Experimental study on curing of bisphenol A epoxy resin

WANG Chun-wen\textsuperscript{1st}, ZHANG Qin\textsuperscript{2nd}, CHANG Xin-long \textsuperscript{3rd}, Hu Kuan \textsuperscript{4th}, ZHANG You-hong \textsuperscript{5th}, MA Renli \textsuperscript{6th}

Xi’an research institution of high-technology, XIAN, CHINA
\textsuperscript{a}e-mail 1786611567@qq.com
\textsuperscript{* Corresponding author: e-mailxiongch@vip.sina.com

Abstract—Taking the bisphenol A epoxy resin system as the research object, the thermal curing and microwave curing experiments were carried out. The relationship between the curing degree and the hardness of the product after thermal curing and microwave curing was analyzed. The thermally cured product and microwave cured product were tested for tensile properties and infrared spectroscopy respectively. The results show that there is a positive correlation between the degree of curing of the product and the surface hardness. Compared with thermal curing, microwave curing can save 50\% of the time, and the microwave cured product does not generate a new structure. The tensile strength of the microwave cured product is about that of thermal curing, 88\% of the tensile strength of the product.

1. INTRODUCTION
As an important component of composite materials, the matrix is esponsible for transferring loads and protecting fibers. The performance of the matrix material affects the mechanical properties of the composite material to a certain extent. Therefore, scientists from various countries have carried out a lot of research in many aspects such as matrix development, modification, synthesis, and curing process\cite{1-11}. Among them, the epoxy resin matrix has low cost, good comprehensive mechanical properties, and excellent process performance\cite{1-11}. It is currently the most widely used polymer matrix. The curing process of composite materials is essentially a process of cross-linking between the components of the resin matrix to form macromolecules. Carrying out experimental research on microwave curing of epoxy resin and in-depth study of the changes in the physical and chemical properties of the resin curing process will help improve the microwave curing process and lay the foundation for subsequent composite material curing experimental research. Therefore, this article takes the bisphenol A epoxy resin system as the research object to carry out the microwave curing test and thermal curing test research, uses a fluorescent optical fiber sensor to monitor the temperature during the curing process of the epoxy resin, and investigates the corresponding relationship between the curing degree and the hardness of the epoxy resin , to discuss the influence of microwave curing on the structure and mechanical properties of the product, and to provide a reference for the subsequent improvement of the microwave curing process of composite materials.
2. EPOXY CURING TEST

2.1 Ement material
During the test, the epoxy resin system used was provided by Xi’an Aerospace Composite Materials Research Institute. The specific components are shown in Table 1.

| Number | Name                  | Grade | Manufacturer                                      |
|--------|-----------------------|-------|--------------------------------------------------|
| 1      | DGEBA                 | E-51  | Hunan Yueyang Petrochemical Plant                |
| 2      | Thinner               | TDE-85| Tianjin Jindong Chemical Plant                   |
| 3      | Mixed curing agent    |       | Xi’an Aerospace Composite Materials Research Institute |

2.2 Specimen preparation and curing process

2.2.1 Curing monitoring test. At a certain temperature, add the curing agent to the epoxy resin in proportion, mix and stir evenly, and then perform vacuum defoaming treatment. Pour the configured epoxy resin glue into two identical beakers A and B, and place fluorescent optical fiber sensors in the center of the beakers. According to the curing process provided by Xi’an Aerospace Composite Materials Research Institute, the curing temperature of the A beaker adopts the thermal curing process to be 70°C/1h+90°C/2h+120°C/2h. Beaker B uses a microwave curing process. In order to ensure a certain reference, the final holding temperature of the resin in beaker B is the same as that of beaker A. The curing process curves of the two curing methods are shown in Figure 1.

![Curing process](image)

Figure 1 Curing process

2.2.2 Production of pouring body. Pour the configured mixed glue into a polytetrafluoroethylene (PTFE) mold, and then divide the 16 test pieces into two groups, respectively, using a thermal curing process and a microwave curing process. The shape and size of the test piece refer to GB/T 2567-2008 “Test Method for Performance of Resin Casting Body”.

2.3 Test equipment and performance test
The main equipment used during the test is shown in Table 2.

| Number | Name                  | Model   | Manufacturer                                      |
|--------|-----------------------|---------|--------------------------------------------------|
| 1      | Microwave curing system | —       | Independent design                               |
| 2      | Electric oven          | LR016   | Chongqing Yinhe Testing Instrument Co., Ltd.      |
| 3      | DSC                   | DSC822  | METTLER TOLEDO                                   |
(1) Curing degree test: Use a differential scanning calorimeter (DSC) to test the curing degree of the sample, the heating rate is 10°C/min, and the temperature range is 25~300°C.

(2) Hardness test: refer to GB/T 2411-2008 "Plastics and hard rubber use durometer to measure indentation hardness (Shore hardness)".

(3) Infrared spectroscopy (FT-IR) analysis: use Fourier transform infrared spectrometer to measure, the resolution is 0.4 cm⁻¹.

(4) Tensile performance test: refer to GB/T 2567-2008 "Resin Casting Body Performance Test Method for Resin Casting Body".

### 3. TEST RESULTS AND ANALYSIS

#### 3.1 Test phenomenon analysis

The actual curing process temperature curves in the two beakers A and B are shown in Figure 2. Both the thermal curing and microwave curing processes realize the predetermined curing process. During the thermal curing process, the resin temperature in the beaker changes smoothly during the early heating and holding stage; finally at the 120°C holding stage, due to the heating method of thermal curing and heat conduction, the air inside the oven is heated, and the temperature response is slow. After reaching the holding temperature, due to the exothermic curing reaction, a peak temperature of 130.5°C was detected inside the resin. During the microwave curing process, under the action of high-frequency microwave radiation, the polar molecules inside the epoxy resin continuously produce polarization phenomena, and the microwave energy is converted into heat energy and dispersed in the resin system. In the heat preservation stage, because the microwave directly acts on the resin in the beaker, the heating rate is faster. After the heat preservation temperature is reached, the microwave power decreases. The resin in the beaker conducts heat to the outside cold air, and the temperature inside the material drops rapidly. Then, the microwave power turn on and reheat the resin. Because the fluorescent optical fiber sensor does not respond quickly to temperature changes and does not feed back information to the control system in time, there are obvious temperature fluctuations in the heat preservation process. There is a difference of ±6°C between the microwave curing process and the predetermined process, and the extreme value is slightly smaller than that of the thermal curing process.

![Figure 2 The actual curing process temperature curve](image)
The final products obtained by different curing processes are shown in Figure 2. It is observed that the appearance of products A and B are basically the same. The resins are both clear and transparent and bright yellow. The thermally cured products have no obvious defects such as bubbles. Micro bubbles appeared at the bottom of the microwave cured product. This is mainly due to the fact that in the early stage of resin curing, the heating rate of microwave curing is faster, and the bubbles expand rapidly when heated and finally leave tiny pores in the product, which may have a certain impact on the final mechanical properties. However, more importantly, under the condition that the total curing time is shortened by 250 minutes, the microwave curing process still obtains cured products that are relatively similar to thermal curing. This shows that microwave curing can cure epoxy resin systems quickly and efficiently, which is of great significance for saving energy and reducing consumption.

3.2 Curing degree and hardness of cured product
The resin curing process is a process in which simple linear molecules undergo cross-linking reactions to form three-dimensional body-shaped molecules. As the curing degree of the resin gradually increases, the strength, hardness, modulus, and viscosity of the material will gradually change. The DSC equipment for measuring the degree of resin curing is expensive and the measurement time is long, which brings a lot of inconvenience to the degree of curing. Hardness test is a simple and easy experimental method in mechanical performance test. In the process of hardness measurement, the indentation hardness is inversely proportional to the indentation depth, which depends on the material's modulus and viscoelasticity. Due to its convenient measurement, hardness is widely used in performance testing. Therefore, in order to obtain the approximate curing degree of the resin simply and quickly, it is possible to qualitatively judge whether the resin is cured completely by measuring the product hardness of the epoxy resin. In order to verify the curing of the cured products of different processes, the uncured resin and the two cured products were respectively subjected to DSC test and hardness indentation test (as shown in Figure 4). In the indentation hardness test, the D-type Shore hardness tester is used to measure the hardness of the product at different curing stages, and the uncured resin is a viscous fluid without hardness testing. Measure the hardness of the product according to GB/T 2411-2008 "Plastics and hard rubber use a hardness tester to determine indentation hardness (Shore hardness)". The results of curing and hardness measurement are shown in the table.

(a) DSC test
The test results of the curing degree and hardness of the heat-cured specimens cured for different times are shown in Table 3.1 It can be seen that the curing degree and the hardness have an obvious positive correlation. With the continuous deepening of the curing process, the crosslinking density of the epoxy resin and the curing agent continues to increase, and the modulus of the cured product will increase, so that the indentation hardness of the surface will increase. Therefore, there is a correlation between the degree of curing and the hardness, which also shows that the hardness test can roughly judge the degree of curing. After the final curing, the curing degree of the cured products of the two curing processes reached 92.4% and 93.5%, respectively, and both exceeded 90%, which indicates that the epoxy resin system has been basically cured under different curing processes. At this time, the respective Shore hardnesses of the two products are 88.6D and 89.2D. It can be preliminarily judged that when the surface hardness of the product reaches 88D, the resin system is basically cured, which is of great value for quickly judging the curing effect.

Table 3 Curing degree and hardness measurement results

| Sample | Curing method      | Degree of cure % | Hardness |
|--------|--------------------|------------------|----------|
| 1      | Heat curing        | 76.5             | 72.4D    |
| 2      | Heat curing        | 79.4             | 76.5D    |
| 3      | Heat curing        | 83.2             | 83.4D    |
| 4      | Heat curing        | 86.3             | 85.5D    |
| 5      | Heat curing (End of curing) | 92.4   | 88.6D    |
| 6      | Microwave curing (End of curing) | 93.5   | 89.2D    |

3.3 Infrared spectrum analysis

Infrared spectroscopy (FT-IR) analysis refers to irradiating the material to be tested with different wavelengths of infrared light. The infrared rays of different wavelengths can be absorbed by specific molecular groups, so that the infrared absorption spectrum of the material can be obtained, and the molecular structure of the material can be judged. Infrared spectroscopy analysis is one of the important methods to study the molecular structure changes during polymer curing.

According to the source of the absorption peak, the infrared spectrum is roughly divided into two characteristic regions: the characteristic frequency region (4000cm⁻¹–1300cm⁻¹) and the fingerprint region (1300cm⁻¹–600cm⁻¹). Among them, the wavelength absorption peaks in the characteristic frequency region are sparsely distributed, have obvious characteristics, are easy to identify, and can be used to identify functional groups. For example, the characteristic wave number of the carbonyl group (C=O) is around 1700cm⁻¹. Therefore, in ketones, acids, esters or amides and other carbonyl-containing compounds, there will always be a strong absorption peak around 1700cm⁻¹. The absorption peak distribution in the fingerprint region is more complicated, mainly caused by the stretching vibration of single bonds such as C—O, the bending vibration of hydrogen-containing groups such as C—H, and the vibration of the C—C skeleton. When the molecular structure is
different, there will be a certain difference in the distribution of absorption peaks in this region. Therefore, the fingerprint area is very important for identifying the unknown molecular structure.

Figure 5 shows the infrared spectra of specimens obtained by different curing methods. Curves a, b, and c are the infrared spectra of uncured, thermally cured, and microwave cured, respectively. First, observe the curve a, there are obvious double absorption peaks of primary amino groups (—NH2) at 3461 cm\(^{-1}\) and 3370 cm\(^{-1}\), and the characteristic wavenumber of epoxy groups (CO—C) is also obvious at 915 cm\(^{-1}\) Peak. After the curing reaction, observe the thermal curing infrared spectrum curve b, the double absorption peak of the primary amino group (—NH2) disappears, the absorption peak of the epoxy group is also significantly smaller, and the C at 1250cm\(^{-1}\) and 1120cm\(^{-1}\) The peak of —O group has obvious change. This shows that in the epoxy resin system, during the curing process, the epoxy group (C—O—C) is broken and the ring-opening reaction occurs. The epoxy group and the active hydrogen on the primary amino group are added together, consuming the primary amino group (— NH2) and epoxy groups (C—O—C), the molecular structure changes, and absorption peaks of C—N (amine) bond and C—O (alcohol) bond appear at 1340cm\(^{-1}\) and 1120cm\(^{-1}\), The epoxy resin system is also cross-linked by chain monomers to form a three-dimensional network structure. Comparing the infrared spectra of products b and c of different curing methods, the absorption spectra of the two do not generate new absorption peaks, and there is no obvious difference in the characteristic peaks between the two in the fingerprint area, which indicates that the microwave cured product and the thermally cured product are molecularly cured products Have a similar chemical structure. It can be judged that the microwave curing process does not change the chemical structure of the product. This is mainly because the microwave radiation of 2.45GHz is non-ionizing radiation and cannot cause the molecular chemical bond to fracture resonance [12], so it cannot cause the chemical reaction mechanism. change.

![Figure 5 Infrared spectra of products with different curing methods](image)

3.4 Tensile properties of casting body

After the cured product is demolded, the edge burrs of the cast body specimen are polished to obtain the tensile performance test specimen as shown in Figure 6. Tensile tests were performed on the cured products of epoxy resin castings with different curing processes. The tensile properties are shown in Figure 7.

![Figure 6 Tensile specimen](image)
It can be seen from Table 4 that the tensile strength of the microwave cured product is about 88% of that of the thermal cured product. Compared with the thermally cured product, the microwave cured product has a smaller elongation at break, a larger elastic modulus, and a more brittle product. Analysis believes that this is due to the heating mode of microwave curing "body heat transfer". During the product curing process, the selective heating of microwave curing leads to more concentrated heat, greater internal curing crosslinking density and higher curing degree, which makes the product brittleness greater. Observing the performance dispersion coefficient of the two products, it is obvious that the thermal curing performance is less dispersive, which is caused by the excessively fast heating rate at the initial stage of microwave curing and the presence of tiny bubbles generated by gas expansion in the product. It can be seen that while microwave curing is fast curing, attention should be paid to the control of the curing process. The curing speed should not be overemphasized, and the negative impact of excessive heating rate on performance should not be ignored.

| Cured product  | Tensile modulus /GPa | Dispersion coefficient /% | Tensile Strength /MPa | Dispersion coefficient /% | Elongation at break /% |
|----------------|----------------------|---------------------------|-----------------------|---------------------------|------------------------|
| Heat curing    | 2.28                 | 4.51                      | 91.48                 | 3.30                      | 6.32                   |
| Microwave curing | 2.84                | 6.34                      | 80.97                 | 8.34                      | 3.94                   |

4. CONCLUSION

(1) The thermal curing test and microwave curing test were carried out on epoxy resin-based composite materials. The results showed that the appearance of microwave curing and thermal curing products were basically similar. Compared with thermal curing, microwave curing saved 50% of the curing time. It is of great significance to save energy and reduce consumption.

(2) The DSC test of the microwave curing product and the thermal curing product respectively found that the designed microwave curing process can successfully cure the resin; the hardness indentation test of the thermal curing product and the microwave curing product separately found that the thermal curing and microwave curing process products When the curing degree reaches 92.4% and 93.5%, the corresponding Shore hardness of the two products are 88.6D and 89.2D, indicating that there is a positive correlation between the curing degree of the product and the surface hardness, indicating that the hardness test of the cured product can be Roughly judge the degree of curing, which is of great value to quickly judge the curing effect.

(3) By comparing the infrared spectra of the products of different curing methods, it is found that the absorption spectrum of the microwave curing product does not generate a new absorption peak, which shows that the structure of the microwave curing product is the same as that of the thermal curing product.

(4) By comparing the tensile strength of microwave curing and thermal curing, it is found that the tensile strength of the microwave cured product reaches 80.97MPa, which is about 88% of the thermal
cured product; the elongation at break of the microwave cured product is 3.94%, which is slightly less than that of the thermal cured product. 6.32% of the product; the elastic modulus of the microwave-cured product and the heat-cured product were 2.84 GPa and 2.28 GPa, respectively, indicating that the microwave-cured product was more brittle.

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