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Use of Permapol® P3.1 polymers and epoxy resins in the formulation of aerospace sealants

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Abstract

This paper outlines the performance of aerospace sealants based on Permapol® [1] P3.1 polythioether polymer technology. Due to their chemical structure these liquid polymers have inherent resistance to fuel, water and high temperature and, in addition, exhibit high flexibility at temperatures as low as 213 K. Sealants based on this technology possess excellent physical properties and demonstrate adhesion to a wide range of substrates. The epoxy curing mechanism employed to vulcanise the sealant is ideal as assembly time can be shortened without loss of sealant performance and reliability. The cure profile meets both production and repair operations even at temperatures as low as 278 K. The properties of these sealants are derived from the combination of the patented Permapol® P3.1 polymer technology and the epoxy curing system.

Keywords: A. Sealants; A. Epoxides; D. Cure/hardening; Permapol®

1. Introduction

Conventional aerospace sealant technology produces good sealing materials which nonetheless do not entirely satisfy the needs of the aerospace industry. This is because a great deal of research and development work has been carried out over the past three decades to improve the performance of aerospace sealants but very little has been done on improving product convenience or increasing the environmental friendliness of the sealant products.

Many years of research have been devoted to developing appropriate technology and formulating products that will satisfy the needs of the aerospace industry. Recently developed products, based on patented Permapol® P3.1 technology, have made further advances in that they exhibit excellent cure profiles and adhesion and, despite using little or no solvent, demonstrate outstanding tooling characteristics.

2. Development

The structure of conventional liquid polysulphide polymer is shown in Fig. 1. This polymer has been the mainstay of the aerospace sealant industry for over 40 years. Liquid polysulphide polymer (LP™)[2] is chemically a polymer of bis (ethylene oxy) methane containing polysulphide linkages terminated with mercaptan groups. They are formed by the reaction of bischloroethylformal and sodium polysulphide. Crosslinking is provided by the incorporation of a trifunctional monomer, trichloropropane, into the polymer backbone during polymerisation. The level of chain branching for a particular grade of LP™ polymer is determined by the molar concentration of trichloropropane in the reaction mixture. The concentration of trifunctional monomer varies from 0.2% or 2% w/w depending upon the grade of polymer. LP™ polymers are produced at different viscosities with molecular weights ranging from 1000 to 8000.

Liquid polysulphide polymer is ideal for aerospace use as the formal linkage in the backbone provides

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[1] Permapol® is a registered trademark of PRC-DeSoto International, Inc.

[2] LP™ is a trademark of Toray Fine Chemicals Co., Ltd.

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$HS\text{-}(C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}[S\text{-}S]_{2\text{-}8})_x\text{-}C_2H_4\text{-}O\text{-}CH_2\text{-}O\text{-}C_2H_4\text{-}SH$

Liquid Polysulphide (LP™) Polymer

Fig. 1. Structure of liquid polysulphide (LP™) polymer.

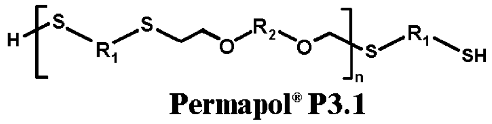


Fig. 2. Structure of Permapol® P3.1 polymer.

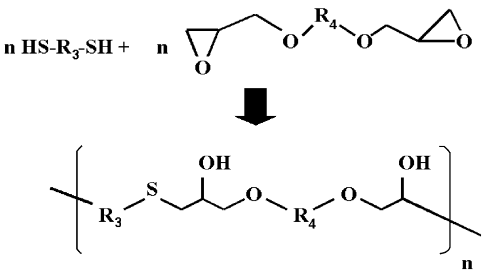


Fig. 3. The reaction of Permapol® P3.1 polymer with an epoxy resin.

flexibility while the polysulphide groups impart the excellent chemical and solvent resistance required for the sealant to perform successfully in the hostile environment of an aircraft fuel tank [1].

However, the presence of polysulphide groups in the backbone places limits on the performance of sealants based on this polymer. The sulphur–sulphur chemical bond is the weakest in the backbone (in terms of bond energy in the diatomic molecular state) [2] and it is this polysulphide linkage which is most prone to either thermal or thermo-oxidative degradation. Scission of the polysulphide linkage can lead to fresh crosslink formation with adjacent polymer chains. Sealants based on liquid polysulphide polymer will therefore demonstrate an increase in hardness and loss of elongation with time or at elevated temperatures.

In aerospace sealants, liquid polysulphide polymers are generally cured using a solid transition metal oxide such as manganese dioxide (MnO_2). This curing mechanism is effective but not entirely efficient in that it is a heterogeneous system (and therefore can be affected by the degree of mixing) and the mercaptan/oxygen condensation reaction is sensitive to the effects of temperature and humidity. The use of an epoxy resin to cure the sealant would convey some benefits. However all efforts to develop an LP™-based, epoxy cured aerospace fuel tank sealant with suitable characteristics have been unsuccessful to date.

Permapol® P3.1 polythioether polymers, due to their unique character, readily lend themselves to the use of epoxy resins as curing agents. The advantages of epoxy cure are those of a homogeneous system (liquid polymer and curing agent) and an additive reaction which is both rapid and relatively unaffected by temperature and humidity.

The structure of the Permapol® P3.1 polymer is shown in Fig. 2. Chemically, it can be described as a polythioether and it is produced through the reaction of a dithiol and a divinylether. The molecular weight of Permapol® P3.1 polymers can be controlled through the selection of the molecular size of the monomers and process manipulation which determines the number of repeat units. Since both monomers are difunctional, Permapol® P3.1 polymers are essentially linear in structure.

However, through the selection of the dithiol and divinylether, the chemical groups shown as R_1 and R_2 in Fig. 2 can be manipulated, giving the Permapol® P3.1 polymer range considerable variety in terms of backbone chemistry. Features that may confer specific properties, such as additional backbone elements or pendant side groups, can be added to the polymer by this means.

Moreover, through the use of an epoxy resin as the curing agent (as shown in Fig. 3), an even greater range of backbone chemistry in the cured sealant is achievable by the selection of the epoxy resin which would allow manipulation of the chemical group identified as R_4 in Fig. 3.

All types of epoxy resins can be used to cure Permapol® P3.1 polymers. Bisphenol A, Bisphenol F and epoxy novolac resins are all suitable. In addition, it is possible to use materials such as diglycidyl ethers as reactive diluents in sealant systems.

Because Permapol® P3.1 polymers are essentially linear in structure the selection of the epoxy resins for curing the sealant is extremely important. The chemical structure and functionality of the individual epoxy resins used will affect both the physical strength and flexibility of the cured sealant. The chemical structure will directly affect the backbone chemistry of the cured polymer matrix and the functionality will determine the crosslink density of the network. As the functionality of the Permapol® P3.1 polymer is 2, the epoxy resin blend must have an average functionality of greater than 2 in order to produce a crosslinked system.

Permapol® P3.1 polymers, due to the presence of sulphur in the polythioether backbone, possess good fuel and chemical resistance. The liquid polymers possess low glass transition temperatures (T_g) which conveys flexibility at low temperatures to the formulated sealants.

Furthermore, through manipulation of the termination step, Permapol® P3.1 polymers may be produced with a range of terminal functional groups such as mercaptan, hydroxyl, epoxy, isocyanate or silanol. This opens up the possibility of producing a range of two-part sealants, based on polythioether polymers, which could be cured as previously mentioned by transition metal oxides or epoxy resins but also by the use of amines or isocyanates. It would be possible to develop one-part sealants which would cure in a similar manner to silicone sealants by reaction with atmospheric moisture.

3. Curing chemistry

Aerospace sealants are normally two-part, room temperature vulcanisation (RTV) materials where the product is mixed, applied and allowed to cure under ambient conditions. Sealants based on LP^{TM} polymers typically use oxygen-donating materials such as transition metal oxides to effect the cure. The first aerospace sealants used lead dioxide (PbO_2) as the curing agent. However, these products were not fully resistant to aviation fuels and required an additional coating of nitrile rubber to prevent reversion of the sealant. The first fully fuel-resistant aerospace sealants used dichromate compounds such as sodium dichromate ($Na_2Cr_2O_7$), calcium dichromate ($CaCr_2O_7$) and magnesium dichromate ($MgCr_2O_7$) as the curing agent. Although these materials remain popular, aerospace sealant products now pre-dominantly use manganese dioxide (MnO_2) as the curing agent.

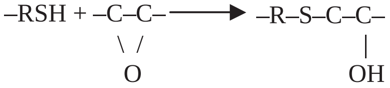
In all these cases the fundamental chemical reaction is the same and involves the surrender of oxygen by the curing agent and its reaction with the terminal mercaptan (–SH) groups of the LP^{TM} polymer, eliminating water and leading to gellation and the formation of a high molecular weight polymer with elastomeric properties.

The mechanism of cure can be expressed most simply as

$$2\text{–RSH} + (\mathrm{O}) \longrightarrow \text{–R–S–S–R–} + \mathrm{H_2O}$$

The process is illustrated more fully in Fig. 4. The mercaptan–oxygen reaction can produce chain extension but also crosslinking if the mercaptan groups are on adjacent polymer chains. As described previously, the crosslink density of the polymer network can be adjusted through the selection of the grades of LP^{TM} polymer in the sealant formulation.

The reaction of a mercaptan-terminated polymer with an epoxy resin has already been shown in Fig. 3 and can be expressed simply as



$$\text{–RSH} + \underset{\substack{\diagdown\ \diagup \\ \mathrm{O}}}{\text{–C–C–}} \longrightarrow \text{–R–S–C–}\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{C}}\text{–}$$

Epoxy–mercaptan cure is therefore an additive, rather than a condensation, reaction. This offers an advantage as a curing agent for an aerospace sealant as it does not produce an unwanted by-product, i.e. water, which causes shrinkage in the cured sealant or could produce microbubbling in a sealant cured at an elevated temperature. For this reason, only specially formulated oxidatively cured sealants can be vulcanised using autoclaves.

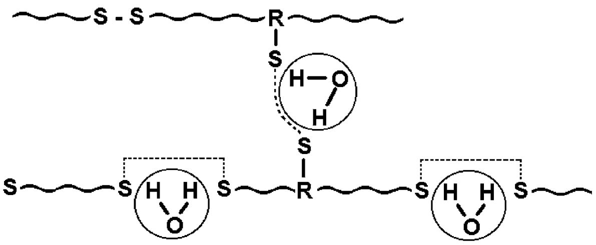


Fig. 4. The oxidative cure of liquid polysulphide (LP™) polymer.

A more significant advantage is that the epoxy–mercaptan reaction is faster than the oxidative/condensation reaction. Sealants cured with epoxy resins demonstrate faster cure, in terms of the development of hardness or elastic modulus, than an oxidatively cured sealant with the same application/pot life. The rate of reaction is also less temperature dependant than the oxidative reaction. The cure rate of epoxy cured sealants is therefore affected less by changes in temperature and they will cure at temperatures where oxidatively cured sealants have effectively stopped (i.e. below 278 K).

Although epoxy resins have been used to cure LP^{TM} polymers for applications in the construction or insulating glass industries, formulating an aerospace fuel tank sealant using the same technology has proved impractical to date. The difficulty has been in balancing the requirements of cure rate, physical properties, chemical resistance and adhesion in the product. It is only by the use of Permapol$^{®}$ P3 and P3.1 polythioether polymers that the advantages of epoxy cure have been fully exploited. Stoichiometry plays an important role in controlling the cure and physical properties of an epoxy cured sealant and the principal reason for the success with the Permapol$^{®}$ P3 and P3.1 polymers is that their manufacturing processes enables them to be produced with a narrow mercaptan equivalent weight range compared to LP^{TM} polymers. This feature of the Permapol$^{®}$ P3 and P3.1 polymers allows the development of products with high reproducibility and good storage stability.

4. Material characteristics

The material characteristics of sealants based on Permapol$^{®}$ P3.1 polymer cured with an epoxy resin are derived in part from the polymer, from the epoxy resin and from a combination of both. The properties of this polymer and sealant are described below and compared to those of LP™ polymers and sealants.

The Permapol® P3.1 polymers, because of their chemical structure, have lower viscosities compared to LP™ polymers of a comparative molecular weight. This facilitates the formulation of sealants with significantly reduced solvent contents and confers a number of benefits, namely reduced VOC emissions, improved user safety and reduced shrinkage of the sealant. The epoxy cure mechanism, because it is an additive reaction, also contributes to the reduction in shrinkage. Because of the efficient distribution of sulphur groups along the backbone, the fuel/chemical resistance of Permapol® P3.1 polymers is equivalent to that of LP™ polymers.

4.1. Glass transition temperature (T_g)

Permapol® P3.1 polymers generally have lower glass transition temperatures (T_g) as their molecular structure provides flexibility and mobility of the polymer chains at low temperatures. In terms of sealant performance, the low temperature flexibility is improved.

The T_g for LP™-based and Permapol® P3.1-based sealants as measured by different experimental techniques are shown in Table 1. The thermal retraction method (ISO2921) involves subjecting a test specimen to a tensile elongation. The sample is then cooled to below T_g and the clamping released at one end. The sample is then warmed slowly and the degree of recovery (as a percentage of the original elongation) is measured as a function of temperature. The test yields a number of retraction temperatures: at 10% recovery (T10), 20% (T20) and 50% (T50). The results shown in Table 1 are for T10.

The other results are by the thermal analytical techniques Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA). A heating rate of $10\,\mathrm{K\,min^{-1}}$ was used in each case.

The results show that the T_g of the polythioether-based sealants are consistently lower than those of the polysulphide-based sealants, regardless of the experimental technique used. The smallest difference is 9.1 K (by DMA) and 14.8 K the largest (by TMA). With the exterior skin of a commercial airliner falling to 218 K at high altitude, this reduction in glass transition temperature can significantly improve the sealant's ability to respond to the movement and vibration in the airframe that occurs in flight.

Table 1
Glass transition temperature (T_g) measured by different experimental techniques

Method	Polysulphide-based sealant (LP™ polymer) (K)	Polythioether-based sealant (Permapol® P3.1) (K)
Thermal retraction	227.0	216.0
DMA	239.5	230.4
DSC	219.8	207.5
TMA	225.7	210.9

Table 2
Effect of elevated temperatures on the tensile properties of sealants

	LP™ polymer MnO_2 cured	Permapol® P3.1 epoxy cured
Tensile strength (MPa)		
Initial	2.88	2.47
After heat cycling	1.71	1.59
Percentage change	41%	36%
Elongation (%)		
Initial	250	430
After heat cycling	50	190
Percentage Change	80%	56%

4.2. Thermal stability

Permapol® P3.1 polymers have improved stability at elevated temperatures because the polysulphide linkages have been eliminated from the polymer backbone. This has increased the thermal and thermo-oxidative stability of the polythioether polymer compared to that of the liquid polysulphide. Exposure at elevated temperatures therefore produces a smaller reduction in tensile strength and, more significantly, in elongation and flexibility.

This is illustrated by the results shown in Table 2. The initial results were obtained after the sealants were allowed to cure for 14 days under standard conditions of 298 K and 50% RH. The heat cycle consisted of 24 h at 400 K, 4 h at 433 K and 6 h at 455 K divided evenly into six portions, each consisting of 4 h at 400 K, 40 min at 433 K and 1 h at 455 K [3].

As the results show, the tensile strength and elongation of the polythioether/epoxy sealant were reduced by 36% and 56%, respectively, while those of the polysulphide/MnO_2 went down by 41% and 80%. Hence, the polythioether/epoxy sealant had significantly better flexibility, both in terms of the residual elongation and the relative reduction in properties, following exposure to demanding thermal environmental conditions.

4.3. Cure properties

The principle benefits of these sealants are in their cure profile and adhesion properties, both of which are, to a large extent, due to the use of epoxy resins as curing agents.

The rate of the epoxy/mercaptan reaction is rapid and, through careful formulation, it is possible to produce sealants with the same pot life as existing LP™

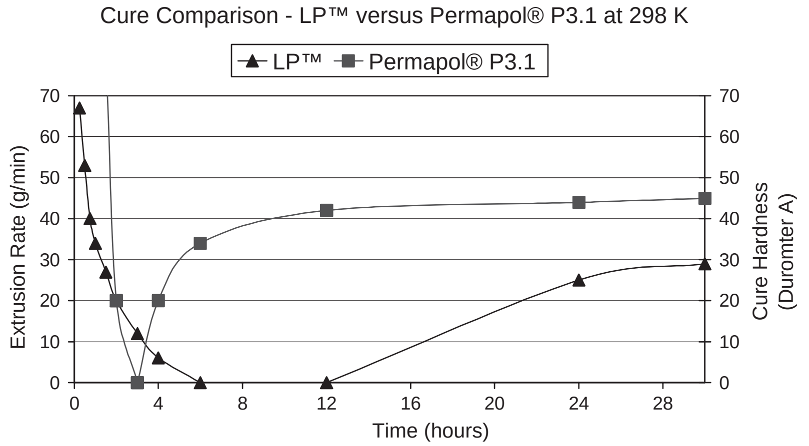


Fig. 5. The comparative cure properties of a manganese dioxide cured LP™ and an epoxy cured Permapol® P3.1 sealant at 298 K.

polymer-based sealants but with significantly faster cure rates.

The time taken for the sealant to become a useful rubber (35 Durometer A Hardness) can be two to three times shorter for a Permapol® P3.1-epoxy cured sealant compared to an equivalent LP™ polymer-oxidative cure sealant. The reaction, because of its lower activation energy, is less sensitive to temperature and therefore the advantages of epoxy cure are even more significant at low temperatures.

The cure characteristics of a Permapol® P3.1 epoxy cured sealant and a manganese dioxide cured LP™ sealant are illustrated in Fig. 5. Both products are designed for the same end use, i.e. they are high viscosity, slump resistant fuel tank sealants (Class B in aerospace terminology) with an application life (pot life) of 2 h. The extrusion rate of the products is plotted on the left-hand axis and the Durometer A hardness on the right-hand axis. It should be noted that after 2 h the extrusion rate of both products is the same, that is to say their application life is the same and therefore the two products can be considered to be equivalent in terms of this material property. After mixing the extrusion rate decreases as the viscosity of the products increases. Eventually the product gels, at which point the extrusion rate drops to zero. The crosslink density of the product continues to increase and the sealant starts to demonstrate a measurable hardness. The hardness can be monitored until ultimate hardness is achieved. The results indicate that the rate of hardness development for the Permapol® P3.1 epoxy cured sealant is significantly greater and that the time for the onset of hardness development is much shorter. This type of behaviour is characteristic of the epoxy cure system and offers benefits during the manufacture of aerospace assemblies.

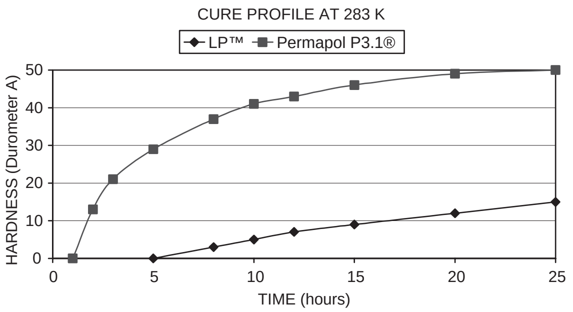


Fig. 6. The comparative cure properties of a manganese dioxide cured LP™ and an epoxy cured Permapol® P3.1 sealant at 283 K.

Table 3
Test results for 180° peel adhesion for Permapol® P3.1 epoxy cured sealant

Substrate	Force value ($N\,mm^{-1}$)	Mode of Failure
Aluminium Alloy	9.32	100% cohesive failure
Stainless steel	10.72	100% cohesive failure
Titanium	9.56	100% cohesive failure
Carbon fibre composite	7.88	100% cohesive failure
Epoxy coating	8.68	100% cohesive failure
Polyurethane coating	9.76	100% cohesive failure

Fig. 6 shows the hardness development results for these materials at low temperature. As the epoxy curing system is less temperature sensitive its advantages are emphasised as the ambient temperature is reduced.

4.4. Adhesion

Good adhesion to a wide range of substrates is an inherent requirement for an aerospace sealant and the adhesion properties of Permapol® P3.1 polymer–epoxy cured sealants are excellent. By adjusting the stoichiometry of the formulation, the epoxy resin acts not only as the curing agent but also as part of the adhesion system. The epoxy becomes bound into the cured polymer network and will resist being leached out by any medium into which the sealant might be immersed. In addition, the low viscosity of the Permapol® P3.1 polymer will assist in surface wetting. Sealants based on this technology show excellent adhesion to aerospace coatings, sealants, metals and plastics. A selection of results for 180° peel adhesion tests is shown in Table 3. The mode of failure, 100% cohesive, does not change after immersion, at a range of temperatures and exposure times, in common aerospace media such as fuel, water, de-icing fluid and salt water.

5. Conclusion

Sealants based on Permapol® P3.1 polymers and cured with epoxy resins offer a convenient cure profile, excellent physical properties, low VOC and robust adhesion to a wide range of substrates. These properties are well tailored to meet the needs of sealant users in the aerospace industry.

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