Application of the Hot Ball Method on Curing Process of an Epoxy Resin

Carlos Calvo Anibarro, Ľudovít Kubičár
Institute of Physics SAV, Dúbravská cesta 9, SK-845 11 Bratislava, Slovakia

Ivan Chodak, Igor Novak
Polymer Institute SAV, Dúbravská cesta 9, SK-845 11 Bratislava, Slovakia

1. Introduction

The paper deals with application of the Hot Ball method on curing process of an epoxy resin. With this method we are able to test the curing stage of the epoxy resin by measuring of the thermal conductivity. Thermal conductivity is a material property that depends on the degree of curing of the polymer. The epoxy resin sample hardens during the curing and the physical properties of the material are changed. We can use this change of the physical properties for identification of the curing process.

Testing of the material property is performed by cycles. In each cycle the thermal conductivity is measured and stored. With the repetition of the cycles a picture on long time material property change is obtained. The curing process has been tested to several temperatures.

2. Description of the Hot Ball method

The Hot Ball method belongs to transient measuring techniques. This method is based on the generation of a constant heat flux by a spherical heat source inside the material to be tested, measuring the temperature response with a thermometer placed in the center of the heat source.

Fig.1. Photo of the hot ball sensor

The constant heat flux is generated by the passage of an electrical current through a resistance assembled to the spherical heat source (r_b). The heat flux penetrates inside the hot ball sensor surrounding (R).

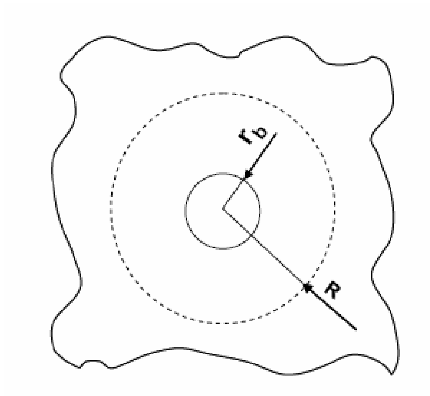

Fig.2. Ideal model

A thermometer placed in the center of the heat source measures a temperature response. While the heat transfer to the surrounding medium is being produced, the temperature of the sample is increased up to a maximal value (T_m), in which the temperature is stabilized.

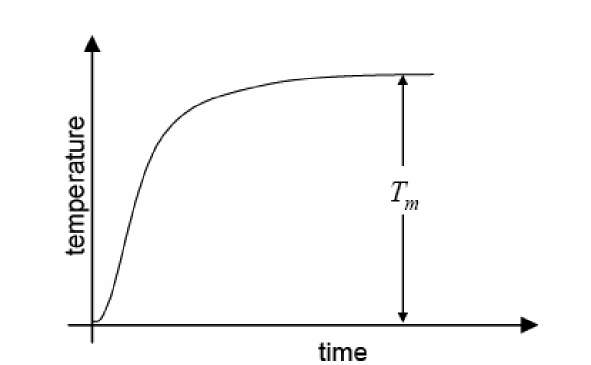

Fig.3. Ideal temperature response

This maximal value of the temperature response is used to calculate the thermal conductivity of the material by the relation

$$\lambda = \frac{q}{4\pi r_b T_m (t \to \infty)}$$

where λ *[Wm⁻¹K⁻¹]* is the thermal conductivity, q *[W]* is the heat flux, r_b *[m]* is the heat source radius and T_m *[K]* is the stabilized temperature value.

In order to obtain a picture on long time thermal conductivity change, testing of the material property is performed by cycles. Each cycle consists on the measuring of the ball temperature (obtaining the base line), the generation of a constant heat until obtaining the stabilized temperature value after some time, and a stabilization stage produced when the heat generation is interrupted.

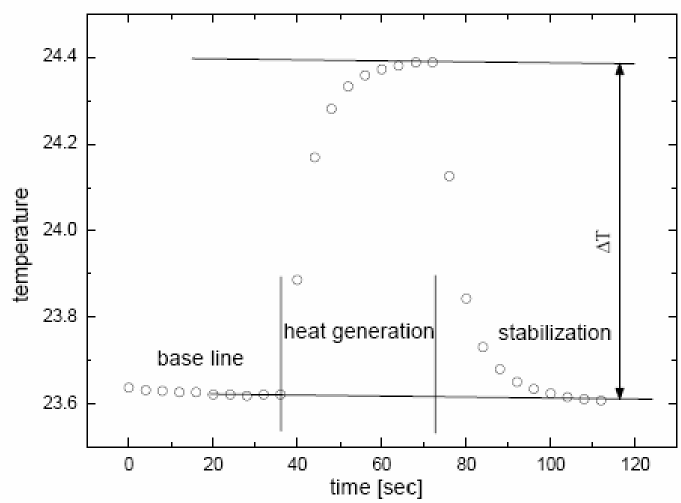

Fig.4.Measuring cycle

Results of each cycle are stored in the data logger and transferred into computer, obtaining automatically the thermal conductivity for each measuring cycle.

3. System

An epoxy oligomer named *ChS Epoxy 513* was used. It is a low-molecular weight epoxyacrylate resin. Its molecular weight is 800 and its viscosity is 400 mPa. A catalyst based on a boric fluoride compound was used as hardener. The sample was prepared by the Polymer Institute of the Slovak Academy of Sciences.

A polymerization following a cationic mechanism is observed. In this kind of polymerization, the catalyst activates an epoxy monomer by forming an oxonium active center.

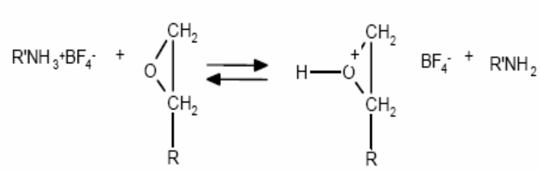

Fig.5.Cationic polymerization initiation

These protonated epoxy molecules can then reacted with other epoxy monomers and proceed in cationic chain propagation by the activated chain end or activated monomer mechanisms.

In the activated chain end mechanism, tertiary oxonium ions are formed and the chain propagates by repeated addition of monomer molecules.

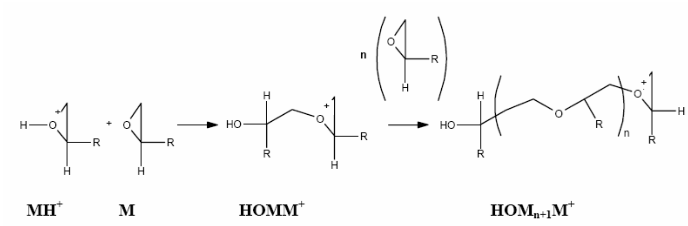

Fig.6.Activated chain end mechanism

Another possibility is the activated monomer mechanism. As the oxiranium ring opens, hydroxyl groups are formed, and with a high formation of active centers, more hydroxyl ions will form. Reaction with these hydroxyls containing species followed a transfer of charge with a monomer to generate the activated monomer, which is again added to a hydroxyl containing species. Thus this path becomes more important as the hydroxyl concentration increases with increasing initiation.

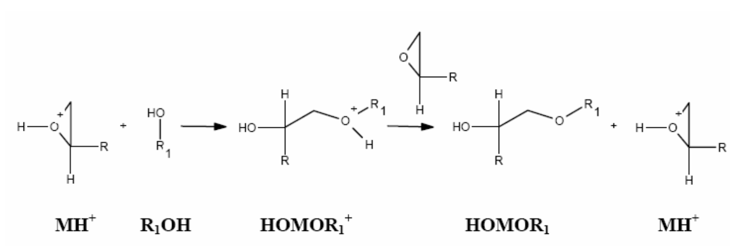

Fig.7.Activated monomer mechanism

A system was prepared in order to realize the measurements. The sample was put inside a metallic recipient, and the hot ball sensor was placed in the middle of this recipient.

A first chamber is placed over the recipient and a second chamber is placed over the first one to have an isothermal process. The temperature inside the chamber is controlled by a thermostat.

The hot ball sensor is connected to an electronic unit that realizes the required functionalities to obtain data on thermal conductivity and to store the corresponding data. Those data are transferred to a computer.

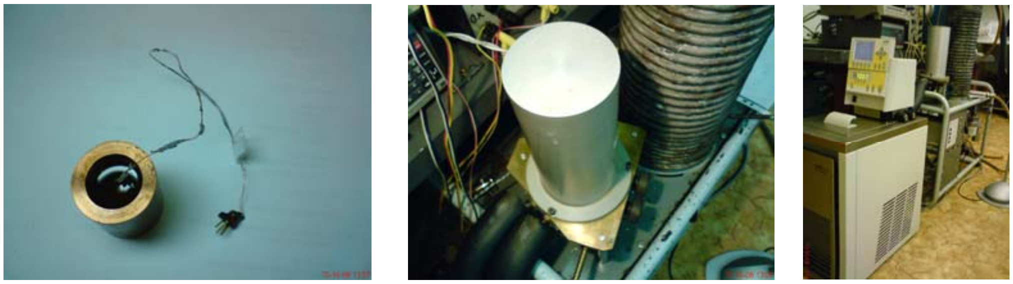

Fig.8.Picture of the hot ball sensor inside the sample

4. Experiment

The calibration of the hot ball sensor is based on the relation

$$q / T_m = 4\pi r_b \lambda = A\lambda$$

The ratio q/T_m is a linear function of thermal conductivity that will be tested using certified materials, namely porofen, calcium, PMMA and glycerol. A calibration function was obtained.

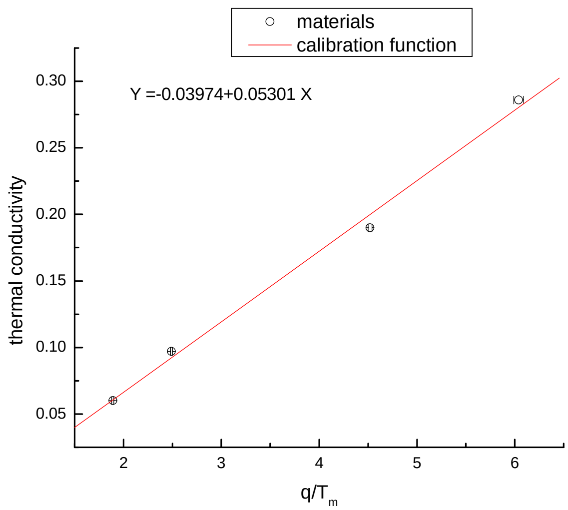

Fig.10.Calibration function

In order to start the monitoring of the curing process, the temperature was set at 30°C. When this temperature was stabilized, the mixture of the epoxy resin was put in the recipient and the hot ball sensor was introduced in the middle of the mixture. The recipient was put into the chamber.

After five days, it was observed that the process was running very slowly. The decision taken was set the temperature at 50°C, in order to accelerate the process.

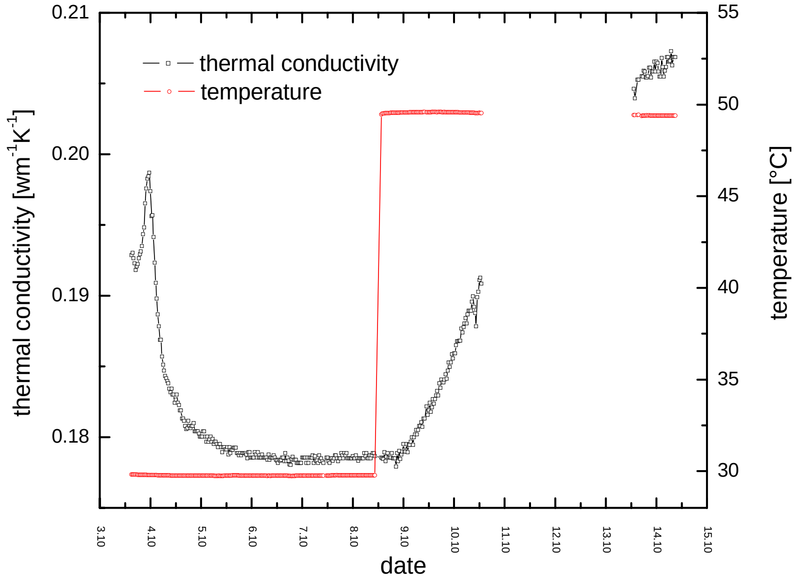

Fig.11.Variation of the thermal conductivity during curing process of the epoxy resin

Fig.11 shows changes of the thermal conductivity and temperature during the experiment. The experiment started at 30°C. Firstly we could observe how the thermal conductivity was going to lower values. It was due to a homogenization of the initial mixture of the two components. When this homogenization had been get, a constant value of the thermal conductivity was obtained. After five days, this constant value was still obtained. We decided to increase the temperature up to 50°C. An increasing in the thermal conductivity was observed, due to the stiffening of the sample. After one week from the beginning of the experiment and due to a problem with the battery of the RTM device, a wide range of measurements were lost. When this problem was solved, the increasing of the thermal conductivity was still running.

5. Conclusion

The application of the Hot Ball method to monitoring curing process of an epoxy resin has been presented.

An epoxy resin based on boric compound has been used for the experiment.

Initially, a lowering of the thermal conductivity was produced, due to a homogenization of the mixture formed by the epoxy resin and the hardener.

The thermal conductivity is increased during the curing process due to the stiffening of the sample.

6. Acknowledgements

This work was supported by project APVV/0497/07.

Authors would like to express thanks to Mr. Markovič for technical assistance and to Mr. Bohač, Mr. Stofanik and Mr. Vretenár for fruitful discussions.