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THERMALLY STIMULATED DISCHARGE IN FRACTIONAL COMPONENT AND MOISTURE EFFECT STUDIES OF EPOXY ENCAPSULANTS

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Thermally stimulated discharge (TSD) is used to characterize fractional components of epoxy encapsulation systems used on semiconductor devices. Previous work is reviewed. Present results based on individual components and component interactions are detailed. Various resin/hardener systems are examined and are not found to be major contributors to TSD structure when balanced by epoxy equivalent weight. Catalyst additions reveal increased TSD structure, especially for low levels. TSD is suggested as a cure indicator for epoxy systems. Moisture is found to resolve thermogram structure, and TSD is found to be a viable method of studying moisture effects.

Key words: thermally stimulated discharge, epoxy encapsulants, polarization, semiconductor encapsulants.

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Introduction

Thermally stimulated discharge (TSD) is a technique used to study molecular level effects in dielectric substances. Basically, the method consists of a poling procedure wherein samples of the dielectric are exposed to high electric field strengths at elevated temperatures. Following this the specimens are allowed to cool under the effects of the applied field. In this way charges are separated and are immobilized within the dielectric material. Such permanently charged materials are known as electrets. Though having been recognized for over fifty years, these arrays of separated charge have only recently found commercial use and are presently used to study the physical processes occurring within the materials in which they can be formed. This is accomplished by taking current measurements.

Upon subsequent heating the separated charges randomize within the dielectric and cause current flow within attached external circuitry. This procedure is called depoling. The process is summarized in Fig. 1 where the poling and depoling apparatus is shown in separate branches of the circuitry. The current flow, when measured as a function of temperature, is characteristic of the dielectric material investigated. Particularly, thermograms so developed may be used to study molecular and ionic effects occurring during electret discharge.

Previous work(1) has demonstrated a correlation between live device performance and TSD charge storage in the encapsulant. Specifically, when performed on epoxy samples, TSD has been shown to be of aid in screening encapsulation candidates for live device testing performance under high temperature reverse bias (HTRB) tests. Table I is an example of the correlation found between leakage current and TSD in n-p-n transistors. The process can be instrumental in saving time and money needed to perform live device tests.

Many authors(2) have studied TSD in highly ordered dielectric systems and have developed techniques to mathematically analyze their thermal

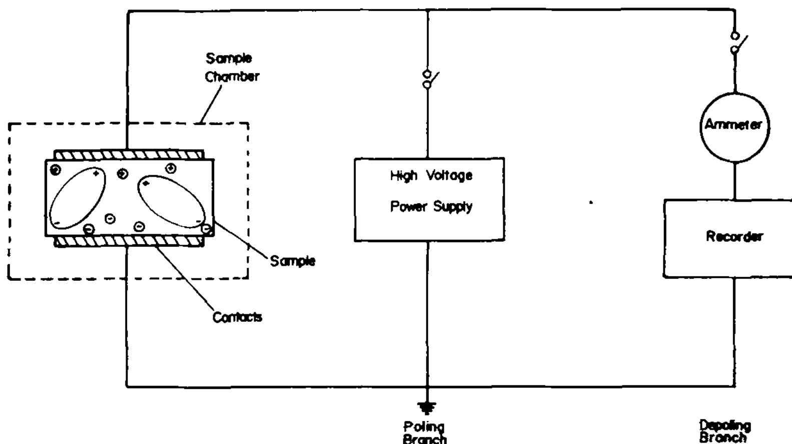

Fig. 1. TSD Apparatus

behavior. In the case of epoxy encapsulation systems, the chemical interactions are very complex, and the TSD performance is so variable after small changes in chemistry that we have deemed it impractical to undertake exact mathematical analysis in the present investigations. Rather, we have elected to establish whatever correlations might apply to live device results and to center our study around the changes in physical behavior as they depend on chemical differences in epoxy encapsulation compounds.

Table I. Leakage Current As Related to TSD

Stored Charge (Area Under TSD Curve) ($\times 10^{-7}$ Coul)	NPN Transistor Data % Leakage Current Change After Exposure To 150°C At 40 V Reverse Bias For 48 Hours
4	13
9	105
65	7,490
108	11,240

Having demonstrated TSD correlation with live device results, we are now attempting to understand the interactions that occur between the various formulation components in an epoxy encapsulation system, and what it is that causes them to give either good or bad live device testing results.

Resin/Hardener Combinations

We have begun by analyzing the TSD characteristics of samples compounded from only epoxidized resins and hardeners. The basic chemistry of these processes is demonstrated in Fig. 2. An epoxy resin and a hardener representative of those used in this study with their resultant reacted product is shown. In the present study three different epoxy resins have been compounded in different combinations with three distinctly different hardeners. Fig. 3 shows typical TSD thermograms taken after poling at 150°C for 30 minutes using 5 kV/mm of sample thickness. The samples shown have been post cured at 190°C for 16 hours. Their glass transition temperatures, Tg,are all approximately 170°C. In what follows we will denote the three resins as A, B, and C, respectively, and the three hardeners as 1, 2, and 3, respectively. Descriptive information concerning these materials is contained in the Appendix. Each of the systems shown in Fig. 3 is compounded in the resin/hardener stoichiometric ratio of 1/1 (100%) without the use of any reaction enhancer or catalyst except in the case of A/1 which has a reaction initiator built into the resin system. As can be seen, the pure resin/hardener systems give fairly flat TSD curves. On this basis and on that of our previous work one would expect these systems to give good electrical performance.

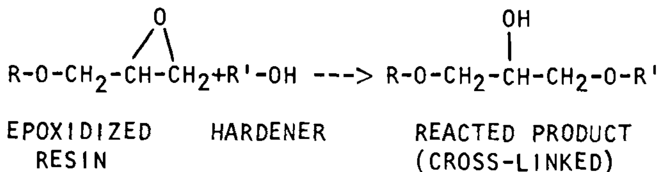

Fig. 2. Basic Epoxy Chemistry

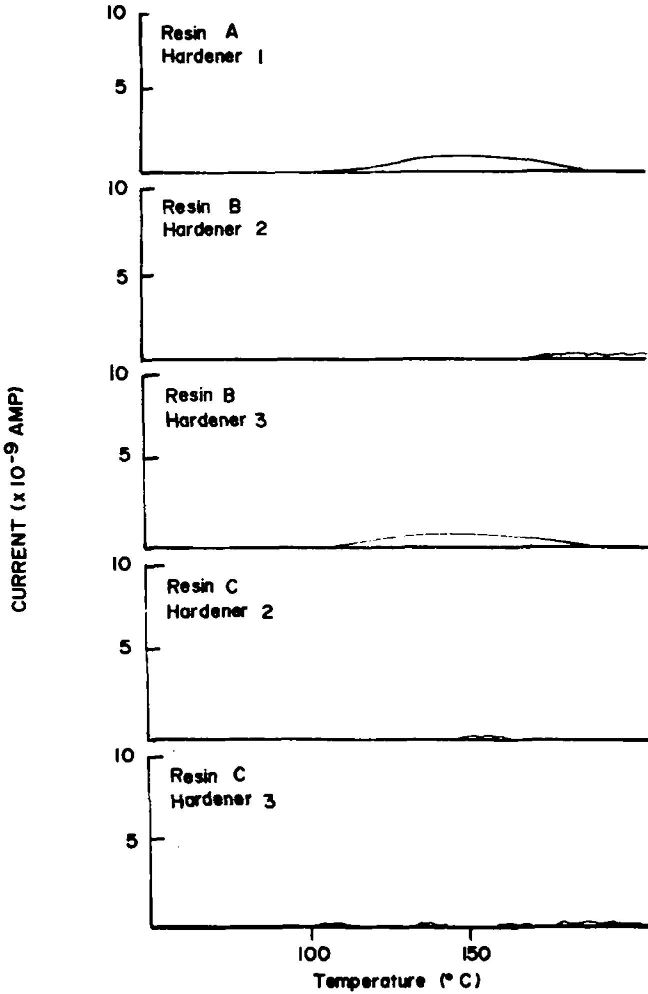

Fig. 3. Resin/Hardener Systems At 100% Stoichiometry

Having seen the above unstructured behavior, we next wanted to know how changes in cure, stoichiometry, and mobile impurity species would affect TSD. First looking at the effect of stoichiometry, we quickly discovered that an optimization occurs giving a flat TSD structure for many resin/hardener systems. For most of the systems tested this optimization occurred at a 1/1 resin/hardener ratio (100% stoichiometry). Fig. 4 demonstrates the type of result found for varying stoichiometries.

The performance shown in Fig. 4 led us to question the dependence of TSD on cure state. A good indication of this is shown in Fig. 5 where the cure state of two of the systems is shown after 2 hours and after 16 hours both at 190°C. Though this may seem like a long cure time, recall that these are pure resin and hardener systems with no catalyst and that the cure process must proceed without activation of the reaction species(3). Fig. 5 shows the effects of an advanced state of post cure as indicated by glass transition temperature, Tg, and suggests that TSD might be suitable for use as a degree of cure indicator. This will be discussed further in connection with catalysts.

Since TSD thermogram structure is generally believed to arise from either dipolar orientation of molecules or space charge separation, the resin/hardener studies allowed us to identify the types of TSD curve that might be expected from molecular dipole orientation. To ensure the absence of mobile charge we took the partially cured systems from Fig. 5 and subjected them to surface removal studies. The surface removal procedure(1) entails a lengthy poling process (approximately 4 hours at 150°C, 5 kV/mm) followed by a slow abrading away of the surface.

After removal of the surface the samples are depoled and a TSD thermogram is taken. Our work has shown that the effect of this procedure is to reduce structure and hence flatten the thermogram. In most cases repetition of the surface removal procedure increasingly flattens the curve with the discharge current approaching a limit.

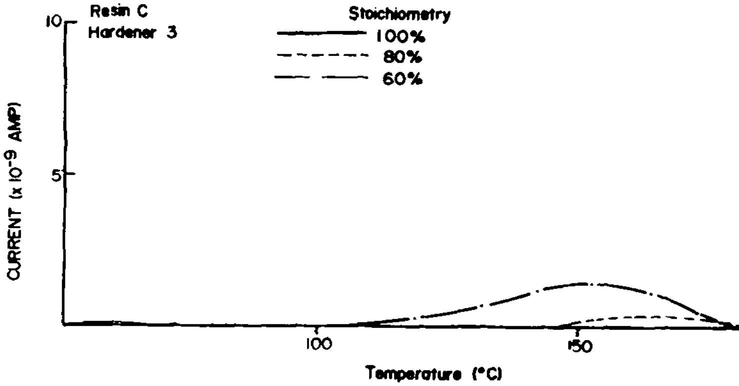

Fig. 4. Typical Stoichiometric Dependence For A Resin/Hardener System

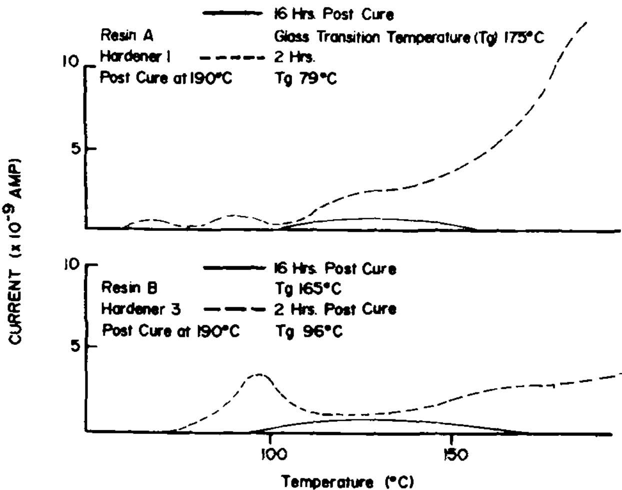

Fig. 5. Dependence Of Resin/Hardener Systems on Post Cure (100% Stoichiometry)

While we cannot eliminate the possibility of unknown surface effects caused by the abrasion (e.g., generation of stable surface states), it seems peculiar to us that the thermograms would continue to flatten with successive polings, surface removals, and depolings if surface state generation were solely responsible for the effect.

Our previous work(1) on this curve flattening indicates that the effect is at least partially due to the removal of mobile charge from the interior of the samples, and that any residual structure remaining after several successive surface removals is due to the discharge of molecular dipoles.

Fig. 6 shows the residual dipolar orientation data from TSD's taken on the samples of Fig. 5 after surface removal. As seen, the resultant curves show a reduction in amplitude after subsequent poling and depoling. We attribute this behavior to the progress of post cure as the samples are heated in the poling and depoling procedures. The poling before surface removal takes place at 150°C for 3-4 hours, and sequential TSD generation requires about 2 hours at temperature. Thus, Fig. 6 will also give some feeling for the manner and rate at which post cure proceeds.

Effects of Catalyst Addition

We next consider the effects of adding small amounts of catalyst to each system at varying stoichiometries. We will discuss four chemically different catalysts in all, denoted by a, b, c and d, respectively (see Appendix).

The general chemical mechanism involved in this process is demonstrated in Fig. 7. Here, we believe that the reaction is speeded by the catalyst through the formation of alkoxide ions. Fig. 7 shows the route to the cross-linked structure since the resins and hardeners used are novolacs.

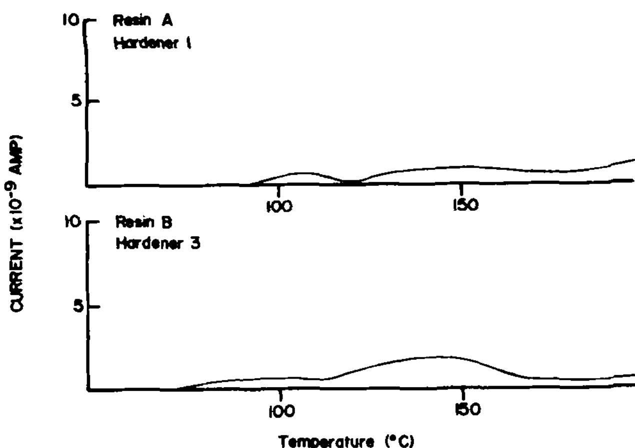

Fig. 6. TSD After Surface Removal For Partially Cured Resin/Hardener Systems

Considering first the TSD dependence on resin/hardener stoichiometry, Fig. 8 shows the stoichiometric dependence usually found for a variety of catalysts. Again the flattest TSD curves occur for 100%

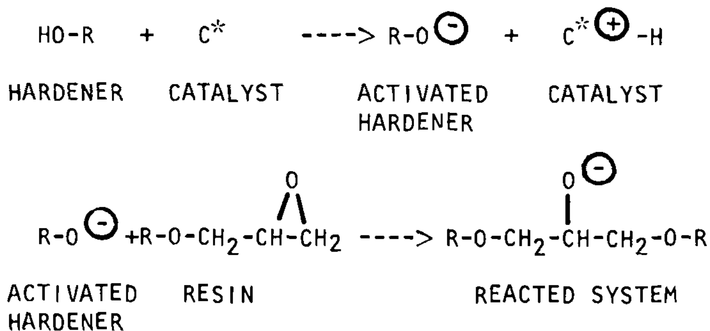

Fig. 7. Proposed Catalysis In An Epoxy Novolac Reaction

stoichiometry. Of course, there are always exceptions and Fig. 9 demonstrates one of these for system C/3/a where the best TSD curve occurs for 80% stoichiometry (1/0.8 resin/hardener ratio).

Since surface removal studies indicate that reaction fragments are primarily responsible for TSD structure(1), a flatter curve might well indicate the absence of these fragments and thus represent a more completely reacted system. This is reasonable in light of the fact that the stoichiometry is based on the epoxy equivalent weight of the system. However, there have been indications in the literature(3) that an exact balance between resin and hardener is not necessary to obtain reaction completion, and this may be responsible for the results of Fig. 9.

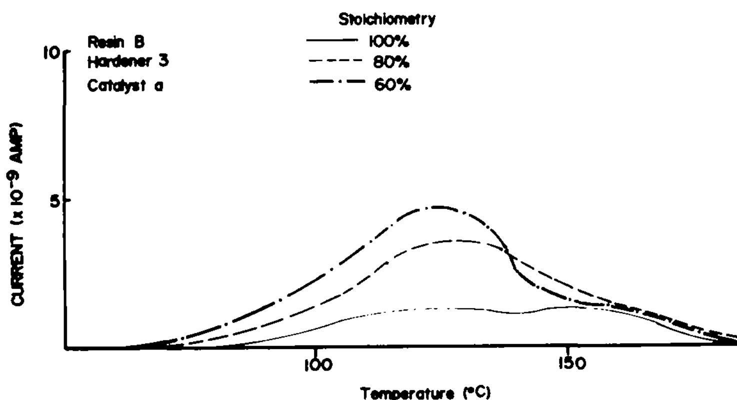

Fig. 8. Most Typical Dependence On Stoichiometry

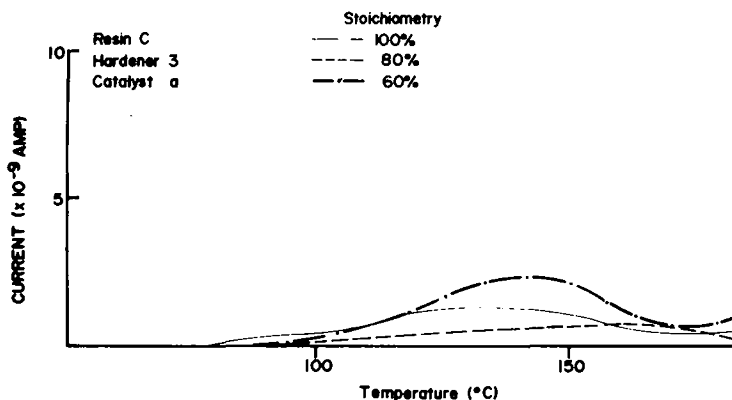

Fig. 9. Less Frequent Dependence On Stoichiometry

Although this again suggests that TSD may be used as an indication of degree of cure, one cannot immediately draw such a conclusion. The addition of the catalyst complicates the situation immensely. As seen in Fig. 7, upon reaction completion the catalyst remains available as a free polar species. Hence, the TSD structure shown may be totally dependent on the free mobility of these catalyst fragments. In turn this mobility will depend on the density of cross-links in the completed system which is known to depend at least partially on the stoichiometry. Hence, the general result shown in Fig. 8 would be just that expected if catalyst fragments were responsible for the thermogram structure.

Fig. 10 gives results for resin/hardener/catalyst systems at low and high catalyst levels. As can be seen from the figure, the higher level of catalyst apparently drives the chemical reactions toward completeness, increasing the cross-link density and immobilizing the catalyst fragments which result in the flattened curve. Tg measurements show a rise from 180°C to 200°C for higher catalyst levels which

confirms the completeness of cure. It would appear that these catalytic species do not participate in the mechanism of thermogram formation at least for the present samples. In this context the possibility of attributing the structure in Fig. 8 and 9 to unreacted mobile species becomes evident. It follows that TSD may indeed be a valid indicator of cure state in some epoxy systems.

Surface Behavior of Free Species

Ninety percent of all device failures are known to be associated with the device surface. Many of these are believed to be caused by the presence of mobile charged species at the device/encapsulant interface, which have been extensively studied by several authors (6-11). Shockley et al.(8) and Schlegel et al.(9) have found a voltage dependence on the silicon oxide surface at a distance x from a voltage source. Their work indicates that an inversion layer may be formed below such a surface by the spreading of the available mobile charge. This inversion layer, I(x), has a time dependence:

$$I(x) \propto t^{0.5}$$

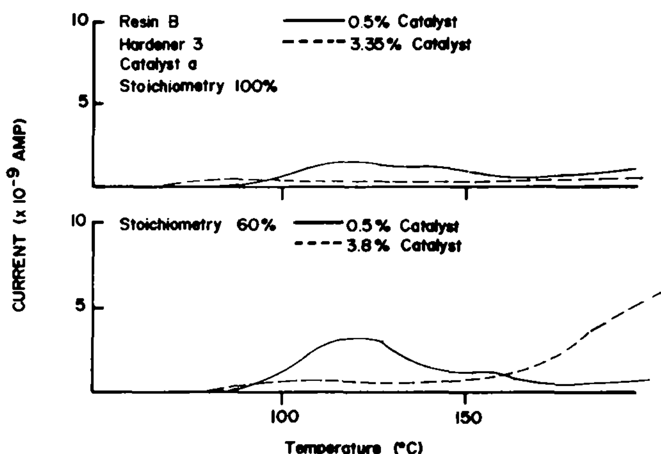

Fig. 10. TSD Dependence On Catalyst Level

Wakashima et al.(11), including encapsulant bulk effects, have put the dependence at

$$I(x) \propto t^{0.8 \sim 1.0}$$

The mobile charged species are known to interfere by causing inversion layers and leakage currents on the device surface.

It was suggested that ionic impurities (e.g., chlorides) may be responsible for TSD results. However, repeated attempts to associate TSD performance with impurity content have led us to believe that these effects are of secondary importance. Of primary importance to TSD and its associated high temperature reverse bias (HTRB) performance are what appear to be reaction fragments as revealed by surface removal studies using TSD. It is our contention that for epoxy systems these are the most important ionic degradative species. At this point we also note that in highly cross-linked systems, repeated surface removal runs are necessary to obtain an unstructured TSD curve, but that a relatively unstructured curve can be obtained. This would be expected because of free volume limitations on the mobility of larger reaction fragments within the polymer.

Moisture Effects

Moisture has a history of ill effects on epoxy encapsulants. To help develop our understanding of moisture degradation, we have begun preliminary studies of TSD results as they pertain to the effects of moisture absorption in epoxies. Fig. 11 shows a comparison of a typical epoxy encapsulation system before and after exposure to an 85°C at 85% relative humidity environment. The main effect has been to move the first peak in the curve to a lower temperature. A similar situation is shown in Fig. 12, where resolution of an additional peak results from 85/85 exposure.

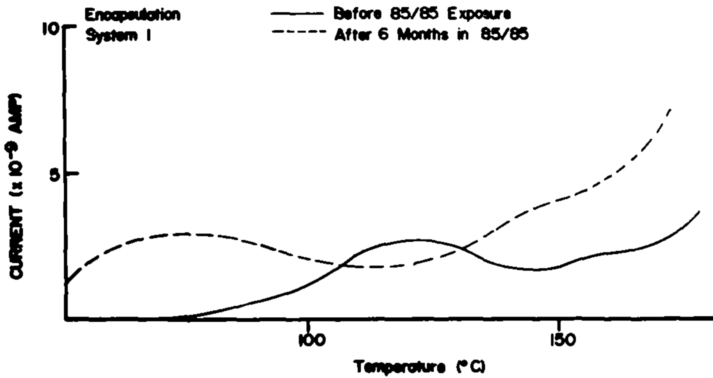

Fig. 11. Moisture Effects In Encapsulation System

TSD experiments as done on highly ordered polymer systems(2) enable resolution of a number of thermogram peaks. One of those occurring at the lowest energies is attributed to thermally stimulated free rotation of the side chains associated with hydrogen bonding. Such an effect is believed evidenced by the figures. We think that the peak shift in Fig. 11 and the peak resolution of Fig. 12 are due to the solvation effect of the moisture on the epoxy side chains(12-15). This solvation would allow the peak, in the case of Fig. 11, to occur at a lower temperature and would associate this peak with rotation of the side chains. The system shown in Fig. 12 on the other hand has permitted the solvation effect to break hydrogen bonds, allowing free rotation to occur and enhancing the mobility of any existent space charge through the removal of steric effects.

Such resolution of individual molecular processes is the real advantage of moisture effect studies. This information when combined with other more common measurements not only allows one to better understand

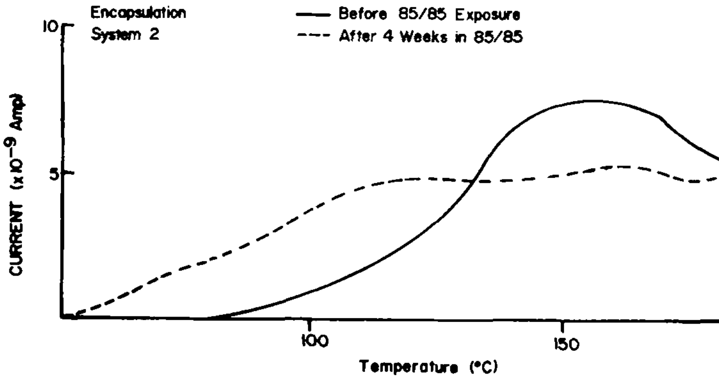

Fig. 12. Moisture Effects In Encapsulation Systems

the chemical processes in an encapsulant but to investigate water absorption mechanisms separately.

Summary

Thermally stimulated discharge (TSD) has been applied to determine polarization processes in components of epoxy encapsulation systems. Polarization effects due to molecular dipole space charge mechanisms have been separated, and the use of TSD for cure state determination has been demonstrated. The effect of resin/hardener stoichiometry and of catalyst level on TSD thermograms has also been detailed. Generally, 100% stoichiometry was found to minimize TSD thermogram structure. Surface removal studies indicate that the most important contributors to TSD are unreacted fragments of the chemical composition. TSD is shown to be effective in studying moisture effects in polymer encapsulants allowing individual molecular processes to be resolved, and absorption mechanisms to be clarified.

Acknowledgments

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Appendix

Code No.	Type Of Material	Approximate Molecular Weight	Epoxy Equivalent Weight
A	Epoxy Novolac Resin	900	200
B	Epoxy Novolac Resin	1,200	220
C	Epoxy Novolac Resin	1,200	220
1	Novolac Hardener	650	
2	Novolac Hardener	700	
3	Novolac Hardener	650	
a	Amine Catalyst	*	
b	Amine Catalyst	*	
c	Amine Catalyst	*	
d	Organo-Phosphorous Catalyst	*	

*Proprietary

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