Effect of temperature cycling on performance of epoxy resin and evaluation of state

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Abstract. Epoxy resin samples were prepared according to the most common types of epoxy resins and curing agents in the market. The material was temperature-circulated at -40 to 150°C to investigate the effect of temperature cycling on the dielectric properties and bending properties of the material. The results show that with the increase of the number of temperature cycles, the relative dielectric constant, dielectric loss, flexural strength and flexural modulus of epoxy resin increase first, then decrease and then increase, and the electrical conductivity increases. Based on the samples of various performance values of epoxy resin in different times, an evaluation model based on BP neural network was established to evaluate the state of epoxy resin.

1. Introduction

Epoxy resin has good electrical properties and high mechanical strength, and is commonly used in the insulation of electrical equipment such as low-voltage grade cast-in transformers. Especially in cast-in-place transformers, epoxy resin has long been subjected to the internal heat of the transformer and the temperature change of the external environment, and its performance directly affects the performance of the transformer.

As an electrical insulating material, epoxy resins are often subjected to thermal shock. The stability of the epoxy resin is especially important when the temperature changes drastically. When the surface of the material is rapidly heated or cooled, the outer layer and the inner layer of the material form a temperature transition of thermal expansion and shrinkage unevenness, resulting in uneven stress, cracking, and deterioration of mechanical and electrical properties [1, 2, 3].

Dielectric properties and mechanical properties are important parameters for evaluating insulating materials. The dielectric properties directly reflect the material's savings and loss characteristics for electrostatic energy [4]. The mechanical properties reflect the material's ability to withstand mechanical loads. Therefore, it is important to study the influence of temperature cycling on the electrical and mechanical properties of epoxy resin and the evaluation of the state of epoxy resin.

Before, domestic and foreign research scholars have done a lot of research on the damp heat aging of epoxy resin. Li Bo [5] studied the dielectric properties and static mechanical properties of epoxy resin under four types of damp heat aging, and proposed the life prediction of epoxy resin by Arrhenius extrapolation method. YUE Ying-juan [6] studied the tensile properties of epoxy resin by
hydrothermal aging test. Gao Kun [7] et al. studied the effects of damp heat aging on compressive strength, flexural strength, shear strength, dynamic mechanical properties and dielectric properties of glass fiber/epoxy composites. Most of the research on epoxy resin is focused on the wet heat aging of materials. It is rare to study the effect of temperature cycling on the performance of epoxy resin and state evaluation.

In this paper, samples were prepared for the most common types of epoxy resins and curing agents in the market. The material was subjected to a temperature cycle test at -40 to 150℃, and the dielectric properties and bending properties of the sample were tested. The effect of temperature cycling on the dielectric properties and bending properties of epoxy resin was investigated. Based on the test results, a training sample was formed and a BP neural network based method was proposed to evaluate the epoxy resin.

2. Experiment

2.1. Experiment material
Bisphenol A type epoxy resin E-51: epoxy value 0.48 ~ 0.54, Kunshan Lvxun Electronic Materials Company; Hardener: polyetheramine D-230, IPDA, molecular weight 230, 170.25, Kunshan Lvxun Electronic Materials Company; Release agent: silicone grease, Axel Corporation of the United States.

2.2. Sample preparation
Due to the different sample sizes for testing dielectric properties and mechanical properties, the casting was performed with two different moulds according to the requirements of the test instrument and national standards.

The residual material on the surface of the mould was removed, and the mould and mortar were dried in an incubator at 70℃ for 30 minutes until water droplets could not be observed by the naked eye. The mould was taken out, cooled to room temperature, and a small amount of release agent was applied to the mould bonding surface and the casting tank. Tighten the screws to make the mould fit better and minimize the air gap inside the mould. The mass ratio of the epoxy resin to the curing agent was weighed to 3:1, and the epoxy resin and the curing agent were successively poured into a mortar and stirred with a grinding rod for 10 minutes. The mixed liquid was slowly injected into the mould tank, and the mould was placed in a vacuum drying oven for vacuum degassing for 20 minutes. After the degassing was completed, the mould was placed in an incubator at 70℃ for 12h. Remove the mould, cool to room temperature, take out the sample, and smooth the surface of the sample. Finally, a dielectric property sample having a diameter of 30mm and a thickness of 1mm and a bendable sample having a length of 60mm, a width of 12mm, and a thickness of 3mm were obtained.

2.3. Experiment method

2.3.1. Temperature cycle test. The dielectric property sample and the bending property sample were grouped into three samples each, and the sample was placed in a temperature chamber, exposed to the air. The temperature cycle test was carried out in accordance with GB/T 2423.22-2002. The high temperature is set to 150℃, the low temperature is set to -40℃, the temperature change rate is 2℃/min, and the sample is exposed to high and low temperature for 30 min. One temperature cycle time is 4h10min.

2.3.2. Dielectric performance test. The dielectric properties of the samples were tested using a broadband dielectric impedance spectrometer from Novocontrol, Germany, in conjunction with Novocontrol’s BDS 1200HV sample holder. The test was carried out under vacuum at room temperature. The electrode with a diameter of 30mm was selected and tested in the frequency range of 100 to 102 Hz, and the measurement results at 50 Hz were selected as the test results for analysis.
2.3.3. Bending performance test. The bending performance of the sample was tested by a microcomputer-controlled electronic universal material testing machine. Adjust the span to 50mm to ensure that the centre of the specimen is at the midpoint of the span. The loading head is perpendicular to the base and the loading speed is 2mm/min until the sample breaks. The strain-displacement curve of the sample was recorded.

3. Test results

Figure 1 is a comparison of the appearance of epoxy resin dielectric properties after different temperature cycles. As can be seen from Figure 1, as the number of cycles increases, the colour of the resin deepens. Under normal conditions, the epoxy resin without any modifier added is colourless and transparent, and after being subjected to alternating high and low temperature effects, the appearance of the resin changes from colourless to pale yellow, and then from pale yellow to deep yellow.

![Figure 1. Comparison of the appearance of different temperature cycling samples.](image1)

Thermal oxygen will have an effect on the colour of the epoxy resin. Figure 2 is a preparation process of a bisphenol A type epoxy resin, which is obtained by chemical reaction of epichlorohydrin and bisphenol A under the catalysis of NaOH. For aromatic epoxy resins, the bisphenol A type structure is easily oxidized to form a carbonyl group to form a yellowing group. At the same time, the epoxy resin will directly polymerize with the free amine in the amine curing agent, so that the local temperature rises and accelerates yellowing [8, 9].

![Figure 2. Preparation method of bisphenol A epoxy resin.](image2)

3.1. Dielectric performance test results

In order to investigate the effect of temperature cycling on the dielectric properties of epoxy resin, epoxy resin samples were divided into 10 groups and subjected to temperature cycling of 0 to 10 times. After each cycle is completed, the relative dielectric constant, dielectric loss tangent and conductivity are measured by a broadband dielectric impedance spectrometer. The data are shown in Table 1.

**Table 1. Dielectric performance test results for different cycle Times under power frequency.**

| Times | \( \varepsilon_r \) | \( \tan \delta/10^2 \) | Conductivity /10^{-15} S·cm^{-1} |
|-------|---------------------|-----------------|---------------------------------|
| 0     | 3.130               | 0.582           | 5.25                            |

3.1.1. Analysis of relative dielectric constant results. The relative dielectric constant curve obtained from the relative dielectric constant data in Table 1 is shown in Fig. 3.

![Figure 3. Relative permittivity variation trend.](image)

In the first stage (0 to 3 times), the relative dielectric constant increases in a relatively stable trend. In the early stage, the exposure time of high temperature is not enough, and the viscosity of the medium is relatively large, which is not conducive to the establishment of polarization [10]. The dipole turn cannot keep up with the change of the applied electric field, so the dielectric constant increases slowly. The high temperature exposure time increases, the intermolecular viscosity becomes smaller, and the dipole turn gradually follows the change of the electric field, so the dielectric constant increases as the number of cycles increases.

In the second stage (3 to 5 times), the relative dielectric constant decreases to some extent. This is because the post-curing reaction of the bisphenol A epoxy resin and the polyether amine which are not completely cured in the epoxy resin cured product occurs. Post-cure effect increases the molecular crosslink density, van der Waals force is enhanced, dipoles are difficult to turn, and polarization is weakened. Post-cure can be carried out at different temperatures and the time required is inversely proportional to temperature. The effects of post-cure and low-temperature regions are superimposed and the relative dielectric constant decreases.

When the cycle enters the third stage (6 to 10 times), the relative dielectric constant begins to rise. At this time, the post-cure effect is no longer significant, and the influence of the high temperature zone is dominant. As the number of cycles increases, the water repellence of the material decreases, causing the absorbed moisture to increase and present in the form of ions, resulting in an increase in dipole concentration. At the same time, the epoxy resin begins to age and the molecular chain breaks, which also leads to an increase in dipole concentration. Under the combined effect of these two aspects, the degree of polarization is enhanced, the relative dielectric constant of the sample becomes larger, and the rate of change gradually becomes stable.

3.1.2. Analysis of the results of dielectric loss tangent. The variation curve of the dielectric loss tangent value in Table 1 can be obtained as shown in Fig. 4.

|   | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|---|----|----|----|----|----|----|----|----|----|----|
|   | 3.228 | 3.323 | 3.452 | 3.558 | 3.172 | 3.216 | 3.379 | 3.428 | 3.496 | 3.570 |
|   | 0.732 | 0.747 | 0.768 | 0.786 | 0.663 | 0.675 | 0.790 | 0.853 | 0.874 | 0.899 |
|   | 5.94 | 6.45 | 6.88 | 7.31 | 7.46 | 7.79 | 8.07 | 8.19 | 8.31 | 8.70 |
In the low temperature region, dipole rotation is difficult, and polarization loss changes little in a low temperature environment. The temperature gradually rises, the dipole starts to rotate, and energy needs to be consumed during the polarization process, at which time $\tan \delta$ gradually increases. In the high temperature zone, the polar group turns more easily, the polarization loss increases, and the $\tan \delta$ increases.

In Fig. 4, the value of $\tan \delta$ first increases and then decreases and then increases. Continue to cycle, $\tan \delta$ gradually increases. Finally, the number of temperature cycles increases, the epoxy resin ages, the molecular chain breaks, the dipole concentration increases, the polarization increases, and the dielectric loss becomes large. The water repellence of the material is weakened, the water absorption is increased and exists in the form of ion conductance, which greatly increases the conductance loss.

3.1.3. Conductivity analysis. The change curve obtained from the conductivity data in Table 1 is shown in Fig. 5. The conductivity of a composite material is due to the presence of a certain amount of free charge inside the material, including electrons, holes, and positive and negative ions. Due to the presence of an electric field, they produce directional motion and generate current. Therefore, the conductivity of the composite material is closely related to the number of carriers it contains and the speed of movement of the carriers. It can be seen from the variation curve that the conductivity continuously increases because the concentration of carriers is increasing during the cycle. From the initial degradation of the residual curing agent, to the accelerated water absorption by temperature [11, 12], and finally to the aging of the molecular chain, the concentration of the carrier has been increasing, resulting in the test results.

3.2. Bending performance test results

The samples to be tested are divided into 5 groups, and the number of samples in each group is 3, and 0, 4, 6, 8, and 10 cycles are respectively taken for the samples. After the end of the cycle, the samples were subjected to bending strength and flexural modulus measurements by a universal material testing machine. The test results of bending strength and modulus under different cycle times are shown in Table 2.

| Times | Bending strength | Flexural modulus /MPa |
|-------|------------------|-----------------------|
|       |                  |                       |

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**Figure 4.** $\tan \delta$ variation trend.

**Figure 5.** Conductivity variation trend.
| Times | Bending Strength (MPa) | Modulus (MPa) |
|-------|-----------------------|--------------|
| 0     | 86.667                | 278.228      |
| 4     | 93.903                | 295.020      |
| 6     | 89.232                | 280.575      |
| 8     | 84.678                | 271.726      |
| 10    | 87.224                | 250.605      |

It can be seen from Fig. 6-7 that the relationship between the bending strength, the modulus and the number of times of the epoxy resin is basically the same, and both tend to rise and then decrease. When the number of temperature cycles is less than 4 times, the bending strength of the epoxy resin is slightly increased. This is because the high temperature causes the epoxy resin to post-cure [13, 14, 15], the crosslink density increases, and the bending strength increases. When the epoxy resin is completely cured, the bending strength will reach a peak. The time increases and the epoxy resin ages. Degradation occurs inside the material, the molecular chain breaks, irreversible damage occurs, and the matrix hydrolyses to produce cracks. Therefore, under the long-term temperature cycle, the mechanical properties of the epoxy resin will gradually deteriorate, and the variation principle of the flexural modulus is similar to the bending strength.

Figure 6. Trend of bending strength.

Figure 7. Trend of bending modulus change.

4. State evaluation method based on BP neural network

4.1. State assessment method

The electrical performance indicators measured in the previous tests, such as relative dielectric constant, dielectric loss tangent, and electrical conductivity; mechanical properties such as bending strength and flexural modulus are normalized and summarized into one sample.

The status assessment steps are as follows:

a. Set the number of BP neural network layers: It has been proved theoretically that a single hidden layer network can solve most problems, and only need to appropriately increase the number of neurons in the hidden layer to achieve arbitrary nonlinear mapping. Set the network model one input layer, one hidden layer, one output layer, that is, the number of BP neural network layers established is three.

b. Set the number of input nodes: In this paper, five parameters of $\varepsilon_r$, $\tan\delta$, electrical conductivity, bending strength and flexural modulus of epoxy resin are measured, so the number of input nodes is five.
c. Set the number of hidden layer nodes: The number of hidden layer nodes is determined mainly by the empirical formula.

\[ M = \sqrt{n + m + a} \]  

(1)

Where \( n \) is the number of neurons in the input layer, \( M \) is the number of hidden layer nodes, \( m \) is the number of nodes in the output layer, and \( a \) is a constant between 1 and 10.

d. Set the number of neurons in the output layer: The output is the aging condition of the epoxy resin, so the number of output layers is 1.

Based on the data measured at room temperature, the rate of change of each physical property index value is greater than 30% as aging. The rate of change \( u \) is defined as:

\[ u = \frac{|x - x_0|}{x_0} \times 100\% \]  

(2)

Where \( u \) is the rate of change, \( x_0 \) is the value of the physical quantity measured at normal temperature, \( x \) is the physical quantity under the state to be tested.

When \( u \in [0\%, 10\%] \), the epoxy resin condition is normal. When \( u \in [10\%, 20\%] \), the epoxy resin condition is good. When \( u \in [20\%, 30\%] \), The condition of the epoxy resin is general. When \( u \in [30\%, \infty) \), the epoxy resin condition is aging.

According to the temperature cycle test method of 2.3.1, the sample was subjected to multiple temperature cycle tests, and the test time, parameter value and rate of change of each performance index at different rate of change were recorded as training samples. The training samples are trained several times to form an evaluation model. The sample to be tested is used as the input signal of the model, and the output signal is the rate of change \( u \). The insulation state of the sample to be tested can be obtained by \( u \).

4.2. Status assessment result

Several sets of samples at different times were selected as inputs to verify the rationality of the model. The sample parameters were normalized by using the data measured at room temperature as the reference value. Several sets of sample parameters are shown in Table 3. From top to bottom, the normalized dielectric constant, dielectric loss tangent, electrical conductivity, flexural strength, and flexural modulus are normalized.

| Time | 8h  | 168h | 1152h |
|------|-----|------|-------|
| Samples | 1.0313 | 1.1415 | 1.2806 |
|       | 1.2577 | 1.3196 | 1.5447 |
|       | 1.1314 | 1.2285 | 1.6571 |
|       | 1.0835 | 0.9766 | 0.7123 |
|       | 1.0604 | 0.9771 | 0.6966 |
| u    | 0.0785 | 0.1462 | 0.5741 |

From the evaluation results of the model, it can be seen that the sample is in a normal state at 8h, the sample at 168h is in a good state, and the sample at 1152h is in an aging state. According to the definition of the rate of change of a single indicator, the evaluation results are basically in line with the actual situation.

5. Conclusion

In this paper, the dielectric properties and bending properties of epoxy resin after temperature cycling were studied experimentally. The number of temperature cycles increases, and the relative dielectric constant and dielectric loss tangent become larger overall, but a certain degree of decline occurs in the process due to the effect of post-cure. The conductivity is increased with the increase of the number of times, and is not affected by the post-cure effect. In the early stage, the bending strength and flexural modulus of the epoxy resin will increase due to the presence of post-curing, but as time increases, the molecular chain inside the material breaks and the matrix ages and hydrolyses. Therefore, the bending
strength and the flexural modulus are smaller and smaller, and the bending property of the material is deteriorated.

Epoxy resin is a common insulating material in transformers. During long-term operation, epoxy resin may deteriorate electrical and mechanical properties due to heat aging, resulting in a decrease in insulation performance. Therefore, it is necessary to pay attention to the aging state of the insulating materials in time, establish a reasonable state evaluation process and method, and timely discover the defects existing in the insulating materials. On this basis, the evaluation method of the insulation state of epoxy resin was proposed, and the state of the test was used to evaluate the state.

6. References

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