

Effect of Curing Agents on Some Properties of a Polysulfide Sealant

R. RAMASWAMY and P. SASIDHARAN ACHARY, *Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Trivandrum 695 022, India*

Synopsis

The effect of curing agents on the properties of a polysulfide sealant composition was investigated. Commercially used curing agents, namely, lead dioxide, manganese dioxide, and ammonium dichromate, were selected for this study. It was established that curing agents affect joint strengths, stress-strain properties, dynamic mechanical properties, and thermal stability of the sealant. Sealant cured with ammonium dichromate had highest shear bond strength, ultimate tensile strength, modulus, and thermal stability, whereas these properties were lowest for lead-dioxide-cured sealant. Peel bond strength and elongation at break were highest for lead-dioxide-cured sealant. The observed changes in properties were attributed to the difference in crosslink density of the cured sealant, produced by the curing agents. The curing agents have no appreciable effect on the fuel resistance of the polysulfide sealant.

INTRODUCTION

Sealants based on polysulfide liquid polymers are widely used in aircraft industry, construction, ship building, and gas main sealing. Polysulfide sealants will continue to grow in application, as performance demands increase.¹ Some of the advantages of polysulfide polymers are:

1. Excellent adhesion to a variety of substrates when properly compounded with specific additives.
2. Maintenance of integrity in the seal under extension and compression by relieving the stress under fixed strain through interchange of disulfide linkages.²
3. Outstanding fuel resistance because of the sulfur linkages in the chain which enhances the solubility parameter of the polymer.²
4. Excellent resistance to ozone, sunlight, and weathering because of the oxygen saturated backbone.
5. Very low gas and vapor permeability.

Polysulfide sealant development was initiated by Thiokol Chemical Corp. in 1932 acquiring sole right to the patent.³ Liquid polysulfide polymers form the basic ingredient of the sealant formulations. The chemistry, cure mechanisms, reinforcement, and various applications of liquid polysulfide polymers are discussed in detail by Berenbaum and Panek.⁴

In addition to polysulfide liquid polymer, a sealant generally contains other ingredients like fillers, adhesion promoter, plasticizer, and curing agent. A wide variety of curing agents have been used to convert liquid polysulfide polymer to an elastomer.⁵ In this study the effect of curing agents on the properties of a polysulfide sealant have been examined. Although a

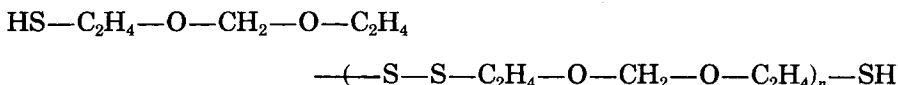
number of curing agents are used, it was decided to restrict the study to commercially used curing agents namely lead dioxide (PbO_2), manganese dioxide (MnO_2), and ammonium dichromate $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]$. The cure reaction proceeds at room temperature with these curing agents by oxidation of terminal—SH groups to form disulfide linkages as shown below:



The curing agents serve as oxygen donor (electron acceptor) and yield disulfide linkages by linking two thiol groups with the liberation of water as byproduct. To minimize other undesirable side reactions of —SH groups, only high molecular weight liquid polysulfide polymers having low —SH content (1–2%) are generally used.⁶ To effect complete dispersion of the curing agent throughout the polymer, the curing agent is added with plasticizer or solvent in the form of paste or liquid. As would be expected, the cure rate is accelerated by alkaline environment and retarded by acidic condition. Temperature and humidity also affect the cure reaction. Accelerators are used to effect a complete cure.

EXPERIMENTAL

The liquid polysulfide resin used in this study is the mercaptan-terminated polymer having the formula



with 2% of thiol-terminated branched chains. It is synthesised in our laboratory by a conventional procedure.² Table I illustrates the characteristics of the resin used in our experimental study.

The basic sealant formulation used for this study is shown in Table II. The resol phenolic resin was prepared in the laboratory from phenol and formaldehyde using sodium hydroxide as catalyst and was used as a 70% solution in methyl ethyl ketone. Other ingredients used are commercially available materials. A single batch of raw materials was used throughout the study to minimize variations in the properties.

A master batch of component A was made by mixing polysulfide resin, phenolic resin, TiO_2 , and silica in a three-roll mill. The phenolic resin was used to extend the application time of the sealant and to improve adhesion.⁷ Fillers titanium dioxide and silica were added to modify the physical properties of the sealant. Component B was made separately by mixing curing agent, dimethyl formamide (solvent) and diphenyl guanidine (accelerator). For lead dioxide and manganese dioxide, component B was in the form of

TABLE I

—SH content of the resin	1.71%
Mol. weight by VPO	3125
Viscosity at 25°C	35,200 cP
Sp. gravity	1.303

TABLE II

Component A	
Polysulfide liquid polymer	100 g
Phenolic resin	3 g
Titanium dioxide	40 g
Silica	10 g
Component B	
Curing agent	Varies
Dimethyl formamide	10 mL
Diphenyl guanidine	2.5 g

soft paste and for ammonium dichromate in the form of solution, as it was soluble in dimethyl formamide. Appropriate amounts of component A and component B were mixed together and adhesion test specimens and slabs were prepared. The specimens were cured for 24 h at room temperature followed by 24 h at 70°C, stored at room temperature before conducting the tests.

Adhesion, stress-strain property, and crosslink density of the sealant were measured using Instron as per procedures reported earlier.^{7,8} Hardness was determined from the slabs by Durometer. Dynamic mechanical properties were measured using Rheovibron. A vibration frequency of 35 Hz was applied to the test piece (20 mm length, 10 mm wide, 1.5 mm thick) from -80 to +50°C. The output data from the apparatus was recorded and calculated with a computer.

The thermal stability of the sealant samples were checked by thermogravimetric analysis using a DuPont 951 Thermogravimetric Analyzer. The cured sealant sample (7 ± 1 mg) was heated at a rate of 10°C/min in N₂ atmosphere.

Fuel resistance was checked by the resistance of the sealant to swell or dissolve in fuel. Approximately 5 g cured sealant sample was kept immersed in 50 g of fuel ATRK-50 at 30°C for 30 days. The weight increase of the sealant sample was determined after blotting it dry with filter paper and the percentage of swelling was determined. Fuel after the immersion was evaporated, and the dry residue content determined.

RESULTS AND DISCUSSION

Optimum Mix Ratios of Curing Agents

Even though we can readily calculate the stoichiometric ratio of the curing agent for polysulfide resin from the —SH content, it has been our experience that this ratio is not necessarily the optimum. Hence we determined the optimum mix ratios of the curing agent from tensile strength tests on cured slabs. The curing condition of 1 day at room temperature followed by 1 day at 70°C was kept constant throughout the study. Results shown in Figure 1 indicates that mix proportion of the curing agent is important for optimum results. Maximum tensile strengths were obtained at a level of 10 phr PbO₂, 6 phr MnO₂, and 2.5 phr (NH₄)₂Cr₂O₇, and these mix ratios were chosen for the study.

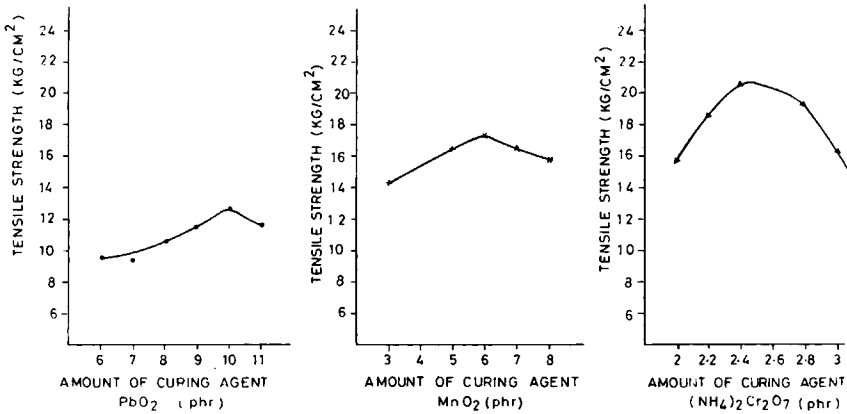


FIG. 1. OPTIMUM MIX RATIOS OF CURING AGENTS
FOR POLYSULPHIDE SEALANTS

Fig. 1. Optimum mix ratios of curing agents for polysulfide sealants.

Adhesion

Good adhesion of the sealant to the substrate is an essential factor in maintaining the seal and in utilizing the mechanical strength of the sealant. The adhesion of the sealant was measured as the force required to separate the sealant from the aluminium substrate in terms of shear and peel bond strength. The results summarized in Table III indicate that cohesive failure is observed irrespective of the curing curing agents. However, with the three curing agents, different peel and shear bond strengths were obtained. This can be attributed to the changes in mechanical properties of the sealant with the curing agent as indicated in Table IV. Kaelble⁹ showed that for cohesive failure, a direct proportionality exists between peel bond strength at 180° angle and the work to fracture parameter (S_c) of the adhesive. Kaelble's expression for work to fracture parameter is

$$S_c = \sigma_0^2/2Y$$

where σ_0 is the failure force and Y is the Young's modulus of the adhesive. From Figure 2, the following order could be assigned for the work to fracture parameter: PbO_2 -cured sealant > $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ -cured sealant > MnO_2 -cured sealant. The same order can be seen for the peel bond strength of the

TABLE III
Effect of Curing Agents on the Adhesion of Polysulfide Sealant

Polysulfide sealant	Peel strength ^a (kg/cm)	Shear strength ^a (kg/cm ²)
(i) Cured with PbO_2	10.4 ^c	11.6 ^c
(ii) Cured with MnO_2	5 ^c	15.2 ^c
(iii) Cured with $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	8.14 ^c	20.4 ^c

^a c indicates cohesive failure in sealant.

TABLE IV
Effect of Curing Agents on the Mechanical Properties of Polysulfide Sealants

Polysulfide sealant	Tensile strength (kg/cm ²)	Elongation (%)	Stress at 100% elongation	Hardness
(i) Cured with PbO ₂	12.6	440	5.4	50
(ii) Cured with MnO ₂	17.3	178	12.6	58
(iii) Cured with (NH ₄) ₂ Cr ₂ O ₇	20.6	182	14	64

sealants. Highest shear bond strength was obtained for ammonium-dichromate-cured sealant which possesses highest tensile strength and modulus.

Stress-Strain Properties

Probably the most widely used mechanical test for the sealant is the stress-strain behavior. The stress-strain curve provides the load-deflection relationship of the sealant. The effect of the three curing agents on the stress-strain curve of the sealant is depicted in Figure 2. All the three curves exhibit a monotonic increase in stress with increasing strain. The ultimate tensile strength, elongation at break, and the stress at 100% elongation taken from the stress-strain curve are listed in Table IV. The difference in the stress-strain properties of the sealant are due to the differences in the crosslink densities of the sealant produced by the curing agents. The effect of curing agents on the crosslink densities are shown in Table V. Among the three sealant samples, ammonium-dichromate-cured sealant has the highest crosslink density which shows highest modulus and tensile strength. The lowest crosslink density is for the PbO₂-cured sealant

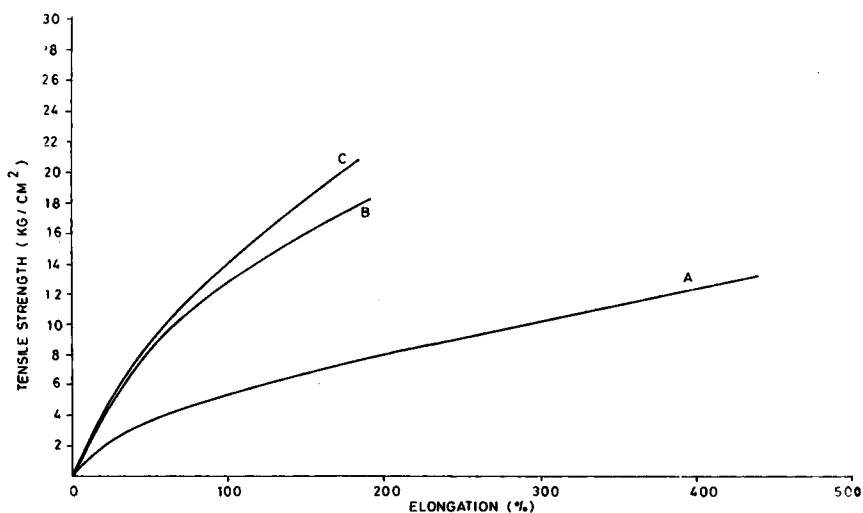


FIG. 2. STRESS-STRAIN CURVE FOR POLYSULPHIDE SEALANT

A. CURED WITH PbO₂ B. CURED WITH MnO₂ C. CURED WITH (NH₄)₂Cr₂O₇

Fig. 2. Stress-strain curve for polysulfide sealants. Cured with: (A) PbO₂; (B) MnO₂; (C) (NH₄)₂Cr₂O₇.

TABLE V
Effect of Curing Agents on the Crosslink Density of Polysulfide Sealant

Polysulfide sealant	Crosslink density $\nu_e \times 10^{-5}$ (mol/cc)
(i) Cured with PbO_2	2.51
(ii) Cured with MnO_2	3.14
(iii) Cured with $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$	6.64

sample, which gives highest elongation and lowest modulus and tensile strength.

Dynamic Mechanical Properties

Dynamic mechanical test measures the deformation of the material in response to vibrational forces.¹⁰ Polysulfide sealant has good vibrational damping properties, but the modulus is very sensitive to temperature and frequency.¹¹ Elastic modulus E' and damping parameter $\tan \delta$ measured as a function of temperature for the polysulfide sealant cured with the three curing agents are shown in Figures 3–5. The maximum found in the

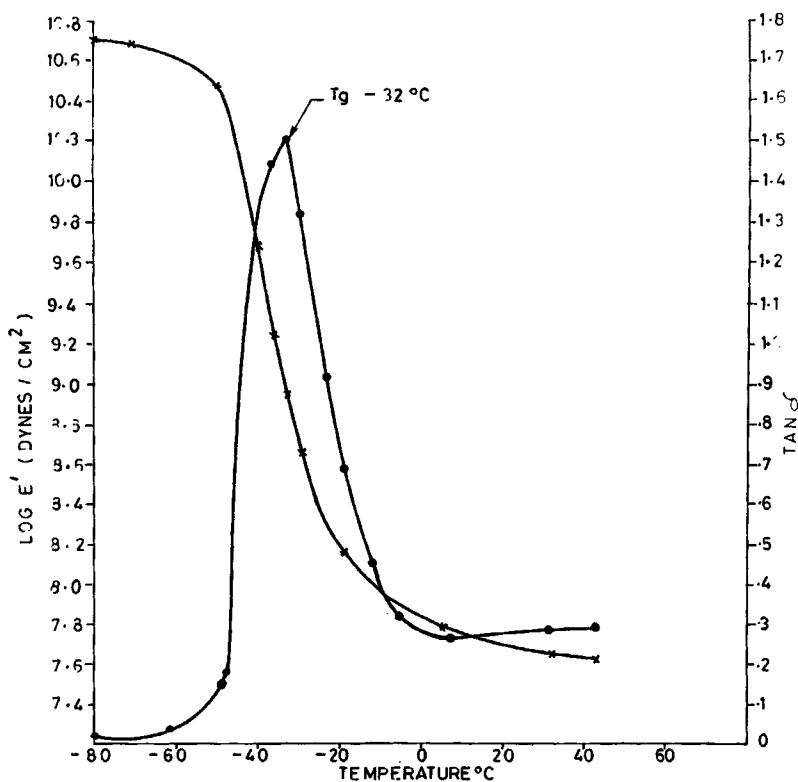


Fig. 3. Dynamic mechanical properties of polysulfide sealant cured with PbO_2 : (●) $\tan \delta$; (X) $\log E'$.

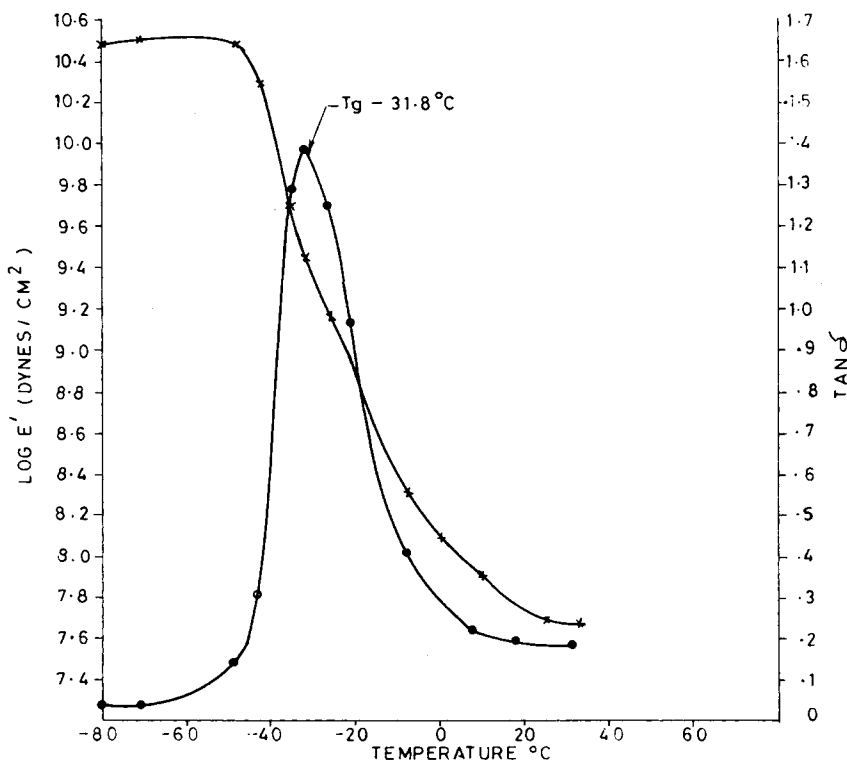


Fig. 4. Dynamic mechanical properties of polysulfide sealant cured with MnO_2 : (●) $\tan \delta$; (X) $\log E'$.

damping curve and the gradual decrease in modulus E' must be associated with the glass transition of the sealant. This is located at about -32°C . In this region the material changes from rubbery state to glassy state. The greater height of damping peak for lead-dioxide-cured sealant indicates its greater energy absorbing capability compared to the manganese-dioxide- and ammonium-dichromate-cured sealants. The higher value of $\tan \delta$ for lead dioxide cured sealant may be due to the lower crosslinking.¹²

Thermal Stability

We investigated the thermal stability of the polysulfide sealant cured with the three curing agents by means of TGA. The thermogravimetric traces of the polysulfide sealant cured with the three curing agents namely, lead dioxide, manganese dioxide, and ammonium dichromate, are given in Figure 6, and the weight loss data, IDT (initial decomposition temperature), and T_{\max} (the temperature where the rate of weight loss is maximum) are compiled in Table VI. Based on the results, one might assign the following thermal stability ranking to the polysulfide sealant cured with the three curing agents. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ -cured sealant > MnO_2 -cured sealant > PbO_2 -cured sealant. This can be attributed to the differences in the crosslink densities of the sealant produced by the curing agents (Table V). Increase

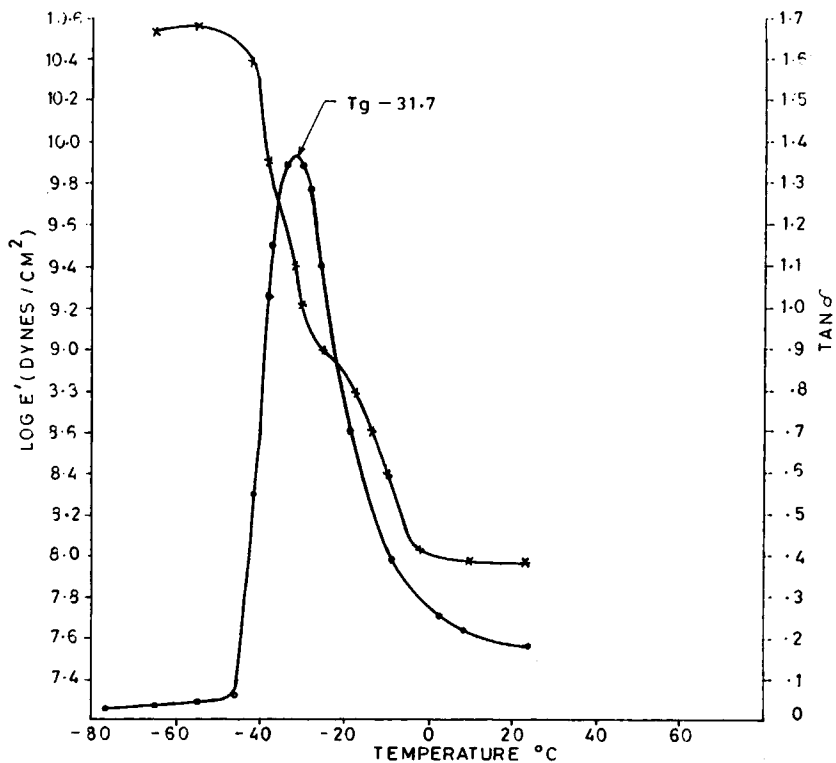


Fig. 5. Dynamic mechanical properties of polysulfide sealant cured with $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$: (●) $\text{tan } \delta$; (X) $\text{log } E'$.

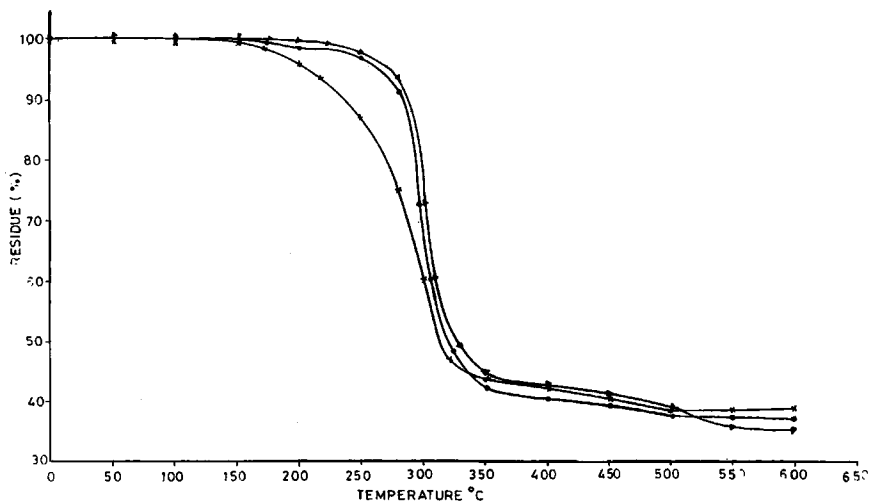


Fig. 6. Thermogravimetric traces of polysulfide sealant in N_2 atmosphere. Cured with: (X) PbO_2 ; (●) MnO_2 ; (Δ) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

TABLE VI
Effect of Curing Agents on the Thermal Stability of Polysulfide Sealant

Polysulfide sealant	Temp of various % weight loss (°C)						IDT (°C)	T_{max} (°C)
	10%	20%	30%	40%	50%	60%		
(i) Cured with PbO ₂	215	250	265	275	285	292	140	290
(ii) Cured with MnO ₂	270	280	292	295	300	305	160	300
(iii) Cured with (NH ₄) ₂ Cr ₂ O ₇	275	290	300	305	307	320	200	305

in crosslink density results in an increased thermal stability simply because more bonds will have to be broken before the total network breakdown occurs. The highest thermal stability of ammonium-dichromate-cured polysulfide sealant can be attributed to its higher crosslink density.

Fuel Resistance

For applications in aircraft fuel tanks, the sealant must maintain fuel resistance and also must contain minimum extractable materials. The fuel contamination test in combination with the amount of swelling is a good guide for evaluating the resistance of the sealant in a fuel. The effect of the three curing agents on the resistance of the sealant to swell or dissolve in aviation fuel ATFK-50 is shown in Table VII. It can be seen that curing agents have no appreciable effect on the fuel resistance of the sealant. The fuel resistance of the sealant is dependent largely on the percentage of sulfur content in the base polymer. Higher sulfur content gives better fuel resistance. The presence of sulfur in the backbone enhances the solubility parameters (δ) of the polymer and resist the dissolution or swelling of the polymer in hydrocarbon fuels and retain its properties even after prolonged exposure.⁴

CONCLUSIONS

Some properties of a polysulfide sealant, cured with three commercially used curing agents, were investigated. Based on the experimental results obtained, it has been shown that curing agent has an influence on the mechanical, adhesive, and thermal properties of the sealant. These changes are due to the variations in crosslinking density of the cured sealant produced by the curing systems. Fuel resistance of the polysulfide sealant is unaffected by the curing agents.

TABLE VII
Effect of Curing Agents on the Fuel^a Resistance of the Polysulfide Sealant

Polysulfide sealant	Swelling in fuel (%)	Fuel contamination (%)
(i) Cured with PbO ₂	1.49	0.044
(ii) Cured with MnO ₂	1.27	0.051
(iii) Cured with (NH ₄) ₂ Cr ₂ O ₇	1.25	0.045

^a ATFK-50.

References

1. T. C. Lee, *Eur. Rubber J.*, **165**, 26 (1983).
2. A. V. Tobolsky and W. J. MacKnight, *Polymeric Sulphur and Related polymers*, Polymer Reviews Vol. 13, Wiley-Interscience, New York, 1965, p. 39.
3. J. Patrick, U.S. Pat. 1890191 (1932).
4. M. B. Berenbaum and J. R. Panek, in *Polyethers, Part III*, N. G. Gaylord, Ed. Wiley-Interscience, New York, 1962, p. 43.
5. J. R. Panek in *Polyethers Part III*, N. G. Gaylord, Ed., Wiley-Interscience, New York, 1962, p. 165.
6. R. H. Gobran and M. B. Berenbaum, *Polymer Chemistry of Synthetic Elastomers*, J. P. Kennedy and E. G. M. Tornquist, Eds., Wiley-Interscience, 1969, Vol. XXIII, p. 805.
7. R. Ramaswamy and P. Sasidharan Achary, in *Adhesive Joints, Formation, Characteristics and Testing*, K. L. Mittal, Ed., Plenum, New York, 1984, p. 31 (in press).
8. R. Ramaswamy and P. Sasidharan Achary, *J. Adhesion*, **11**, 305 (1981).
9. D. H. Kaelble, *Adhesion and Cohesion*, P. Weiss, Ed., Elsevier, New York, 1962, p. 84.
10. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974.
11. N. J. DeLollis, in *Adhesives, Adherends, Adhesion*, Krieger, New York, 1980, p. 228.
12. T. Murayam, *Dynamic Mechanical Analysis of Polymeric Materials*, Material Science Monograph, Elsevier, New York, 1978, p. 86.

Received December 4, 1984

Accepted January 11, 1985