QUANTITATION OF BURIED CONTAMINATION BY USE OF SOLVENTS

First Interim Report

Part I. Solvent Degradation of Amine Cured Epoxy Resins

February, 1972

Supported by

NASA Grant NGR 35-001-012

Submitted to the

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

by the

Department of Polymers and Coatings
North Dakota State University
Fargo, North Dakota 58102

(NASA-CR-126306) QUANTITATION OF BURIED CONTAMINATION BY USE OF SOLVENTS. PART 1: SOLVENT DEGRADATION OF AMINE CURED EPOXY RESINS A.E. Rheineck, et al (North Dakota State Univ.) Feb. 1972 22 p CSCL 07D G3/06
N72-22116
Unclas
26291

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INTRODUCTION

1. Background

The objectives of the overall project are: (1) to develop non-sporicidal methods for solvent degradation of cured polymeric resins that are used in spacecraft, and (2) to determine if reaction conditions during resin cure cause decontamination of the component that is being fabricated. This interim report deals with the first objective; more specifically, it describes the application of solubility parameter methods to the degradation of amine cured epoxy resins. The research described herein was carried out by Robert A. Heskin* under the direction of Alfred E. Rheineck. The death of Dr. Rheineck on August 10, 1971 prevented him from submitting a report on this work.

Of the plastics used as potting compounds and adhesives in space vehicles, epoxy resins are the most prevalent (1). The three epoxy resins used in this study were obtained from the Plastics and Resins Division of Shell Chemical Company and can be identified by their trade names, Epon 815, Epon 836, and Epon 1001. The structure of the uncured resins can be represented as:

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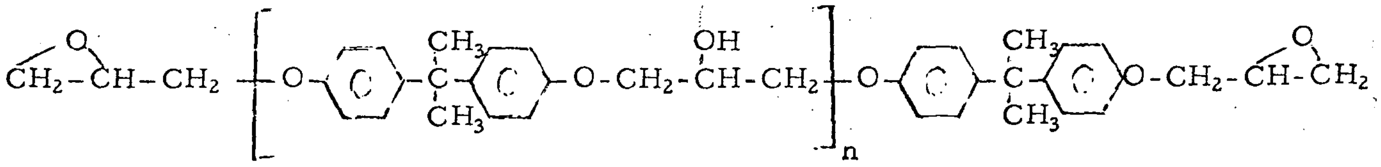
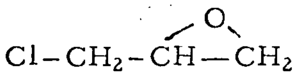


Epoxy resins of this type are known as glycidyl ethers of bisphenol A. They are prepared by the reaction of epichlorohydrin (I) with bisphenol A (II) under basic conditions (2).



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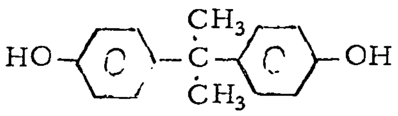


II

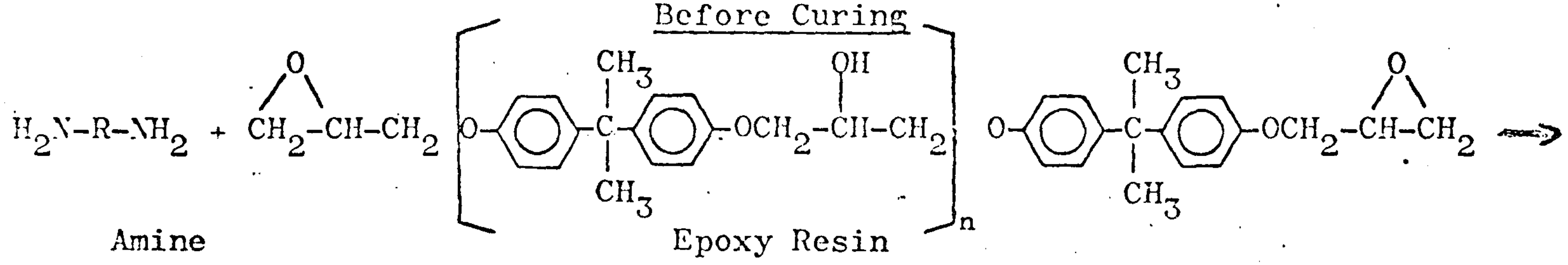
The curing of an epoxy resin using an alkyl diamine is shown in Figure 1. Crosslinking occurs by attack of amine on the oxirane group of the resin. As indicated in Figure 1, both amine groups react in some cases while in others only one -NH_2 of the diamine reacts. Attack of the oxirane by hydroxyl groups present in the resin does not occur at an appreciable rate in the absence of catalysts.

Crosslinked polymers are essentially insoluble. However, such polymers can be swollen by appropriate solvents. Selection of the solvent can be facilitated by use of the solubility parameter concept (3). Recovery of buried contamination from crosslinked polymers is currently a difficult problem. Pflug (4) pointed out that recovery of seeded spores from piece parts by grinding or pulverising is generally poor. Petersen (5) recently reported that use of the biodetection grinder resulted in 5.7% recovery from a seeded model system composed of laminated polystyrene. Values of 0.1% recovery for seeded methyl methacrylate and 1.2% recovery for

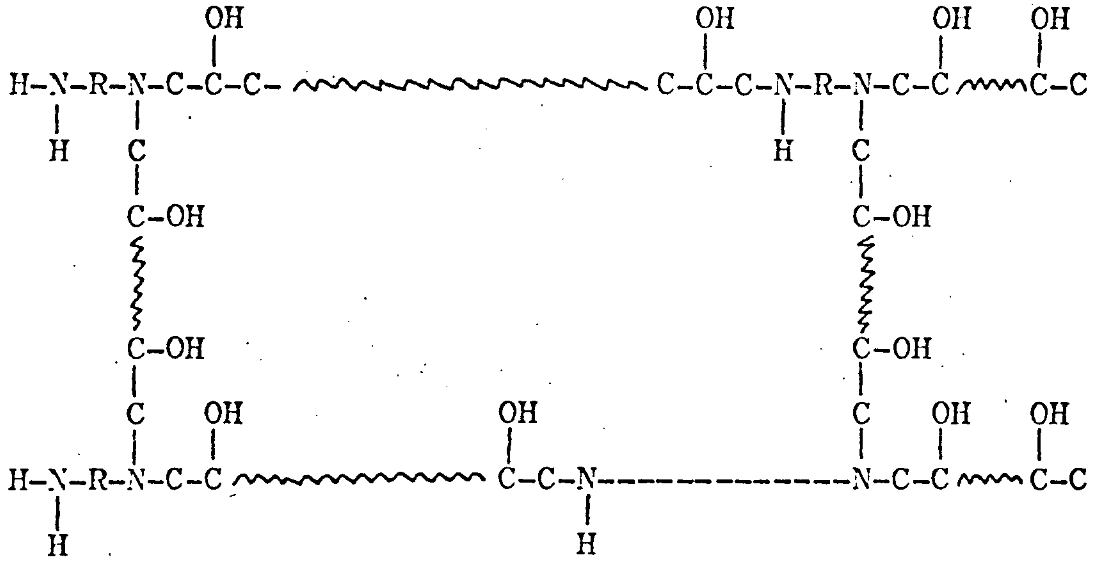
FIGURE 1

Structure of a Model Epoxy Compound Before Curing

Before Curing



After Curing



Where ∿∿∿ represents the epoxy resin chain
R represents some alkyl group

seeded Eccobond had been reported previously (5). The rationale of the present study is that mechanical degradation of a swollen cured resin in the presence of a suitable solvent may increase recovery substantially. Complete dissolution in a non-toxic solvent yields a higher recovery than grinding or pulverizing for piece parts in general (4); however, for cross-linked polymers it is very doubtful that complete dissolution can be achieved. A possible exception may occur when a chemical reaction takes place between solvent and polymer to cause depolymerization.

2. Solubility Parameter

The development of thermodynamic treatment of non-electrolyte solutions has been reviewed by Hildebrand and Scott (6). Scatchard (6) introduced the term "cohesive energy density" into Hildebrand's theory in 1931, and the square root of the cohesive energy density was subsequently named "solubility parameter". The application of solubility parameter concepts to polymer solutions was described by Burrell (3). As Burrell pointed out, the most useful equation developed by Hildebrand is

$$\Delta H_m = V_m \left[(\Delta E_1/V_1)^{1/2} - (\Delta E_2/V_2)^{1/2} \right]^2 \phi_1 \phi_2 \qquad (1)$$

where ΔH_m = enthalpy of mixing components 1 and 2
V_m = volume of mixture
ΔE = internal energy of vaporization of 1 or 2
V = molar volume of 1 or 2
ϕ = volume fraction of 1 or 2

The terms mentioned above are defined as:

cohesive energy density $= \Delta E_i / V_i$
Solubility parameter $= \delta_i = (\Delta E_i / V_i)^{1/2}$

Rearranging equation (1) and introducing the definition of solubility parameter, one obtains

$$\Delta H_m / V_m \phi_1 \phi_2 = (\delta_1 - \delta_2)^2 \qquad (2)$$

Since the difference on the RHS is squared and V_m, ϕ_1, and ϕ_2 are all positive by their definitions, ΔH_m is always positive according to the assumptions of this treatment. The most common thermodynamic criterion for spontaneity of a process is that the change in free energy, ΔG, be less than zero. The familiar equation

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (3)$$

can then be used to interpret the significance of solubility parameters. The entropy change, ΔS_m, is always positive for a mixing process; thus, the second term on the RHS ($-T\Delta S$) is always negative (T = absolute temperature). As long as ΔH_m is not too positive, ΔG_m will be negative and mixing or dissolution will be possible. If ΔH_m is larger than $T\Delta S_m$, ΔG_m will be positive, and dissolution will not be possible at the temperature of the experiment. If we consider component 2 to be the polymeric solute, then from equation (2) it is seen that one must select a solvent with a similar solubility parameter so that the difference $(\delta_1 - \delta_2)$ is not too large. The most favorable situation corresponds to $\delta_1 = \delta_2$ because then $\Delta H_m = 0$ according to equation (2) and $\Delta G_m = -T\Delta S_m$ by equation (3). In other words, if the δ values of two substances are nearly equal, the substances will be miscible.

Once the practical applications of the solubility parameter approach were realized, semi-empirical and purely empirical extensions developed to expand the range of applicability. For instance, Small (7) assigned group values (and atomic values) for fragments of molecules which when added and normalized by density and molecular weight gave the solubility parameter of any molecule for which the structural formula was known. Small's "molar attraction constants", as the group values are known, yield δ's within about ± 1 unit in most cases. It was soon found that hydrogen bonding strength was not adequately accommodated by the theory. Better solubility predictions were obtained if solvents were classified into three categories (3):

Class I	Poorly hydrogen bonded
Class II	Moderately hydrogen bonded
Class III	Strongly hydrogen bonded

Typical solvents in each class are given in Table II, page 11.

Solubility parameters of solvents can be obtained most directly from experimental determination of the heat of vaporization. The internal energy change can be computed from the heat change ($\Delta H = \Delta E - RT$), and then δ can be obtained from the definition of solubility parameter. Burrell (3) describes several other methods including use of Small's molar attraction constants. For polymers the precise structure is seldom known and vaporization cannot be achieved without decomposition. Therefore, solubility parameters of polymers are usually obtained from solubility experiments. A list of solvents within a given class and with gradually increasing δ is prepared. Solubility in each solvent is then tested. The solubility parameter of the polymer is assigned as the midpoint of the range of δ values for solvents which dissolve or, in the case of crosslinked polymers, swell the polymer. Although this method is similar to trial and error, it should be noted that it is necessary to use only one solvent of a group with similar δ values in preparation of the list of solvents or "solvent spectrum" as this list is called. A solvent spectrum was used in this study to obtain the solubility parameter of the cured epoxy resins.

EXPERIMENTAL

1. Preparation of Amine Cured Epoxy Resins

The properties of the commercial epoxy resins as given in a Shell Chemical Company bulletin are shown in Table I. With reference to the structure indicated on page 2, Epon 815 has $n \cong 0$, Epon 836 has $n \cong 1$ and Epon 1001 has $n \cong 2$. In addition to the bisphenol A derivative, Epon 815 contains a small amount of a monofunctional epoxy diluent. The epoxide equivalent given in Table I is defined as the number of grams of resin containing 1 mole of oxirane groups. Oxirane contents were determined

TABLE I

Properties of Epon Resins

	Epon 815	Epon 836	Epon 1001
Weight per Gallon, lb. 20 °C	9.5	9.9	9.9
Hydroxyl content, equiv. OH/100 g. resin	0.05	0.21	0.28
Average Molecular Weight	330	710	900
Melting Point, °C	---	40-45	65-75
Flash Point, Tag open cup, °F	> 175	> 175	> 175
Epoxide Equivalent	175-195 (170.8)*	280-350 (325)*	450-570 (467)*

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* Determined in this laboratory.

by titration with hydrogen bromide in glacial acetic acid according to the method of Durbetaki (8).

At room temperature Epon 815 is a liquid of relatively low viscosity, Epon 836 is a viscous liquid, and Epon 1001 is a solid. The physical state of Epon 836 and Epon 1001 required that solutions be prepared in order to reduce the viscosity and facilitate mixing of the curing agent. Solutions containing 75% resin by weight in methyl ethyl ketone were used. Epon 815 was cured in the absence of solvent. Four amine curing agents were used: ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetraamine (TETA) and tetraethylenepentaamine (TEPA). Samples containing 20 grams resin were cured with sufficient quantities of each amine to correspond to reaction of 1/3, 2/3, and all of the oxirane groups. Thus, there were thirty six model systems in all (4 amine curing agents) x (3 resins) x (3 levels of cure).

The Epon 836 and Epon 1001 were baked at 140°C for four hours in all runs to maximize cure and remove solvent. The Epon 815 was cured without baking in some cases since no solvent was present, and in other cases this resin was also baked at 140°C for four hours. The three model compounds obtained from Epon 815 cured with TETA were analyzed by infrared spectroscopy using the potassium bromide pellet technique.

2. Solubility Parameter Determination

The solubility parameter ranges of the 36 model compounds were determined by the solvent spectrum method described by Burrell (3). A series of solvents of gradually increasing solubility parameter were obtained for each of the three classes of hydrogen bonding. It was soon noted that none of the solvents in Class III (strongly hydrogen bonded) dissolved the epoxy polymers. Thus, Class III solvents, mainly alcohols, were excluded.

The model amine cured epoxy polymers were prepared in 4 oz. brown glass bottles. The sample size was 20 grams. In order to effectively realize the action of the solvents towards dissolution or swelling of the polymers, the sample size had to be reduced to 20-30 mesh particles with a hacksaw. A blade containing 32 teeth per inch was used. The epoxy particles (0.04 gram) were weighed into a 10 mm. by 75 mm. pyrex test tube. The solvent was added by means of a pipet to make a 2% solution by weight. The test tubes were placed in a dry ice bath and allowed to freeze. The test tubes were then sealed with a gas-oxygen torch.

The samples were now ready to be placed in a constant temperature water bath. The temperature was maintained at 60°C for all solubility tests. The samples were agitated by a vacuum windshield wiper assembly operated in reverse. The test tubes were wired onto rods submerged in the water bath and connected to the windshield wipers which were run on compressed air. The samples were agitated at 60°C for 48 hours and then inspected visually for swelling or dissolution.

RESULTS AND DISCUSSION

Table II is representative of the data obtained using the solvent spectrum method. These data are for Epon 836 cured with sufficient triethylenetetraamine (TETA) to correspond to complete reaction of oxirane groups. The thirty-five other model systems were treated in a similar manner. The solid lines within the body of the table bracket those solvents which caused either swelling or dissolution. The solubility parameters of the bracketed solvents establish the solubility parameter range of the model epoxy polymer for Class I and Class II solvents. No solubility or swelling was noted in Class III solvents for the model system considered in Table II, and similar results were obtained for the other model systems. In certain cases a solvent well outside the solubility range caused swelling; benzonitrile, a Class I solvent, is an example in Table II. This behavior corresponds to a specific interaction between solute and solvent. Frequently the nature of the interaction is not known (3).

The solubility parameter ranges for all thirty six model epoxy polymers are compiled in Table III. An entry of "Ins." indicates that the polymer was not dissolved or swollen by any of solvents tested. An entry of a single number, rather than a range, indicates that the polymer was dissolved or swollen by only one of the solvents used in the test. The width of the range observed for a solute is symbolized by $\Delta\delta$ and reported as a $\pm$ tolerance (3). The greatest tolerance reported in Table III is for Epon 836 cured with 33 1/3% or 66 2/3% ethylenediamine in Class I solvents.

TABLE II

Determination of the solubility parameters at 60°C of Epon 836 cured with triethylenetetraamine (TETA) corresponding to 100% reaction of oxirane. Inspection after 48 hours of sealed ampules containing 2% by weight of 20-30 mesh particles.

Class I Solvents

Solvent	Solubility Parameter	Observation
Hexane	7.3	
Heptane	7.4	insoluble
Mineral Spirits	7.6	
Varsol 1	8.1	
Turpentine	8.1	
Benzonitrile	8.4	swollen
Dipentene	8.5	
Carbon tet.	8.6	
p-Chloro toluene	8.6	
Toluene	8.9	insoluble
Benzene	9.2	
Trichloroethane	9.3	
Chlorobenzene	9.5	insoluble
Tetralin	9.5	
1, 1, 2-trichloroethane	9.6	
Tetrachloroethane	9.7	slightly soluble
Ethylene dichloride	9.8	
2-nitro propane	9.9	
Nitro benzene	10.0	soluble
1-nitro propane	10.3	slightly soluble
Acrylnotrile	10.5	insoluble
1-bromonaphthalene	10.6	
Nitro ethane	11.1	insoluble
Acetonitrile	11.9	insoluble
Nitro methane	12.7	reacted

Result: Solubility parameter range, 9.7 to 10.3

TABLE II (cont'd)

Class II Solvents

Solvent	Solubility Parameter	Observation
Ethyl benzoate	8.2	insoluble
Sec. amyl acetate	8.3	
Methyl isobutyl ketone	8.4	
Methyl n-amyl ketone	8.5	
Carbitol acetate	8.5	
Ethyl acrylate	8.6	
Cellosolve acetate	8.7	insoluble
Butyl acrylate	8.8	
Butyl cellosolve	8.9	
Ethyl acetate	9.1	
Tetrahydrofuran	9.1	slightly soluble
Diacetone alcohol	9.2	
Methyl ethyl ketone	9.3	
Methyl acetate	9.6	
p-Dioxane	9.9	soluble
Acetone	10.0	
Methyl benzoate	10.5	swollen
Methyl cellosolve	10.8	
Aniline	11.8	swollen
Dimethyl sulfoxide	12.0	
Dimethyl formamide	12.1	
Dimethyl phosphite	12.5	insoluble
Propylene carbonate	13.3	insoluble
Methyl sulfone	14.5	
Ethylene carbonate	14.7	

Result: Solubility parameter range, 9.1 to 11.8

TABLE II (cont'd)

Class III Solvents

Solvent	Solubility Parameter	Observation
Carbitol	9.6	insoluble
n-Octyl alcohol	10.3	insoluble
t-Butyl alcohol	10.6	
n-Amyl alcohol	10.9	
n-Butyl alcohol	11.4	insoluble
Isopropyl alcohol	11.5	
n-Propyl alcohol	11.9	insoluble
Diethylene glycol	12.1	
Ethanol	12.7	insoluble
Methyl alcohol	14.5	insoluble
Ethylene glycol	14.6	
Glycerol	16.5	
Formamide	19.2	insoluble

TABLE III

Solubility Parameter Ranges in Class I and Class II Solvents at 60°C.

	Epon 815		Epon 836		Epon 1001	
Curing Agent	I	II	I	II	I	II
EDA						
33 1/3%	9.5-10.3	9.9-12.1	8.4-12.7	8.2-12.0	9.5-10.0	8.2-9.9
66 2/3%	8.4	9.9-11.8	8.4-12.7	8.4-11.8	10.0-10.3	9.9
100%	Ins.	Ins.	8.4-11.1	8.8-12.0	10.0-10.3	9.9
DETA						
33 1/3%	9.5-10.0	9.9-11.8	8.4-10.0	9.3-12.5	10.0	9.9-12.1
66 2/3%	9.7-10.0	9.9-11.8	8.4-10.0	9.1-11.8	Ins.	9.9-12.1
100%	9.7-10.0	11.8	8.4-9.9	9.9-11.8	Ins.	11.8
TETA						
33 1/3%	9.5-10.0	9.1-11.8	8.4-11.1	8.2-12.5	9.7-10.0	11.8
66 2/3%	9.5-10.0	9.1-11.8	8.4-10.0	9.1-11.8	9.7-10.0	11.8
100%	9.7-10.0	11.8	9.7-10.3	9.1-11.8	10.0	11.8
TEPA						
33 1/3%	9.5-10.0	9.9-11.8	9.5-11.1	8.2-12.0	10.0	11.8
66 2/3%	10.0	10.5-11.8	9.5-10.0	9.3-11.8	10.0	11.8
100%	Ins.	10.5-11.8	9.5-10.0	11.8	10.0	11.8

EDA = Ethylenediamine, DETA = Diethylenetriaamine, TETA = Triethylenetetraamine
TEPA = Tetraethylenepentaamine

The range reported is 8.4 to 12.7; thus, the tolerance is $\Delta\delta = \pm (12.7-8.4)/2 = \pm 2.2$. Hildebrand and Scott (9) have considered tolerance from a theoretical point of view. They computed that a hypothetical high molecular weight polymer would have $\Delta\delta \cong \pm 1.1$ while a nonpolymeric liquid would have $\Delta\delta \cong \pm 3.5$. The observation of tolerances between 1.1 and 3.5 suggests that curing has not produced high molecular weight polymers for all of the model systems prepared in this study.

Trends in tolerances can be noted in Table III. As expected, the tolerance decreases as the amine level increases. An increase in amine level will cause an increase in crosslink density and possibly also an increase in the average molecular weight of agglomerates. The observation of a maximum in tolerance for cured Epon 836 ($n \cong 1.0$) as compared to Epon 815 ($n \cong 0$) and Epon 1001 ($n \cong 2.0$) is somewhat unexpected. One might expect a smaller tolerance for Epon 815 because there is less distance between oxirane groups, and therefore, a higher crosslink density. The narrower tolerance for cured Epon 1001 (compared to Epon 836) may simply reflect a higher molecular weight in the cured state. Thus, an increase in n has two opposing effects on the tolerance. First, the crosslink density decreases as n increases tending to increase the tolerance. Second, the molecular weight of the cured polymer may increase as n increases tending to decrease the tolerance. R. A. Heskin (10) has discussed variations in tolerance at greater length.

Interpretations of the effect of amine levels and the structure of the amine used in the curing process are complicated by incomplete reaction of the amines with oxirane groups. Infrared spectra of the Epon 815 resin cured with 100% of the stoichiometric amount of amine required for complete cure indicate that only about 80 to 90% of the oxirane groups have actually reacted. This result was noted for samples that were cured without baking, but baking at 140 °C for four hours did not noticeably decrease the amount of unreacted oxirane. With 66 2/3% of the amine required for complete reaction, infrared results indicated that about 50% of the oxirane groups had reacted and in the case of 33 1/3% amine about 25% of the oxirane groups had actually reacted. Infrared spectra and a more complete discussion of the interpretation of infrared results are given by Heskin (10).

The solubility parameters of uncured epoxy resins are given in Table IV. The uncured resins have a much greater tolerance, especially in Class II solvents, than the cured resins considered in this study. Of course, most of the resins in Table IV have a much higher molecular weight (large n) than the resins used in this study, but since they are not cured, crosslinking would be minimal.

TABLE IV

Solubility Parameters of Uncured Epoxy Resins
From Reference (11)

Epon Resin	n	Class I	Class II	Class III
Epon 864	1.5	9.5-12.7	8.5-14.7	0
Epon 1001	2	10.6-11.1	8.5-13.3	0
Epon 1004	5.5	0	8.5-13.3	0
Epon 1007	14	0	8.5-13.3	0
Epon 1009	21	0	8.5- 9.9	0

POTENTIAL APPLICATIONS

The preceding section identifies solvents which would be useful in solvent assisted degradation of cured epoxy resins. If solvents that have been tested prove to be toxic to spores, other solvents having solubility parameters within the tolerance established by this study can be tested for sporicidal activity. Thus, determination of the solubility parameters and tolerance of epoxy polymers make it possible to screen potential solvents without carrying out solubility tests. Although Table II contains an extensive list of solvents, this list is only a fraction of the solvents that could be tested. Since the number of solvents is so large, a purely trial and error approach to finding a solvent with the required properties could be very tedious without the information provided by the solubility parameter method. The solubility parameters of 366 solvents and many resins are compiled in a DuPont bulletin (12).

As indicated in the introduction, determination of buried contamination is difficult because grinding and pulverizing procedures are toxic to spores. If the solubility results of this study make complete dissolution of epoxy piece parts possible, determination of buried contaminants will be greatly facilitated. However, for highly crosslinked epoxy polymers, complete dissolution seems unlikely. Swelling of crosslinked polymers is likely to occur in properly selected solvents rather than complete dissolution. It appears very likely that mechanical degradation of the swollen polymers could be achieved with less severe grinding than is required for the dry polymer. Therefore, the methodology recommended for testing recovery of seeded spores from cured epoxy polymers includes the following steps:

1. Initial reduction of massive objects by sawing or dicing to pieces the size of a 1/2 cm cube.
2. Soaking the pieces in a non-sporicidal solvent until swelling ceases.
3. Gentle grinding of the swollen pieces under solvent in a mortar and pistle.
4. Determination of recovery by accepted bioassay techniques.

In order to check for inadvertent contamination during the test, samples that have been heat sterilized should be treated in a manner identical to that for seeded samples. Pflug (4) has discussed the need for negative controls of this type.

SUMMARY

The solubility and/or swelling of cured epoxy resins has been studied by the solubility parameter method. Determination of the solubility parameters will facilitate solvent selection for solvent assisted degradation of cured epoxy polymers used in spacecraft. A method for improving recovery of seeded spores is suggested. It is anticipated that the results will be useful in assaying buried contaminants.

Three commercial epoxy resins (Epon 815, Epon 836, and Epon 1001) were cured using four different alkyl amines. For each resin-amine combination, three levels of amine were used corresponding to 33 1/3%, 66 2/3% and 100% of the amine required to react with the oxirane groups of the resin. The solubility parameters (δ) of the 36 resulting model compounds were determined in Class I (poorly hydrogen bonded) and Class II (moderately hydrogen bonded) solvents. None of the Class III solvents (strongly hydrogen bonded) caused dissolution or swelling. The tolerance ($\Delta\delta$) of cured resins is discussed in terms of polymer structure.

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