

# C H A P T E R 4

## MICROWAVE CURING OF A --- SPIROORTHOESTER-EPOXY SYSTEM ---

*Increasing production demand of thermoset polymers have promoted the development of alternative curing methods. Microwave irradiation is a promising alternative to conventional heating for the curing of thermosets, with a significant increase in the reaction rate.*

*This chapter describes the copolymerization of a spiroorthoester with diglycidyl ether of bisphenol A under microwave irradiation and its comparison with conventional heating.*

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## 4.1 INTRODUCTION

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Increasing production demand of epoxy resins, due their application in the growing aerospace and microelectronics industries, has promoted the development of alternative curing methods that accelerate this process, which is the bottleneck in the production process of these materials.

Whilst thermal curing increases the cure rate and thus lowers the cure time, this is limited by the fact that the maximum rate of reaction for any given curing system already has an optimum temperature. Heating it to a temperature higher than this optimum would not increase its rate of reaction, but instead lead to thermal degradation of the material.

The incentive for using alternative non thermal curing methods is typically to accelerate the curing process and thus reduce the time of cure. These include the use of ultraviolet light, gamma rays and electron beams. Ultraviolet light has limited application due to its poor penetration ability. Gamma rays are from naturally radiating sources such as Cobalt-60, with enormous radiation hazards and environmental issues. Electron Beam curing has proved to be an accelerated and efficient curing method, but requires often unacceptably high capital outlay. In many systems, the use of microwave irradiation has shown to be a viable alternative for the curing of thermosets polymers, with a significant increase in the rate of reaction.<sup>1 - 8</sup>

The use of microwave irradiation as an alternative heat source is becoming more and more popular in chemistry. Its good acceptance in inorganic and organic synthesis arises from the immense increase in reaction speed, which

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<sup>1</sup> Bogdal, D.; Penczek, P.; Pielichowski, J.; Prociak, A. *Adv Polym Sci* 2003, 163, 193.

<sup>2</sup> Clark, D. E.; Sutton, W. H. *Ann Rev Mater Sci* 1996, 26, 299.

<sup>3</sup> Marand, E.; Baker, K. R.; Graybeal, J. D. *Macromolecules* 1992, 2243.

<sup>4</sup> Tanrattanakul, V.; SaeTiaw, K.; *J Appl Polym Sci* 2005, 97, 1442.

<sup>5</sup> Jacob, J.; Chia, L. H. L.; Boey, F. Y. C. *J Mater Sci* 1995, 30, 5321.

<sup>6</sup> Jayanthi, J.; Boey, F. Y. C.; Chia, L. H. L. *Am Ceram Soc. Ceram Trans* 1997, 57.

<sup>7</sup> Boey, F. Y. C.; Yap, B. H.; Chia, L. *Polym Testing* 1999, 18, 93.

<sup>8</sup> Boey, F. Y. C.; Yap, B. H. *Polym Testing* 2001, 20, 837.

compares favorably with conventional heating for a large number of reactions. Apart from this main advantage, significant improvements in yield, reduction of side reactions and cleaner products have been observed.<sup>9-11</sup>

A simple explanation of the above phenomena is the different mechanism of heating. Traditionally, chemical synthesis has been achieved through conductive heating with an external heat source. Heat is driven into the substance, passing first through the walls of the vessel in order to reach the solvent and reactants. This is a slow and inefficient method for transferring energy into the system because it depends on the thermal conductivity of the various materials that must be penetrated. The thermal equilibrium between the temperature of the vessel and the reaction mixture can take hours.

Microwave heating, on the other hand, is a very different process and it is based on dielectric heating, where the polar molecules, that have a permanent dipole moment, try to align to the applied electromagnetic field resulting in rotation, friction, and collision of molecules, and thus, in heat generation. As a result, the heating rate and efficiency of microwave heating strongly depends on the dielectric properties and the relaxation times of the reaction mixture.<sup>10,12,13</sup>

The use of microwave irradiation in polymer chemistry is an emerging field of research.<sup>14,15</sup> As a result, the number of publications on microwave-assisted polymerizations per year has been growing rapidly (Figure 4.1). Also, in the last few years special attention has been given to microwave curing of thermoset materials.

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<sup>9</sup> *Microwaves in Organic Synthesis*; Loupy, A. Ed.; John, Wiley & Sons, NY 2006.

<sup>10</sup> Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* 2001, 57, 9225.

<sup>11</sup> Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J. P.; Petit, A. *Tetrahedron* 1999, 55, 10851.

<sup>12</sup> *Microwave Synthesis: Chemistry at the Speed of Light*; Hayes, B. L. CEM Publishing, Matthews 2002.

<sup>13</sup> Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S. J.; Mingos, D. M. P. *Chem Soc Rev* 1998, 27, 213.

<sup>14</sup> Wiesbrock, F.; Hoogenboom, R.; Schubert, U. S. *Macromol Rapid Commun* 2004, 25, 1739.

<sup>15</sup> Hoogenboom, R.; Schubert, U. S.; *Macromol Rapid Commun* 2007, 25, 1739.

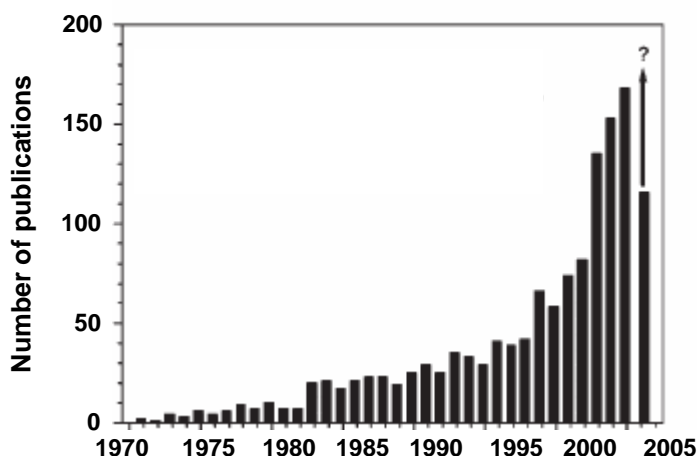


Figure 4.1. Number of publications on microwave-assisted polymerization per year.

Microwave curing of epoxy resins has been investigated by many scientists in terms of structure, dielectric properties, mechanical properties, degradation, percentage of cure, and glass transition temperatures. Thullier<sup>16</sup> studied the influence of continuous and pulsed microwave radiation in the curing of a mixture of diglycidyl ether of bisphenol A (DGEBA) with 4,4'-diaminodiphenylsulfone (DDS) as a curing agent, showing that a low pulse repetition induced the homopolymerization of DGEBA together with the reaction of DGEBA with DDS, while a continuous pulse only promotes the reaction with amines. Other authors<sup>17,18</sup> studied the same reactive curing system and observed that when it is exposed under microwave irradiation, the power absorbed by the sample first increased to a maximum and then decreased before reaching a constant value. Moreover, a significant increase in the reaction rate for the microwave curing of DGEBA/DDS system has been observed by different authors.<sup>19,20</sup> However, other authors<sup>21,22</sup> observed a lower degree of cure and

<sup>16</sup> Thullier, F. M.; Jullien, H.; Loustalot, M. F. G. *Polym Commun* 1986, 27, 206.

<sup>17</sup> Teffal, M.; Gourdenne, A. *Eur Polym J* 1983, 19, 543.

<sup>18</sup> Beldjoudi, N.; Gourdenne, A. *Eur Polym J* 1988, 24, 53.

<sup>19</sup> Lewis, D. A.; Hedrick, J. C.; McGrath, J. E.; Ward, T. C. *Polym Prep* 1987, 28, 330.

proposed that the microwave irradiation accelerated the curing reaction during the first stages of the process, inducing a rapid crosslinking, which created a rigid network that can trap unreacted functional groups, thus actually causing a lower degree of cure which affects the final properties of the material.

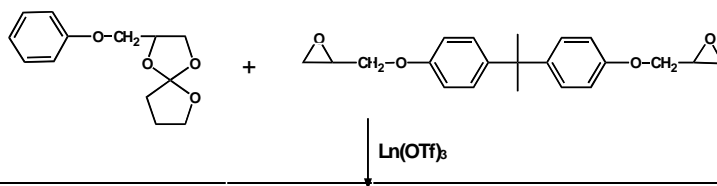
Other epoxy resins<sup>23,24</sup> and curing agents<sup>7,8,25</sup> have also been studied, showing that microwave irradiation is a promising and versatile method to achieve the curing of epoxy materials with considerable reduction in the curing time.

## 4.2 OBJECTIVES

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Although in recent years microwave irradiation has won popularity in the curing of epoxy resins because of the reduction in curing times, no spiroorthoester has been copolymerized with epoxy resins under microwave conditions.

Thus the main objective of the work described in this chapter was to develop new thermosetting materials based on the copolymerization of a spiroorthoester, 2-phenoxyethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-PGE) with the diglycidyl ether of bisphenol A (Scheme 4.1) under microwave conditions and the comparison of the analogous materials obtained under conventional thermal conditions. Moreover, two lanthanide catalysts were used and their behaviour compared.



<sup>20</sup> Wei, J.; Hawley, M. C.; DeMeuse, M. T. *Polym Eng Sci* 1993, 33, 1132.

<sup>21</sup> Jow, J.; Hawley, M. C.; Fingel, M.; Kemp, E. *Polym Eng Sci* 1988, 28, 1450.

<sup>22</sup> Tanrattanakul, V.; Jaroendee, D. *J Appl Polym Sci* 2006, 102, 1059.

<sup>23</sup> Zhang, D.; Crivello, J. V.; Stoffer, J. O. *J Polym Sci Part B: Polym Phys* 2004, 42, 4230.

<sup>24</sup> Wallace, M.; Attwood, D.; Day, R. J.; Frank, H. *J Mater Sci* 2006, 41, 5862.

<sup>25</sup> Fu, Bao.; Hawley, M. C. *Polym Eng Sci* 2000, 40, 2133.



Scheme 4.1

## 4.3 EXPERIMENTAL PROCEDURES AND RESULTS

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The following work includes the experimental procedures and the results of the study performed in this chapter has been submitted for publication in Macromolecular Chemistry Physics and describes the first copolymerization of a spiroorthoester, the 2-phenoxyethyl-1,4,6-trioxaspiro [4,4] nonane (SOE-PGE), with diglycidyl ether of bisphenol A under microwave conditions and its comparison with conventional heating.