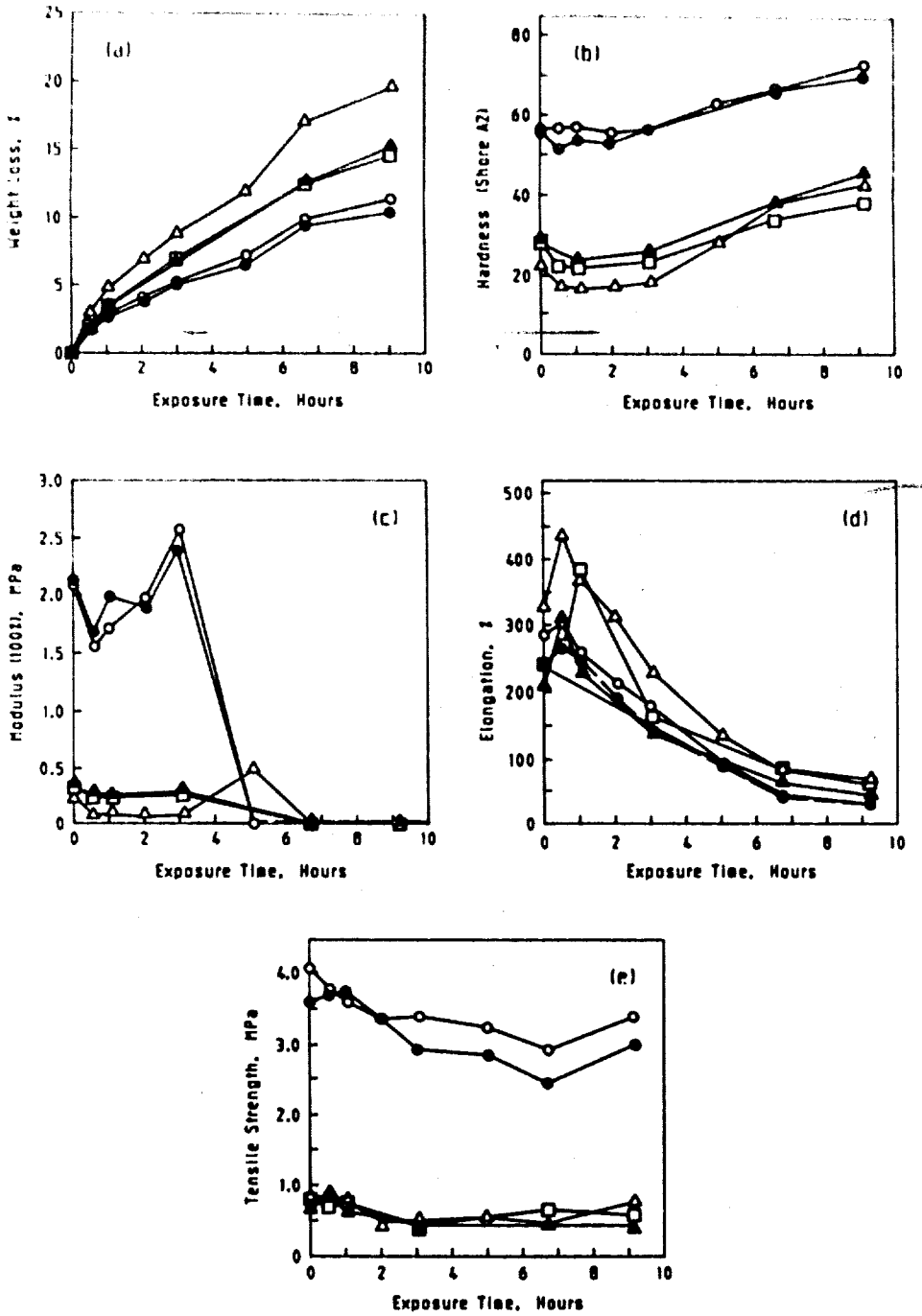

Figure 6: Mechanical properties of sealants after heat ageing at 182°C.
(●) PR-1750 B-2 sealant, (○) PR-1770 B-2 sealant, (△) PR-1770 B-2 prepolymer cured with PR-1770 B-2 cure paste, (▲) PR-1750 B-2 prepolymer cured with PR-1750 B-2 cure paste, (□) PR-1750 B-2 prepolymer cured with PR-1770 B-2 cure paste.

Heat ageing of cured Thiokol LP-21 prepolymer and the prepolymers incorporating DMDS and DMDE result in higher weight losses for the modified prepolymer compared with the unmodified material (Fig. 7a). The weight loss increases with the proportion of added dithiol. After 10 hours of ageing a maximum weight loss of 21% was evident for the specimens with 7.2 phr DMDE and 8.0 phr DMDS which is comparable with that of the PR-1770 B-2 prepolymer (Fig. 6a).

Unlike the elastomers derived from PR-1770 B-2 and PR-1750 B-2, the hardness of the modified LP-32 prepolymers generally decreases rapidly during exposure reaching a minimum after 2 to 5 hours of heat ageing after which it increases again indicating embrittlement (Fig. 7b). The specimens containing the highest concentrations of added dithiol were most affected. These changes are more dramatic than those shown by the PR-1770 B-2 prepolymer.

The modulus measurements at 100% elongation follow the hardness trends with an overall decrease in modulus reaching a minimum between 2 and 5 hours and a subsequent increase after 5 hours (Fig. 7c). There is little difference between the various samples.

Similar trends are evident in the elongation characteristics (Fig. 7d). Maximum elongation is reached after approximately two hours after which there is a steady decrease to pre-exposure values. Of these specimens, unmodified LP-32 prepolymer is least affected with a four fold increase in elongation after two hours of heat ageing compared with an eight fold increase for the 7.2 phr DMDS modified LP-32.

Tensile strength results are consistent with the other trends but there is only a partial recovery in this property after reaching a minimum during three to five hours of heat ageing (Fig. 7e). The subsequent increase in tensile strength is an indication of increasing embrittlement. The results show no apparent improvement in resistance to heat ageing on addition of DMDE and DMDS to LP-32 prepolymer.

Heat ageing of the modified and unmodified cured Thiokol LP-2 prepolymers (Fig. 8a) resulted in weight losses similar to those of the LP-32 analogues (Fig. 7a) whereas the reductions in hardness of the cured LP-2 prepolymers (Fig. 8b) are not as marked as those of the LP-32 analogues (Fig. 7b) and the minimum hardness levels are only slightly less than those of the PR-1750 B-2 prepolymers (Fig. 6b). As with the other modified prepolymers, the extent of weight loss is dependent on the concentration of the added modifying dithiol as this increases the low molecular weight component of the polymer.

Reductions in the modulus of the cured LP-2 prepolymers, after heat ageing (Fig. 8c), are not as substantial as those of the LP-32 series (Fig. 7c) even though the trends are similar with the elastomers showing softening with increase in exposure time followed by an increase in embrittlement after six hours. Specimens containing the highest concentrations of added thiol show a greater increase in embrittlement compared with the unmodified LP-2 with the effect of DMDS being slightly greater than that of DMDE. The PR-1750 B-2 and PR-1770 B-2 cured prepolymers by comparison initially have a lower modulus which gradually decreases on exposure and shows no indication of embrittlement (Fig. 6c).

As expected, the changes in elongation with heat ageing are substantially less in the case of the LP-2 prepolymers (Fig. 8d) than the LP-32 analogues (Fig. 7d). In both cases the maximum elongation prior to fracture of the elastomers is significantly increased on heat ageing compared with the cured PR-1770 B-2 and PR-1750 B-2 prepolymers (Fig. 6d). Specimens with the highest concentration of added thiol are affected to a greater extent with no substantial difference being apparent between the two thiols.

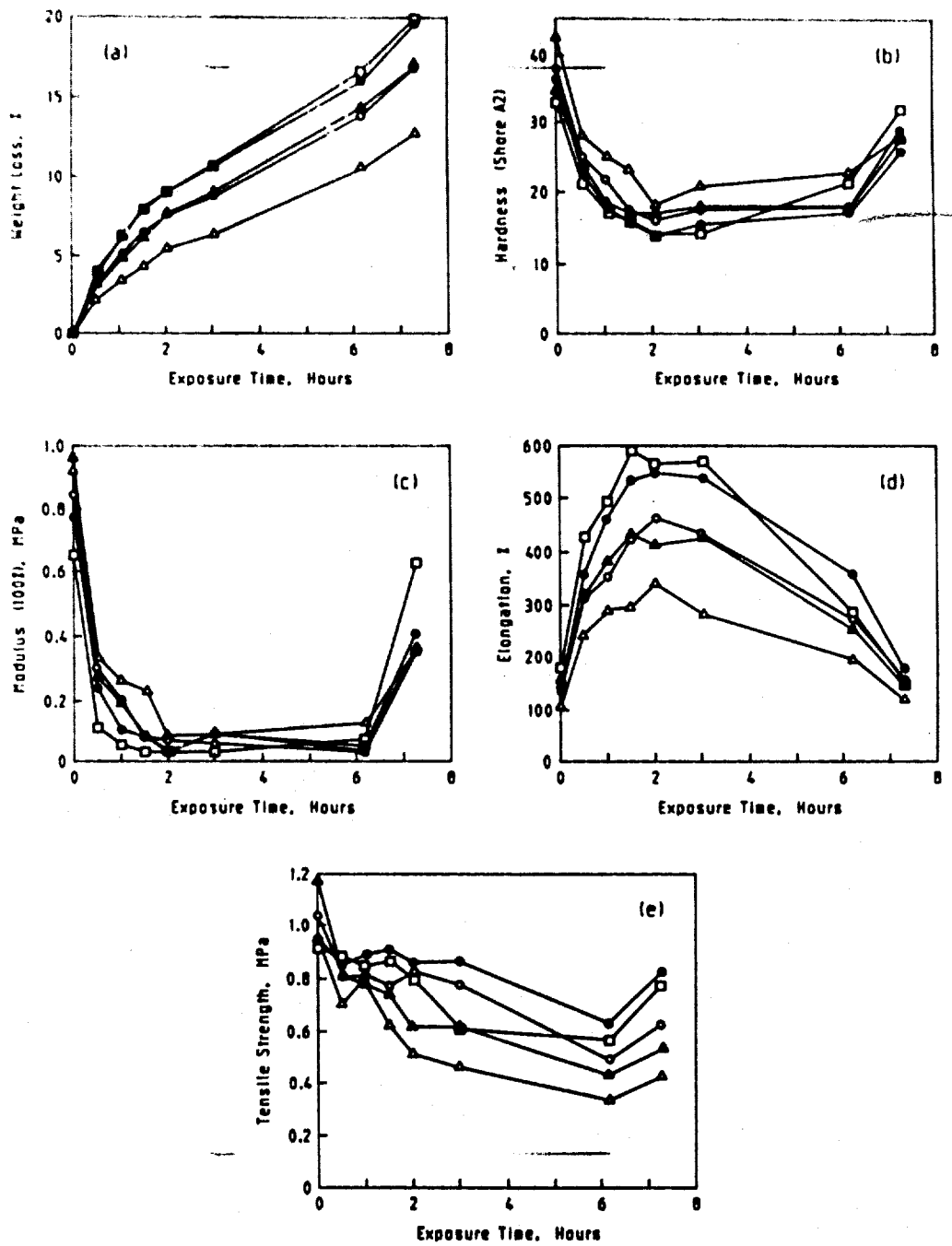

Figure 7: Mechanical properties of sealants after heat ageing at 182°C, in air.
(△) LP-32 prepolymer, (○) LP-32 + DMDE (3.6 phr), (●) LP-32 + DMDE (7.2 phr), (▲) LP-32 + DMDS (4.0 phr), (□) LP-32 + DMDS (8.0 phr).

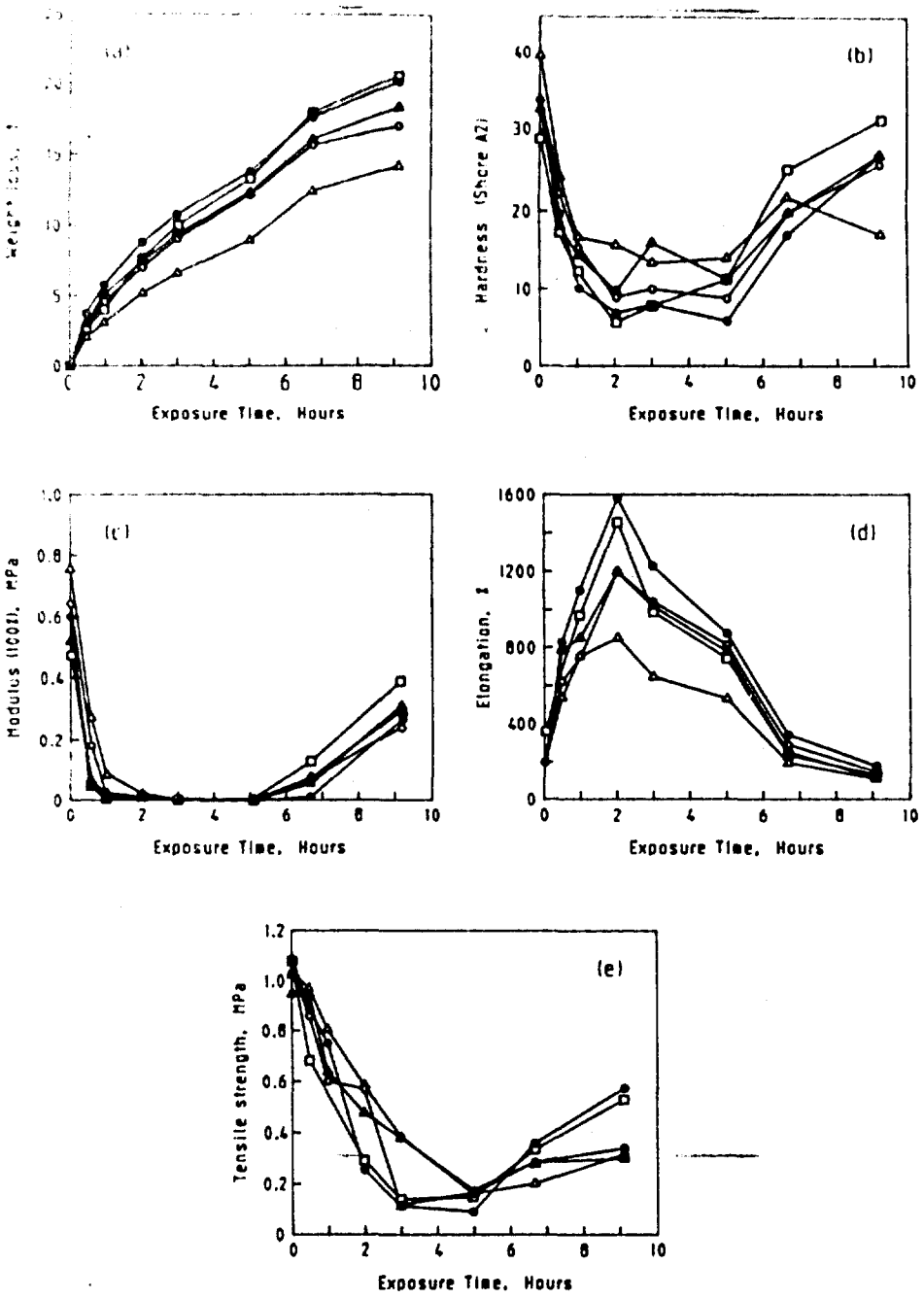

Figure 8: Mechanical properties of sealants after heat ageing at 182°C, in air. (△) LP-2 prepolymer, (○) LP-2 + DMDE (3.6 phr), (●) LP-2 + DMDE (7.2 phr), (▲) LP-2 + DMDS (4.0 phr), (□) LP-2 + DMDS (8.0 phr).

Similarly, changes in tensile strength of the cured LP-2 prepolymers (Fig. 8e) are not affected to the same extent as those of the LP-32 group (Fig. 7e) and are of similar magnitude to those of the cured PR-1750 B-2 and PR-1770 B-2 prepolymers (Fig. 6e). After 7.5 hours heat exposure the tensile strengths of the modified LP-2 prepolymers are slightly higher than the unmodified prepolymer with those containing the highest concentrations of modifying thiol showing slightly higher tensile strengths over the lower concentrations. There is little difference between the two thiols in terms of their effect on the tensile strengths after six hours of exposure.

As the only difference between LP-2 and LP-32 is in the concentration of the crosslinking agent, the difference in properties between the two prepolymers may be attributed to this factor.

While the results indicate that the thermal stability of thiol modified Thiokol prepolymers are not improved compared with the unmodified prepolymers, weight loss measurements published on DMDS and DMDE modified Thiokol LP-12 suggest the reverse [6]. Comparisons of weight losses of cured prepolymers at 182°C after eight hours have suggested that a DMDS modified LP-12 prepolymer was least affected, followed by a DMDE modified LP-12 prepolymer with the unmodified prepolymer having the lowest thermal stability. Similar experiments in our laboratory with Thiokol LP-12 have indicated that the modifications result in increased weight losses of the cured prepolymers compared with that of the unmodified cured LP-12 (Fig. 9). This is consistent with the data for LP-2 and LP-32 thiol modified systems previously discussed. Although the weight losses for the DMDS modified prepolymer appear to be higher than for the DMDE analogue in this case, the behaviour of the other modified prepolymers shows that there is little difference in the effect of the two thiols (Figs 7 and 8).

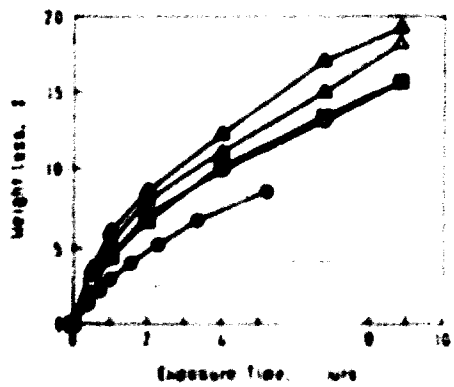

Figure 9: Weight losses of sealants after heat ageing in air at 182°C. (■) LP-12 prepolymer, (○) LP-12 + DMDE (3.6 phr), (●) LP-12 + DMDE (7.2 phr), (▲) LP-12 + DMDS (4.0 phr), (□) LP-12 + DMDS (8.0 phr).

The introduction of a monomeric dithiol into a polysulfide prepolymer increases the content of low molecular weight species and the thiols in the system (Table 1). Consequently, more curing agent is required and there is a greater probability of low molecular weight prepolymer remaining after the curing process. On heat ageing, the latter would be expected to contribute to the weight loss of the cured prepolymer or sealant through volatilization. Under these circumstances it is not surprising that the thiol modified prepolymers show greater weight losses on heat ageing than the unmodified analogues. The presence of the low molecular weight components would also be expected to affect the mechanical properties of the cured polysulfide by acting as plasticizers. Thus the contributions of the thiols introduced into the polysulfide prepolymers may be masked by the behaviour of the low molecular polymer fragments produced by the thiol-disulfide interchange reaction (eq 1).

4. Conclusions

It has been claimed that the thermal stability of Thiokol polysulfide prepolymers may be enhanced by the incorporation of dimercapto ethers (e.g. DMDE and DMDS). A similar modification was undertaken using Thiokol LP-2, LP-32 and LP-12, utilizing the thiol-disulfide interchange reaction. The products were shown to be of similar chemical composition to the Permapol PR-1770 B-2 prepolymer. Heat ageing at 182°C has failed to show a significant advantage of these modifications in improving the resistance of polysulfide prepolymers to exposure at elevated temperatures. Similar conclusions were drawn from the comparison of PR-1770 B-2 with PR-1750 B-2 sealant and the cured prepolymers extracted from the uncured sealants when tested under the same conditions.

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Thermal stability of sealants for military aircraft: Modification of polysulfide prepolymers with ether and thioether monomers

AUTHOR(S)	CORPORATE AUTHOR
P.J. Hanhela and W. Mazurek	DSTO Materials Research Laboratory PO Box 50 Ascot Vale, Victoria 3032

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ABSTRACT

The effect of modifying Thiokol polysulfide prepolymers with dimercapto diethyl ether and dimercapto diethyl sulfide, on the resistance to heat ageing has been examined together with a commercially modified (PR-1770 B-2) and an unmodified equivalent sealant (PR-1750 B-2). Mechanical tests performed on specimens, after heat ageing at 182°C, indicated that the modifications did not improve the heat resistance of polysulfide sealants.

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P.J. Hanhela and W. Mazurek

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