Investigation of Mechanical Properties of High \( T_g \) Epoxy Resin Material

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(Received 21 June 2021, Accepted 27 August 2021)

This study introduces a new type of high \( T_g \) epoxy resin material. Firstly, the viscoelastic behavior of the resin material was investigated through dynamic mechanical analysis and the \( T_g \) value of the resin material was determined. Secondly, the effect of temperature and aging treatment on the mechanical properties of the resin material was investigated by tensile test. The results showed that as the temperature increases, the movement of the polymer chains in the resin material changes from obstruction to flow, and the \( T_g \) value is approximately 230°C. With an increase in the experimental temperature, the elastic modulus and tensile strength of the resin decrease, and the fracture strain increases. With an increase in the aging time, the elastic modulus of the resin increases, while the tensile strength and fracture strain decrease. This is due to the oxidative decomposition reaction of the resin with oxygen in the air during the aging process, which embrittles the resin material. FE-SEM analysis of the fracture surface after the tensile test was performed to determine the state of the resin material under different experimental conditions.

Key Words: Epoxy Resin, Viscoelasticity, \( T_g \), Tensile Test, Mechanical Properties

1. Introduction

With the continuous development of science and technology, resin materials are attractive to more and more industries. Because of its low cost, easy molding, light weight, etc., it has been widely used in electrical products. Among them, epoxy resin is a thermosetting polymer, which has excellent mechanical properties, low shrinkage, corrosion resistance and thermal stability, and has been increasingly used in engineering applications. However, the life of epoxy resin is affected by many factors, such as temperature, humidity, and operation time. These factors can cause physical, mechanical and chemical aging of resin materials\(^1\).\(^4\).

From the viewpoint of its structure, epoxy resin is usually brittle, and its internal polymer chain is very sensitive to temperature changes. Therefore, the effect of temperature on mechanical properties should be considered when using epoxy resin\(^5\)\(^-\)\(^8\). It becomes very important to understand the mechanical properties under different temperature conditions, and the important factor related to temperature is the glass transition temperature (\( T_g \))\(^9\). When using epoxy resin, most of them are used below \( T_g \), because when the temperature is higher than \( T_g \), the epoxy resin will transform to a rubbery state, so it is necessary to study with a higher \( T_g \) epoxy resin\(^10\). From the perspective of chemical aging, epoxy resin has the characteristics of thermal degradation. Under a certain temperature, the macromolecules in the epoxy resin will undergo cross-linking, degradation and other changes, which will change the characteristics of the material. The changes in these structures can be judged by changes in physical properties\(^2\)\(^,\)\(^11\)\(^,\)\(^12\).

In this study, a new type of high \( T_g \) epoxy resin material was prepared. The viscoelastic behavior was investigated through dynamic mechanical analysis, and the \( T_g \) value was measured. Moreover, the effect of temperature and aging time on the mechanical properties of the material was investigated through tensile test. After the tensile test, the fracture surface was observed with a field emission-scanning electron microscope (FE-SEM).

2. Materials and methods

2.1 Materials

High \( T_g \) epoxy resin material was made of bisphenol A diglycidyl ether (DGEBA) and 4,4’-methylenebis (N, N-diglycidylaniline). The hardener was a mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine. The mixing rate of the epoxy resin and hardener was 1: 0.34 (by the weight ratio).

2.2 Specimen preparation

The stirred epoxy resin was put into a vacuum chamber to degas for 90 min. The defoamed epoxy resin was poured into the Teflon mold which was heated at 80°C on a hot plate. The resin-filled mold was put in an oven and heated at 100°C for 2 hours and at 180°C for 4 hours to harden the epoxy resin fully. The specimen was fabricated according to the standard of JIS Z2201 No. 7, and the dimensions of the prepared tensile specimen are shown in Fig. 1(a). The specimen used in the dynamic mechanical analysis was prepared by polishing the tensile test specimen with a #800 water-resistant abrasive paper. The size of the polished
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2.3 Dynamic mechanical analysis

Dynamic mechanical analysis usually applies a small sinusoidal vibration force to obtain information about the mechanical properties of the specimen. It is the most useful technique to investigate the viscoelastic behavior of polymer materials. The parameters that express its viscoelastic behavior include storage modulus ($E'$), loss modulus ($E''$) and loss tangent (tan $\delta$). These moduli can effectively express the properties of the material. The value of the loss tangent is obtained by the ratio between the storage modulus and the loss modulus, and the formula is Eq. (1):\(^1\)

$$\tan \delta = \frac{E''}{E'} \quad (1)$$

A dynamic viscosity measuring device (SII: DMS6100) was used to analyze the viscoelasticity of the new high $T_g$ epoxy resin material and determine its $T_g$. The measurement conditions of the analysis were: the measurement temperature range is 150°C ~ 350°C, and the temperature rise rate was 1°C/min. The measured frequencies were 0.1, 0.5, 1, 5 and 10 Hz, respectively.

2.4 Aging treatment

Aging treatment was conducted to the tensile specimen. The aging temperature was 120°C and the aging time was 250, 500 and 1000 h. Three specimens were prepared under each experimental condition. The appearance of the tensile specimens after aging are shown in Fig. 2.

2.5 Tensile test

The effect of test temperature and aging treatment on the tensile properties of the high $T_g$ epoxy resin material was investigated by tensile test. Under each experimental condition, three specimens were prepared, and the average value of the test results was used to evaluate the elastic modulus, tensile strength and fracture strain. The experiment was carried out by a universal testing machine (INSTRON: 5567). In order to ensure that the tensile specimen does not slip off the chuck of the testing machine during the experiment, a stick #220 sandpaper on the inner part of the chuck of the testing machine was set. The tensile test used two types of tensile specimens, namely a tensile specimen without aging treatment and a tensile specimen after aging treatment. The tensile specimens without aging treatment was tested at 25, 120 and 200°C, respectively. The tensile specimen with aging treatment was tested at room temperature.

Fracture surfaces after tensile test were observed with a FE-SEM (HITACHI S-4300SE/N) under an accelerating voltage of 16 kV and a probe current of approximately 10 μA. In order to improve the clarity of the observed surface, a layer of osmium was coated on the surface of the observed specimen.

3. Results and discussion

3.1 Dynamic mechanical analysis

Fig. 3(a) shows the relationship between the storage modulus of the resin material and temperature at different frequencies. The results show that the storage modulus of all curves decreases stepwise as the temperature rises at different frequencies. When the temperature reaches approximately 225°C, the storage modulus drops significantly, and then the value of the modulus tends to be constant. At different frequencies, the relationship between the loss modulus of the resin material and the temperature is shown in Fig. 3(b). The results show that the loss modulus at different frequencies increases first and then decreases with an increase in temperature, and reaches the maximum at approximately 230°C. The reason for this trend is that the loss modulus is the energy lost by internal friction. When the temperature rises, the movement of polymer molecular chain begins to move from hindrance to movement. When the temperature reaches approximately 230°C, the polymer molecular chain can move, but it can’t keep up with the change of stress, so the lost energy is the largest. This indicates that some changes have taken place in the molecular motion of the polymer at around 230°C, and this transition is the glass transition. Fig. 3(c) shows the relationship between the loss tangent of the resin material and the temperature at different frequencies. When the temperature reaches the glass transition temperature and the frequency is 10 Hz, the loss tangent value is the smallest. The smaller loss tangent value means the greater crosslinking density of the material and the better its heat resistance.
Fig. 4 shows the master curve of the viscoelastic characteristics of the relationship between time and storage modulus, loss modulus, and loss tangent at different temperatures. The curve can extend the measurement results to a wider time range, and at the same time can show the relaxation behavior of polymer materials in a wider time range. It can be seen from the figure that with the passage of time, the storage modulus drops significantly at around 230°C, while the loss modulus and loss tangent reach their peak values, which further proves that the $T_g$ is around 230°C.

### 3.2 Tensile properties

Fig. 5 shows typical stress - strain curves of tensile tests at different temperatures. The results show that as the temperature increases, the tensile stress and elastic modulus tend to decrease, while the strain keeps increasing. When the test temperature reaches 200°C close to the $T_g$, it can be found that the tensile stress drops drastically and the strain drastically increases. This phenomenon may be due to the increase of temperature leading to the increase of polymer chain fluidity, which makes the resin soften and tends to rubber state.
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Fig. 6 shows the relationship between the test temperature and elastic modulus, tensile strength and fracture strain. From the figure, it can be observed that as the test temperature increases, the elastic modulus and tensile strength of the resin material decrease, and the fracture strain increases. In Fig. 6(a) and Fig. 6(c), it is observed that the decrease of elastic modulus and the increase of fracture strain at 120°C are much smaller than those at 200°C. This is because the kinematic activity of the polymer chain increases with the temperature rises. When the temperature is close to the $T_g$, the molecular motion of the polymer chain is activated and prepares to transform from the glassy state to the rubbery state, and thus the rate of change increases. From Fig. 6(b), it is observed that the tensile strength decreases uniformly with the increase of temperature. This is because the tensile strength is greatly affected by the characteristics of the local structure. The increase in temperature causes relative movement of the polymer chains, and thus a greater change can occur when the test temperature is 200°C.

Fig. 7 shows typical stress-strain curves obtained from the tensile test results of the tensile specimen after the aging treatment. The results showed that the fracture strain and tensile strength decreased significantly with the increase of the aging treatment time. Therefore, it was found that long time aging makes the epoxy resin material embrittlement.

Fig. 8 shows the relationship between aging time and elastic modulus, tensile strength and fracture strain. The results show that with an increase in the aging time, the elasticity modulus increases, while the tensile strength and fracture strain decrease. The reason for the above phenomenon is the thermal decomposition reaction of the resin material. When the resin material is heated, the macromolecules begin to crack, causing changes such as cross-linking and degradation. When the aging treatment is carried out, the resin material chemically reacts with oxygen in the air, and thus the aging at a high temperature for a long time causes the resin to oxidative decomposition.

3.3 Fracture surface observation

Fig. 9 shows the typical fracture forms in the vicinity of the initial fracture area. The result shows that the surface of the fracture is represented by three forms. The first type is the crack initiation area (A area), which is the origin of the crack. The crack begins to grow through the origin. Because the surface of this area is smooth, it is called the mirror area. The second type is the transition area (B area) and the surface roughness of this area increases relative to the mirror area, showing a river-like shape.
The third type of fracture area (C area) and the surface roughness of this area increases instantaneously, and thus the surface has no regular shape. Fig. 10(a) is the fracture surface at 25°C, and it was observed that the main manifestation of the surface is the uneven shapes (C area), which can be judged that the surface is a plastic fracture surface. Fig. 10(b) shows the fracture surface at 120°C. This fracture surface mainly presents a river-like appearance (B area). The surface roughness is reduced compared to that of the fracture surface at 25°C. This is due to the increase in temperature. The fluidity of polymer chain is strengthened with an increase in the temperature. In addition, the strain is partially restored due

Fig. 7 Stress-strain curves after aging at 120°C for different aging times.

Fig. 8 Effect of aging time at 120°C on elastic modulus (a), tensile strength (b), and fracture strain (c).

Fig. 9 Typical fracture forms in the vicinity of initial fracture area (without aging, test temperature: 25°C).

Fig. 10 Fracture surfaces of high Tg epoxy resin without aging treatment by tensile test with temperatures of 25°C (a), 120°C (b), and 200°C (c).
to the viscoelastic properties of the polymer. Compared with the fracture surfaces at 25°C and 120°C, the fracture surface at 200°C (Fig. 10(c)) mainly shows the form of A area. This is because the temperature approaches the $T_g$ at 200°C, and the movement of the polymer chain is more intense. Because of the viscoelasticity, the deformation of the fracture surface gradually recovers after the external force is unloaded.

Fig. 11 shows the observation results of the fracture surfaces by the tensile test after different aging time. The results showed that with the increase in the aging treatment time at 120°C, the fracture surface gradually transitioned to the mirror area, thereby confirming that the fracture surface was a brittle fracture surface. The change of the fracture mode seems to be due to the oxidative decomposition of the resin material.

The new high $T_g$ epoxy resin (A1) was compared with the conventional bisphenol F diglycidyl ether epoxy resin (A2)\(^{14}\). The $T_g$ value of A1 is approximately 230°C and the $T_g$ value of A2 is 108.2°C. Fig. 12 shows the fracture surfaces of the A1 and A2 materials at 25°C and 120°C. From the figure, it can be found that the fracture surfaces of both the A1 material and the A2 material show dimple surfaces at 25°C. When the test temperature was 120°C, it was found that the fracture surface of the A1 material shows radial cracks and the surface roughness decreases, while the fracture surface of the A2 material becomes smooth. This is due to the fact that 120°C is higher than the $T_g$ of the A2 material, which makes the A2 material change from the glass state to the rubber state. It is also because the viscoelasticity of the polymer material enables the strain recovery on the fracture surface of the A2 material. From the above, it can be seen that high $T_g$ epoxy resin can work at higher temperature without rubber state transition.

Fig. 13 shows the fracture surfaces of the A1 and A2 materials at different aging times. The results show that the fracture surfaces of the A1 and the A2 materials gradually became more smooth with an increase in aging time, which was caused by the gradual cleavage of the polymer chains and the decrease in
molecular weight. The roughness of the fracture surface of the A1 material is greater than that of the A2 material at the same aging time. This is because the oxidative decomposition reaction of the A2 material is more intense than that of the A1 material at the same aging time, which makes the molecular weight in the A2 material decrease faster. From this result, it is expected that the high Tg epoxy resin has a longer service life than conventional epoxy resin in the same temperature environment.

4. Conclusions

In this study, a new type of high Tg epoxy resin was prepared to conduct dynamic analysis. Moreover, the tensile test was conducted to investigate the effects of test temperature and aging treatment time on the mechanical properties of the resin material. From the results obtained, the following main conclusions can be drawn.

(1) On the basis of the dynamic analysis, the Tg value of the high Tg epoxy resin was determined to be approximately 230°C by the decrease in the storage modulus curve and the peak of loss modulus.

(2) With an increase in tensile test temperature, elastic modulus and tensile strength decreases and fracture strain increases. Since the movement of the polymer chains in the epoxy resin increases with an increase in temperature, the rate of change of elastic modulus and fracture strain increases at the temperature close to the Tg.

(3) As the aging treatment time increases, the resin material undergoes oxidative decomposition. As a result, the resin material becomes brittle, and thus the elastic modulus increases, and the tensile strength and fracture strain decrease.

(4) Through the observation of the fracture surface, it was found that the fracture surface of the specimen without aging becomes smooth with an increase in temperature, which is caused by the viscoelasticity of the resin material. In the aged specimen at 120°C, the fracture surface becomes smooth with an increase in aging time, which is caused by the embrittlement of the resin material.

(5) The high Tg epoxy resin can work at higher temperatures than conventional epoxy resins without rubbery state transition. At the same temperature conditions, the high Tg epoxy resin is expected to have longer service life.

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