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Adhesion Development in a Polysulphide Sealant

R. RAMASWAMY and P. SASIDHARAN ACHARY

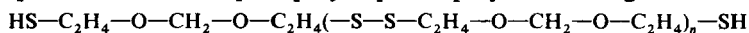
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The necessity for good adhesion in sealants and the mechanism of adhesion development in polysulphide sealants are discussed. The studies reported give the effect of co-reacting polysulphide resin with epoxy resin on the adhesion of a polysulphide sealant composition to an aluminium substrate and also on selected mechanical properties. The sealant was formulated from a mercaptan-terminated liquid polysulphide polymer. The liquid polymer was co-reacted with epoxy resin before formulating the sealant. Modification with epoxy resin improved the adhesion of the sealant. Adhesion is improved because of the presence of hydroxyl groups in the chain after co-reaction. The hydroxyl groups increase the ability of the polymer to remove the loosely adsorbed water layer present on the surface and establish strong interfacial forces with the surface.

INTRODUCTION

Polysulphide sealants find major utility as elastic sealants in aircraft fuel tanks, aircraft runways, ship building and building constructions. They generally contain polysulphide polymer, fillers, adhesion promoter, plasticizer and curing agent. The properties of the sealants are mainly dependent on the physical and chemical nature of the polymeric base used. The polymeric base generally used in polysulphide sealants is the conventional mercaptan-terminated liquid polysulphide polymer having the structure,



with a proportion of thiol-terminated branched chains. By the oxidation of thiol groups, the liquid polymer is cured to a rubber.

Adhesion development in Polysulphide sealant

Sealants are used to fill gaps or joints so as to prevent the passage of liquids or gases. Generally the gap is not a fixed space, but a constantly varying one,

with small movements at high frequencies as in aircraft or large movements at low frequencies as in buildings. To accommodate the movements without the disruption of the seal, good adhesion to the substrate is an essential requirement. Cohesive failure is preferred when the joint is broken.

For the development of good adhesion, the sealant has to wet and spread over the substrate and should establish molecular continuity between the sealant and the substrate. It should also establish strong interfacial forces either by simple van der Waals attractions or by the formation of chemical bonds or hydrogen bonds.¹ For wetting and spreading, the sealant should be in the liquid form and the surface energy of the sealant should be less than or equal to the surface energy of the substrate²

$$\gamma_L \leq \gamma_s$$

where

γ_L = surface tension of sealant (liquid)

γ_s = surface tension of substrate.

The surface energy of substrates like metals, concrete, glass, etc. are very high compared to the liquid polysulphide polymer and therefore wetting and spreading condition is theoretically satisfied and good adhesion can be expected. But it is observed that the adhesion of the polysulphide polymer to the above substrates is poor with interfacial failure. The poor adhesion can be due to the presence of a weak boundary layer³ which results in a failure at the interfaces much below the strength of the polymer. High energy surfaces when exposed to air are covered by adsorbed layers of water which can act as a weak boundary layer.⁴ There is spectroscopic evidence for surface hydroxyls and molecular water on high energy surfaces.⁵ In order to achieve good adhesion, the polymer has to remove the loosely adsorbed surface water layer. The low polarity of the polysulphide polymer suggests that it cannot remove this water layer. The structure also shows it cannot establish strong interfacial forces with high energy surfaces. The capacity to remove the surface water layer is enhanced by blending with appropriate additives called adhesion promoters. Phenolic resins, epoxy resins and mercaptan-terminated silane coupling agents are probably the most widely used adhesion promoters. It is assumed that these additives will migrate to the interface and solvate the water layer present on the surface, thereby achieving better molecular continuity between the sealant and the substrate. Polar groups of the adhesion promoters establish strong interfacial forces by physical interactions and improve the adhesion. Silane coupling agents solvate the water layer and form chemical bonds with high energy substrates.⁶

In the development of a polysulphide sealant from a mercaptan-terminated liquid polysulphide polymer, we used an epoxy resin based on bisphenol A and epichlorohydrin as adhesion modifier. The epoxy resin was incorporated

in the chain by coreacting it with polysulphide resin. The studies reported give the effect of coreacting polysulphide resin with epoxy resin on the adhesion of a sealant composition to an aluminium substrate. We also measured the changes in selected mechanical properties. The variables studied included the effect of various concentrations of an epoxy resin and different epoxy resins at a particular concentration. The liquid polysulphide resin was coreacted with epoxy resins before formulating the sealant.

An epoxy molecule joins two polysulphide molecules as shown in Figure 1. The cure of epoxy coreacted polysulphide resin is accomplished by converting the SH terminals to disulphide by the use of an oxidizing agent.

EXPERIMENTAL

The polysulphide resin used in this study is a mercaptan-terminated liquid polysulphide polymer synthesized in our laboratory from dichloro diethyl formal (DDF) and sodium polysulphide (Na_2S_x , $x = 2$ to 2.2) with 2 mole % trichloropropane (TCP) by a conventional procedure.⁷ Table I illustrates the characteristics of the resin used in our experimental studies.

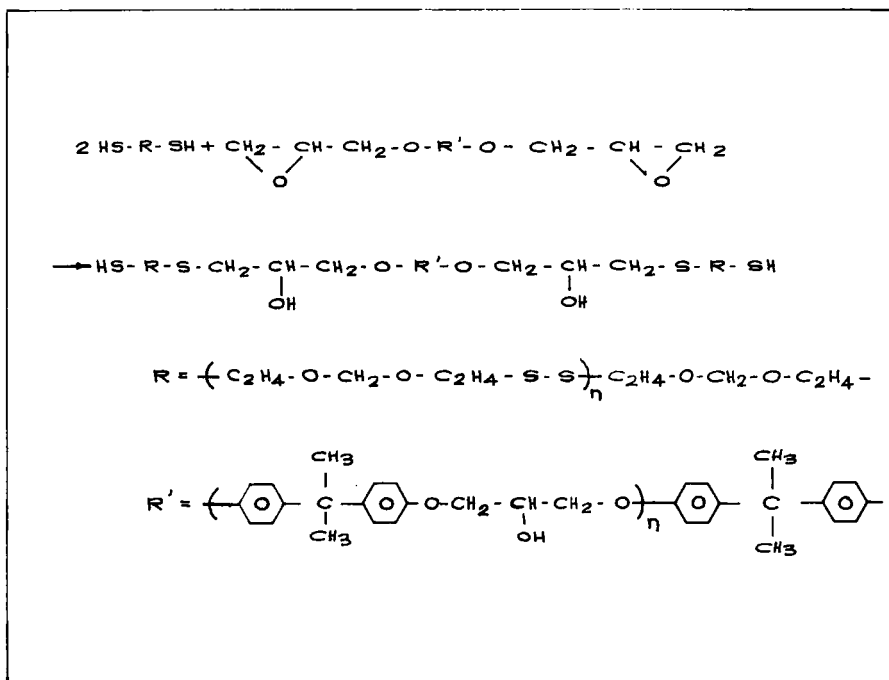


FIGURE 1 Reaction of liquid polysulphide resin with epoxy resin.

TABLE I

SH value	—	1.78 %
Viscosity at 25°C	—	34,560 cp
Molecular weight	—	3070
Specific gravity	—	1.296

The epoxy resins selected were commercially available resins based on bisphenol A and epichlorohydrin (Araldite 6097, Araldite CT 200 and GY 250, supplied by Ciba Geigy India, Ltd.).

The polysulphide resin and epoxy resin were allowed to coreact at 85–90°C. SH values were determined at intervals. The reaction was continued until a constant SH value was obtained. The reduction in SH value was almost equivalent to the epoxy groups.

Table II illustrates a typical sealant composition used for the determination of adhesion and mechanical properties.

TABLE II

<i>Component A</i>		
Epoxy coreacted polysulphide resin	—	100 g
Titanium dioxide	—	40 g
Silica	—	10 g
<i>Component B (Curing Agent)</i>		
Manganese dioxide	—	12.5 g
Dibutyl phthalate	—	4 g
Diphenyl guanidine	—	2.5 g

Component A is a mixture of epoxy coreacted polysulphide resin and fillers. Component B (curing agent) contains an oxidizing agent, plasticizer and accelerator. To minimize the variables in the ingredients, a single batch of raw materials was used throughout.

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 strengths. Figure 2 illustrates the dimensions of the test specimens used. The specimens were made from B51 SWP aluminium. The surface of the specimens were prepared by chromic acid etch.⁸ The nature of failure was visually observed. If the failure occurred at the interface (one surface is free from the sealant) it is recorded as interfacial failure (I). If the failure occurred in the bulk of the sealant it is recorded as cohesive failure (C).

To demonstrate how epoxy resins affect the mechanical properties, sealant slabs were cast in a mold and selected mechanical properties were determined from the dumbbells cut from the slabs. The mechanical properties determined were ultimate tensile strength, stress at 100% elongation, ultimate elongation and hardness.

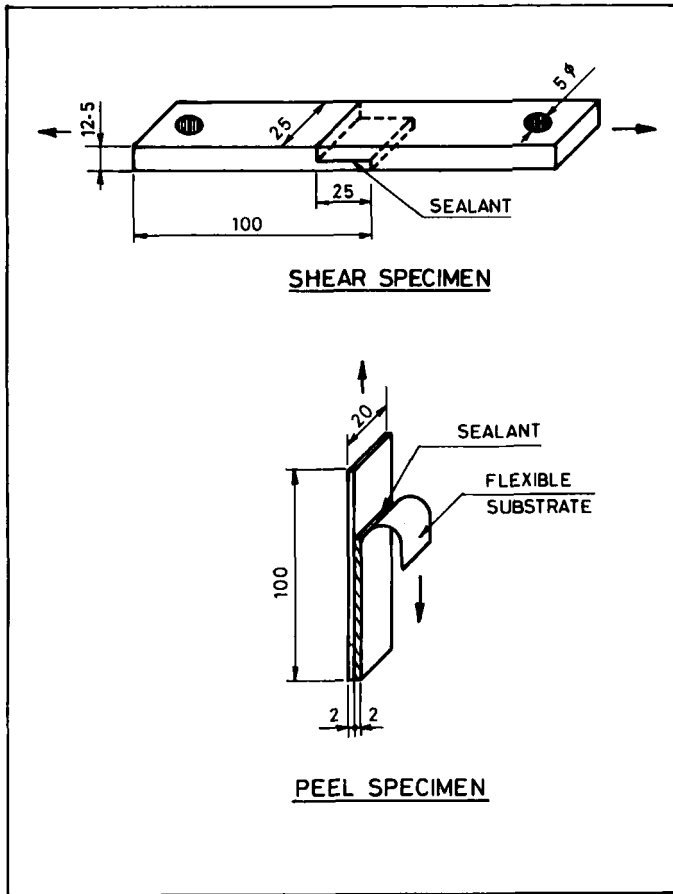


FIGURE 2 Test specimens used for measurements of adhesion of sealant (Substrate-Aluminium). All dimensions in mm.

The resin portion (Component A) and curing agent (Component B) were mixed, adhesion test specimens and slabs were prepared as follows: The test specimens and slabs were cured for 24 hr at room temperature (30°C) followed by 24 hr at 70°C, stored at room temperature for 24 hr and then tested in an Instron at a cross-head speed of 5 cm/min. The results reported are the average of five specimens.

To understand how epoxy resin concentration changes the water absorption of the sealant, about 5 g of the cured sealant from the first series of experiments were cut and immersed in 100 ml distilled water at 30°C and the weight changes determined after blotting dry with filter paper.

RESULTS AND DISCUSSION

Figure 3 and Table III show that coreaction with epoxy resins improved the adhesion of the sealant composition. Figure 3 illustrates the effect of varying the concentration of epoxy resin (Araldite 6097) on the adhesion. Maximum bond strengths were obtained at a level of 5 phr. Below this optimum level the separation of the test specimens occurred at the interface (Interfacial failure) and above this, the break occurred in the bulk of the sealant (Cohesive failure). We propose that the adhesion of the sealant composition improved because of the presence of hydroxyl groups in the polymer chain after the coreaction.^{9,10} The concentration of hydroxyl groups needed to develop good adhesion is small. The hydroxyl groups increase the solvation and diffusion of the loosely adsorbed water layers present on the surface of aluminium, thereby establishing better molecular continuity between the sealant and the substrate. This is supported by the data obtained from the water absorption studies shown in Figure 4. The diffusion of water inside the sealant increases with epoxy resin concentration (hydroxyl group concentration). The hydroxyl groups can also form hydrogen bonds with

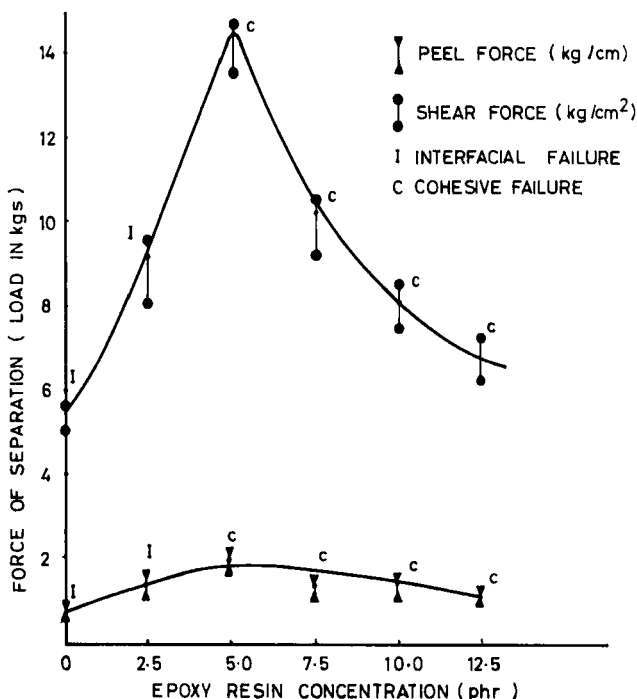


FIGURE 3 The effect of epoxy resin (Araldite 6097) concentration on adhesion of the sealant.

TABLE III

Effect of Various Epoxy Resins on Adhesion and Mechanical Properties of the Sealant Composition
(Concentration of epoxy resin—5 phr)

Properties	Without epoxy resin	Araldite 6097 epoxy value 0.4 g eq./kg	Araldite CT200 epoxy value 2.4 g eq./kg	GY 250 epoxy value 5.1 g eq./kg.
Shear bond strength, kg/cm ²	5.3(I)	14.3(C)	10.5(C)	9.9(C)
Peel strength, kg/cm	0.8(I)	2 (C)	2.4(C)	3.8(C)
Tensile strength, kg/cm ²	10.4	14	9.8	8.5
% of elongation	137	153	152	297
Stress at 100% elongation, kg/cm ²	9.6	11.6	7.7	3.7
Shore A Hardness	58	62	52	50

I = interfacial failure

C = cohesive failure

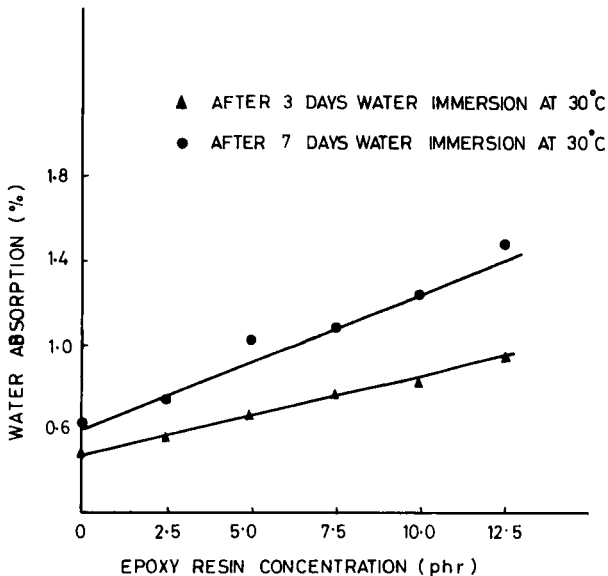


FIGURE 4 The effect of epoxy resin (Araldite 6097) concentration on water absorption of the sealant.

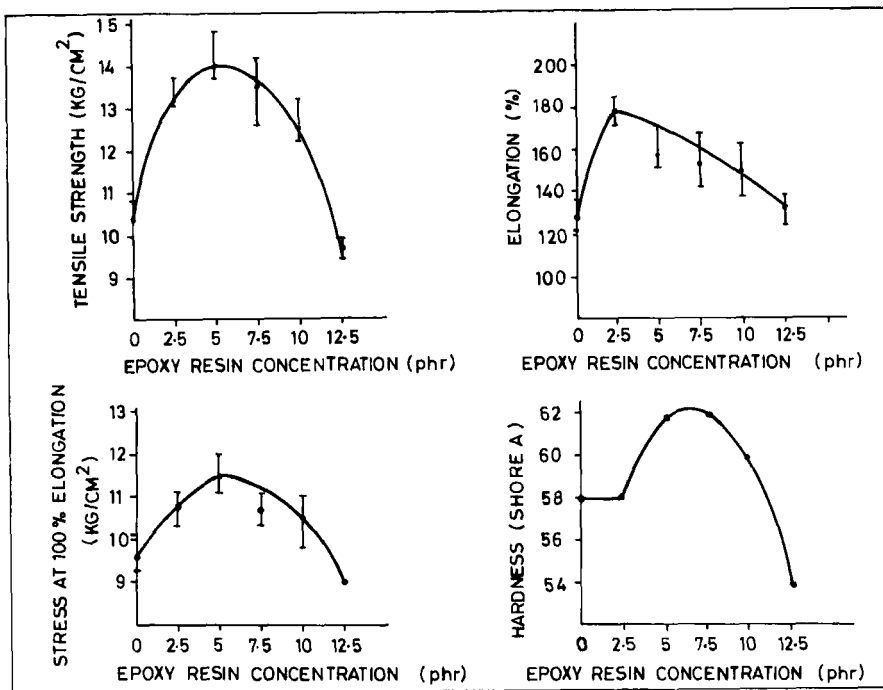


FIGURE 5 The effect of epoxy resin (Araldite 6097) concentration on mechanical properties of the sealant.

the surface, which increase the interfacial forces between the sealant and the substrate, thereby improving the adhesion.

The effect of varying epoxy resin concentration on mechanical properties are shown in Figure 5 and Table III. The coreaction with epoxy resin improved the mechanical properties as expected. With higher levels of epoxy concentrations, there is a tendency for the mechanical properties and hence the bond strengths to lower. This lowering may be due to the decreased extent of cure which is evident from the decreasing trend in stress at 100% elongation, an indicative of modulus.

CONCLUSIONS

Poor adhesion of the conventional polysulphide polymer to high energy substrates can be due to its low polar character. This polymer cannot remove the loosely adsorbed water layer present on the surface of high energy substrates and interact with the surface. Good adhesion can be obtained by increasing the polarity of the polymer chain. Coreaction with epoxy resins

is one of the techniques, described in this paper. The hydroxyl groups formed after the coreaction increases the polarity of the chain. The presence of hydroxyl groups in the chain increases the ability of the polymer to remove the loosely adsorbed surface water layer of the high energy substrates by solvation and diffusion and establish strong interfacial forces with the surface. The concentration of hydroxyl groups needed for good adhesion is small.

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