Storage Life Evaluation and Aging Mechanism Analysis of Epoxy Resin Potting Materials

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Abstract. The tensile shear samples of potting epoxy resin materials were accelerated under 90°C, 100°C and 110°C temperature conditions. The tensile shear strength was used as the aging characteristic index during the aging test. After normalizing the data in the descending section, the storage life evaluation and analysis is performed based on the Arrhenius model. The retention rate of tensile shear strength is 50% as the critical failure condition. The storage life at 25°C is predicted to be 21.7 years. During the thermal oxygen aging process, the epoxy bonding material’s adhesive interface first undergoes post-curing reaction under the action of heat, and then undergoes oxidative degradation under the action of thermal oxygen. The sample interface is more susceptible to oxidative degradation than the interior. In the oxidative degradation stage, the part of the epoxy resin connected to the hydroxyl group is oxidized to the aldehyde group, and the methylene group connected to the N in the curing agent is oxidized to C=O, forming C=O in the amide, and the molecular backbone is broken and produce low molecular weight polymers.

1. Introduction
Epoxy resin materials have excellent insulating properties, mechanical properties, chemical stability, and dimensional stability [1]. They are widely used as encapsulation and casting materials in electrical equipment [2-3]. As a potting material, epoxy resin is widely used in electrical equipment. It is filled in the electronic component circuit, which can strengthen the integrity of the electronic device, improve the resistance to external shock and vibration, and improve the insulation between the internal components and the circuit. It is conducive to miniaturization and light weight of the device, avoids direct exposure of components and lines, improves the waterproof and moisture resistance of the device, and improves the performance and stable parameters [4]. and improve the performance and stable parameters. Current research believes that the aging failure of epoxy resin potting materials is mainly due to the chain reaction of the epoxy resin main chain caused by oxygen radicals at a higher temperature, resulting in the degradation of the epoxy resin main chain, which makes the epoxy resin The performance of the potting material decreased in terms of mechanics and electricity. Therefore, the research on storage life prediction of epoxy resin potting materials is of great significance for the reliability analysis and life evaluation of electronic products [5-9]. In this paper, an accelerated aging
test is carried out on epoxy resin potting materials. The tensile shear strength is used as the aging characteristic index. Based on the Arrhenius model\textsuperscript{[10-15]}, the storage life evaluation and analysis are carried out, and the aging mechanism is discussed.

2. Experimental materials and methods

2.1. Experimental materials
The main raw materials and curing process of epoxy resin potting materials are shown in Table 1. Adhesive shear samples are prepared with reference to the standard "GB/T 7124-2008 Determination of Adhesive Tensile Shear Strength (Rigid Material to Rigid Material)". The preparation process of adhesive shear samples is: cleaning of adhesive materials, preparation of adhesives, adhesion and curing. First, use alcohol and acetone to wipe and clean the metal adhesive interface material, and make preparations according to the instructions for the adhesive; prepare according to the requirements of the shear sample preparation standard. To ensure the same pressure during bonding, use the same specification clip to cut. The sample is clamped until it solidifies; and placed under the specified temperature conditions for curing.

| Materials          | Components | Curing process          |
|--------------------|------------|-------------------------|
| Epoxy resin        | E-39-D     | 100°C (2h) + 130°C (6h) |
| Curing agent       | N-7        | + 100°C (2h)            |
| Curing accelerator | DMP-30     |                         |

2.2. Performance test
The mechanical performance test uses the 5582 type precision universal material testing machine of INSTRON company; the microscopic morphology analysis observation instrument is FEI company scanning electron microscope and Japan HIROX company KH-3000VD three-dimensional video microscopy system; X-ray photoelectron spectroscopy analysis test equipment is American Thermo The company's ESCALAB250 X-ray photoelectron spectrometer (XPS) uses an aluminium target monochromator light source; the micro infrared spectroscopy analysis test instrument is the American Thermo Corporation IN10MX type micro infrared spectrometer, using liquid nitrogen to cool the MCT detector.

3. Results and analysis

3.1. Accelerated aging test results
E-39-D material shear samples were accelerated aging test under the conditions of 90 °C, 100 °C and 110 °C, the shear strength increased first and then decreased with the aging time under the three temperature conditions, from the aging characteristics According to the change rule of the index, it is preliminarily judged that the aging process is cross-linked first and then degraded. The result data is shown in Figure 1.
Figure 1. E-39-D accelerated aging test results.

3.2. Analysis of accelerated aging test results

3.2.1 Data processing model for storage life prediction
During the thermal aging process, the relationship between the aging characteristic index $P$ and the aging time $\tau$ can be described by the empirical formula (1).

$$P = A e^{-K\tau}$$

In the formula: $P$ is the aging characteristic index with aging time of $\tau$; $\tau$ is the aging time, d (day); $K$ is the rate constant of performance change, d$^{-1}$ (day); $A$ is a constant. If the test data calculation results show that the linear correlation coefficient of $\ln P$ and $\tau$ is lower than the look-up table value, formula (1) can be modified to formula (2) to describe the relationship between performance index $P$ and aging time $\tau$.

$$P = A e^{-K\alpha\tau}$$

In the formula: $\alpha$ is a constant, the meaning of other parameters is the same as the formula [1]. The relationship between the rate constant $K$ and the temperature $T$ of the aging characteristic index follows the Arrhenius equation:

$$K = Ze^{E/RT}$$

In the formula: $T$ is the absolute temperature, and the unit is K; $E$ is the apparent activation energy, J·mol$^{-1}$; $Z$ is the frequency factor, d$^{-1}$; $R$ is the gas constant, J·K$^{-1}$·mol$^{-1}$.

The aging rate constant under different temperature conditions can be calculated by evaluating the thermal aging test data of the object, and then the aging rate constant under the condition of the predicted storage temperature (usually 25°C) can be extrapolated. Set the retention rate of the aging characteristic index as a certain value as the failure threshold, and calculate the storage life of the evaluation object under the condition that the storage temperature is 25°C.

3.2.1 Data analysis of heat aging test
In the aging process, the post curing and degradation effects make the degree of crosslinking increase first and then decrease, which leads to the increase and then decrease of the bonding strength. The
storage life assessment is based on the data of the descending section in Figure 1, and the data is processed according to the exponential degradation law of shear strength degradation. The normalized data of E-39-D heat aging test is shown in Figure 2. According to the data processing method in 3.2.1, the test results of 90°C, 100°C and 110°C are fitted, and the prediction is made at 25°C, and the results are shown in Table 2.

![Figure 2. E-39-D aging test data processing results.](image)

| Material | α    | r1   | K25   | 25°C     |
|----------|------|------|-------|----------|
| E-39-D   | 0.59 | -0.9961 | 0.002681 | $p/p_0 = 0.8543(e^{-0.002681t^{0.59}})$ |

3.3. Analysis of aging mechanism of E-39-D material

3.3.1. Analysis of Infrared spectroscopy

Figure 3 shows the infrared spectrum test results of samples with different aging cycles. Comparing the infrared spectrums of different test cycles, it can be seen that the infrared spectrum of the E-39-D material before and after the heat aging test does not change significantly, that is the characteristic peaks do not disappear or new peaks occur.
Figure 3. Infrared spectrum during E-39-D material aging test.

3.3.2. Analysis of X-ray photoelectron spectroscopy
Table 3 shows the X-ray photoelectron spectroscopy test results of samples with different aging cycles. The results in the table show that C/O is higher than that in the early stage to the middle stage, and decreases in the middle stage to the late stage. According to the analysis, in the early stage of the thermal aging test, under the effect of temperature, the incompletely cured reactive groups in the molecular chain at room temperature were further cross-linked and cured, the C-containing main chain increased and the C/O ratio gradually increased; thermal aging In the middle and late stages of the experiment, the degradation was dominant, the main chain was degraded and broken, and O atoms intervened in the degradation chain ends, the number of O atoms increased, and the C/O ratio decreased.

| Aging cycle | Atom percentage |
|-------------|----------------|
|             | C1s  | O1s  | Si2p | Na1s | N1s  | Ca2p |
| 17d         | 76.70| 21.41| 0.81 | 0.47 | 0.46 | 0.16 |
| 49d         | 77.94| 20.56| 0.52 | 0.33 | 0.30 | 0.35 |
| 94d         | 75.76| 22.44| 0.43 | 0.65 | 0.39 | 0.33 |

3.3.3. Micromorphology analysis
After carrying out a certain period of aging test at a temperature of 110°C, the shear strength test is completed, and a flat sheet sample is peeled off from the bonding interface of the tensile shear sample to analyze the micromorphology of the bonding interface. Figure 4 shows the 100× condition micromorphology of the interface under different aging cycles under an optical microscope. As the aging time increases, the granularity of the interface has a tendency to refine, but the overall morphology difference is not obvious.
Figure 4. Micro-morphology of the interface under different aging cycles under an optical microscope.

Figure 5 to figure 7 are the scanning electron microscope observation of the microscopic morphology of the interface during different aging cycles. A large number of fine particle morphologies can be clearly observed in the high magnification (6000×) picture. These particles are firmly attached to the interface material, and the denser the particles, the higher the adhesion strength should be. In the figure, the granules are the most dense in the middle of the heat aging test, corresponding to the highest shear strength, while the granules in the early and late stages are relatively sparse, which is the first increase in shear strength due to competition for crosslinking/degradation during the thermal aging of the adhesive. The post-curing phenomenon of post-reduction coincides.
3.3.4. Thermal-oxidative aging mechanism

During the thermal-oxidative aging process, the epoxy adhesive and its bonding interface first undergo a post-curing reaction under the action of heat, and then undergo oxidative degradation under the action of hot oxygen [16]. The surface of the sample is more susceptible to oxidative degradation than the interior. In the oxidative degradation stage, the part of the epoxy resin that is connected to the hydroxyl group is oxidized to an aldehyde group, and the methylene group that is connected to the N in the curing agent is oxidized to C=O, forming C=O in the amide, and the molecular backbone is broken. And produce low molecular weight polymers [17].

4. conclusion

The epoxy resin potting material was accelerated under the temperature conditions of 90°C, 100°C and 110°C, and the tensile shear strength was used as the aging characteristic index. During the aging test, the tensile shear strength first increased and then decreased. Based on the test results of the falling section, and calculation of the Arrhenius model, a 50% drop in tensile shear strength is a critical failure condition, and the storage life at 25°C is predicted to be 21.7 years. The aging mechanism
analysis shows that during the thermal oxygen aging process, the epoxy adhesive and its bonding interface first undergo a post-curing reaction under the action of heat, and then undergo oxidative degradation under the action of the thermal oxygen. The cross-linking/degradation competition during the thermal aging process, and consistent with the post-curing phenomenon.

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