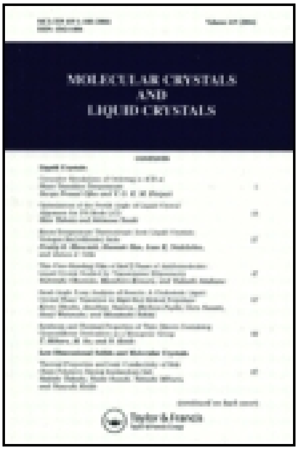

Molecular Crystals and Liquid Crystals

Microwave Assisted Crosslinking Process of Epoxy Resins

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MICROWAVE ASSISTED CROSSLINKING PROCESS OF EPOXY RESINS

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The microwave technique was used intensively in the last few years for synthesis of organic compounds as an alternative method to the classical processes catalyzed by toxic substances. In the present paper the microwave technique was used to obtain composite materials based on the curing process of epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) with different amines as curing agents. Curing tests were performed using meta-phenylene diamine (mPDA), orto-tolidine (o-TOL) and 4,4′-diminodiphenylmethane (DDM) and DGEBA at different temperatures, curing agent concentrations and microwave powers. The curing process was followed by FT-IR Spectroscopy which gives the conversion versus time curves and therefore the curves of reaction rate against time. The results were compared with those obtained in classical processes thermally activated.

INTRODUCTION

The most important aspect regarding the production of thermoset polymer adhesives based on epoxy resins is the curing process which may take place at temperatures depending on the nature of the curing agent. Thus the curing rates and the curing times are strongly influenced by the systems used, the nature and the concentration of the curing agent. Considering the use of epoxy systems as adhesives and encapsulating sealants for the microelectronic industry, the increase of the curing rate is an important demand. However the curing rate exhibits a maximum value which corresponds to an optimum temperature for any given curing system. If the epoxy-curing agent system is heated to a temperature higher than this optimum, the degradation of the resin may occur without any gain in the curing rate.

In the recent years alternative methods to the thermal curing were developed. Many of these studies involved the microwave technique,

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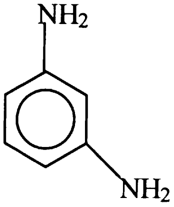
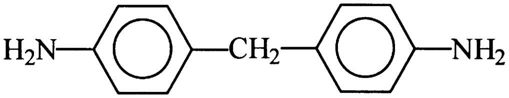
reporting a significant increase in the curing rate [1–6]. The results were influenced by the type of the curing agent used as well as by the microwave conditions [7]. The aim of this work was to compare the curing process of epoxy resins based on diglycidyl ether of bisphenol-A (DGEBA), with different diamines in the classical system (thermal-T) and under the microwave field action (MW).

Tests of curing were carried on using the following amines:

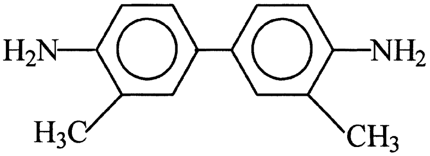
a) meta-phenylene diamine (mPDA)



b) 4, 4′-diaminodiphenylmethane (DDM)



c) orto-tolidine (o-TOL)



One may notice that these amines are primary aromatic diamines which may lead to the DGEBA curing at high temperatures.

The first two amines were reported [6] while the third one (orto-tolidine) was used for the first time as a curing agent for DGEBA.

The curing tests were carried on at different concentration of amines, different reaction temperatures (for thermal curing) and at different powers of the microwave field (for curing under MW).

The kinetics of the curing processes was established by FT-IR Spectroscopy.

EXPERIMENTAL PART

The epoxy resin used was of DGEBA type supplied by DOW CHEMICAL. The diamines were supplied by Merck and Fluka and used as received.

The DGEBA thermal curing processes with the amines were carried on at constant temperature into a MEMMERT oven.

The curing process in the microwave field was performed in a modified domestic microwave oven (Fig. 1).

The curing products corresponding to different reaction times were characterized by FT-IR Spectroscopy, using an FT-IR Schimadzu 8900 equipment.

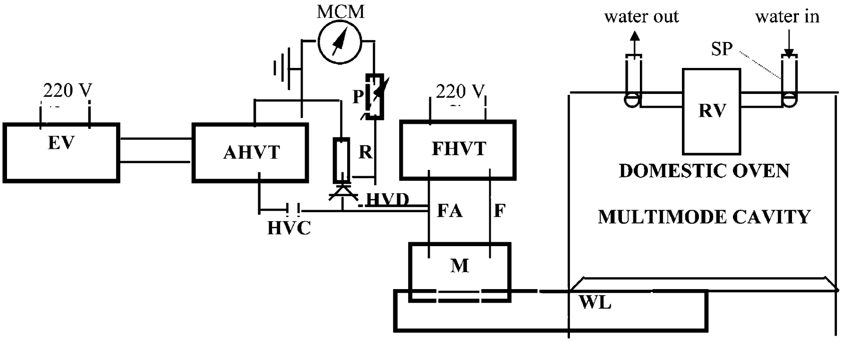
The mixtures obtained from 20 g of DGEBA and different quantities of curing agents were homogenized under stirring by heating at a temperature value less than the curing temperature.

After homogenization the mixtures were pushed in glass phials with a siringe and then introduced in the oven at the desired temperature.

A similar method was applied for microwave curing but only one single phial was introduced in the microwave oven and the MW field was stopped at the desired reaction time.

RESULTS AND DISCUSSIONS

The FT-IR Spectrum of the raw material, DGEBA is shown in Figure 2. The bands followed are one at 905 cm^{-1} (corresponding to the vibration of



WL - waveguide launcher
MCM - magnetron current meter
HVD - high voltage diode
R, P - resistor, potentiometer
EV - electronic variator
AHVT - anode high voltage transformer
FHVT - filament high voltage transformer
M - magnetron
RV- reaction vessel (Teflon)
SP - spiral glass tube

FIGURE 1 Typical system diagram of the microwave installation used for synthetic chemistry.

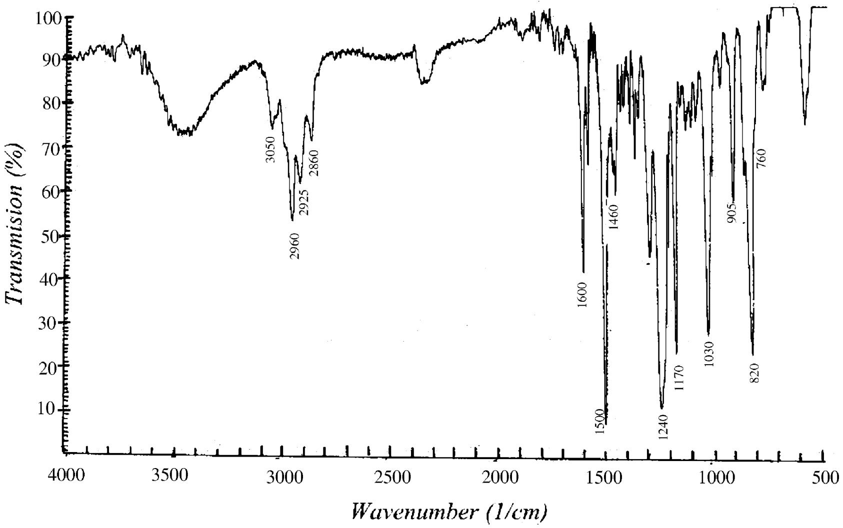


FIGURE 2 FT-IR Spectrum of dyglicydil ether of bisphenol-A (DGEBA) epoxy resin type.

epoxy ring) and one at 820 cm^{-1} (corresponding to the vibration of the C-H bond from the aromatic ring).

The conversion of the curing process was estimated with the formula:

$$\eta = \left[1 - \frac{\left(\frac{A_{905}}{A_{820}}\right)_t}{\left(\frac{A_{905}}{A_{820}}\right)_0}\right] \cdot 100$$

in which:

η-conversion (%);

$\left(\frac{A_{905}}{A_{820}}\right)_t$–the ratio between the absorption at 905 cm^{-1} and 820 cm^{-1} at the precise time t;

$\left(\frac{A_{905}}{A_{820}}\right)_0$–the ratio between the absorption at 905 cm^{-1} at 820 cm^{-1} at the initial moment.

The curing tests were performed for each amine at different concentrations and temperatures.

From Figure 3 one may observe the dependence of conversion against the curing time for the thermal curing process of DGEBA with mPDA at 120°C. The curing process proceeds at a high rate even from the initial moment of the reaction and after 15 minutes the epoxy groups are completely consumed.

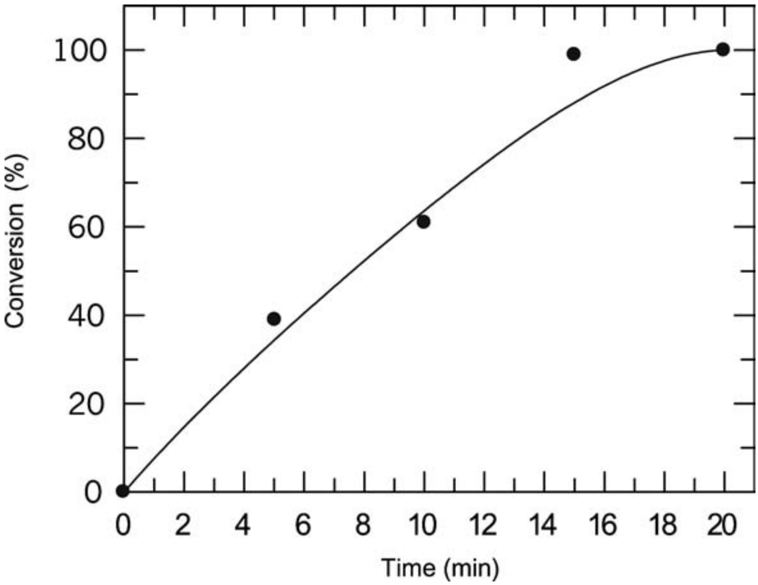


FIGURE 3 The dependence of conversion against time for the thermal curing process of DGEBA with mPDA. Reaction conditions: t = 120°C; [mPDA] = 14.5%.

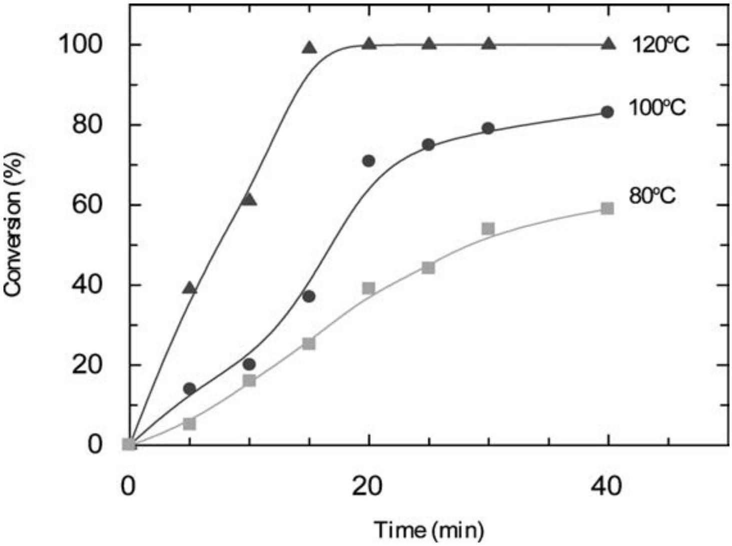


FIGURE 4 The dependence of conversion against time for the thermal curing process of DGEBA with mPDA at three different temperatures. Reaction conditions: [mPDA] = 14.5%.

Curing tests with mPDA were carried on at three different temperatures (120°C, 100°C, 80°C) (Fig. 4).

The conversion vs. time curves exhibit a S shape at 100°C and 80°C, the curing process beginning only after ten minutes, which corresponds to the rearrangement of the polymer chains (DGEBA) in order to be suitable for the attack of the amine group.

The mobility of DGEBA chain at 120°C is very high, thus the curing process starts from the first moment.

The value of the activation energy was calculated as 91 kcal/mol, higher than those mentioned in the literature [5].

The curing tests of DGEBA with mPDA were also done in order to establish the influence of the curing agent concentration on the kinetics.

From Figure 5 one may notice that the curing process starts from the first moment regardless of the mPDA concentration.

For the mPDA concentration of 14.5% the curing reaction occurred with the highest rate. The differences in reaction rates are not significant at low concentrations.

The influence of the curing agent concentration is also shown in Figure 6, where tests of curing with DDM are presented.

For a concentration of DDM lower then 26.6%, the conversion-time curves are similar and the initial rate does not significantly vary.

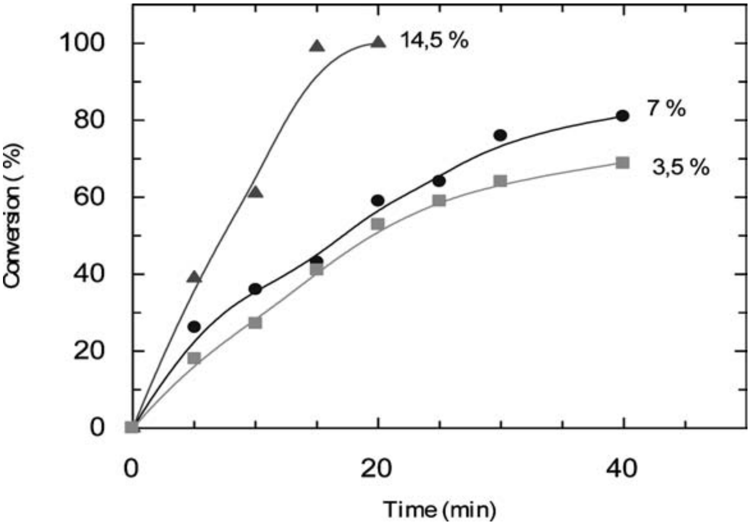


FIGURE 5 The dependence of conversion against time for the thermal curing process of DGEBA with mPDA at different mPDA concentrations. The crosslinking temperature = 120°C.

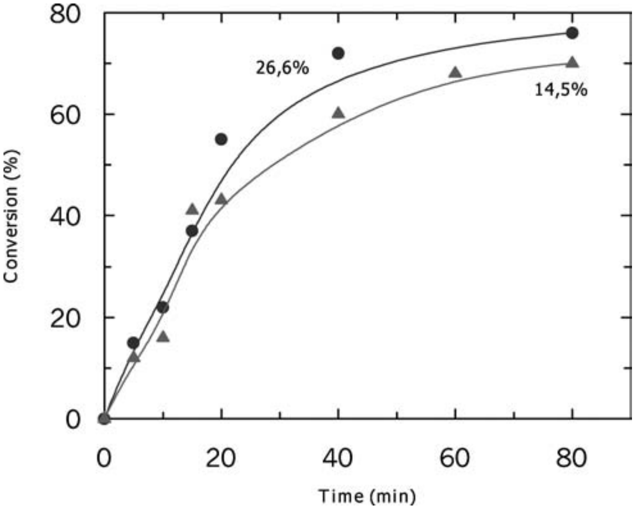


FIGURE 6 Conversion-time dependence for thermal curing process of DGEBA with DDM for two different concentration of DDM. Reaction condition: t = 120°C.

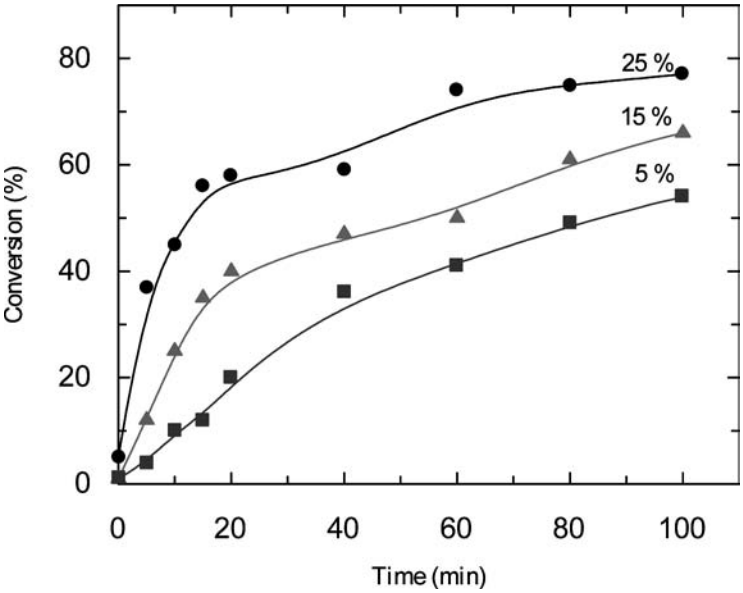


FIGURE 7 The influence of the curing agent concentration against the conversion-time dependence for the thermal curing process of DGEBA with o-TOL. The curing temperature = 130°C.

The results of curing tests of DGEBA with o-TOL, for three different concentration, are shown in Figure 7.

One may observe that all the curing curves exhibit the same shape regardless of the o-TOL concentration. Only in the case of very low concentration ([o-TOL] = 5% wt.) a certain delay in the curing process may be noticed.

The comparison of the behavior of the three amines in the thermal curing process of DGEBA is presented in Figure 8.

Figure 8 shows that mPDA exhibits the highest curing rate. Therefore the curing process ends after 20 minutes. This is due to the very high mobility of mPDA molecules (which include only one aromatic ring) and therefore the attack of epoxy groups is facilitated.

For DDM, the CH_2 group, which is electrodonor, stabilizes the aromatic rings, also increasing the basicity of the NH_2 groups by an additional electrons movement towards these groups. However, due to the two very rigid aromatic rings, the DDM mobility is lower than for mPDA, which may explain the lower rate for the DGEBA curing process with DDM than for mPDA.

The lowest reaction rate is obtained with o-TOL. This can be explained both by high rigidity of the o-TOL molecules which contain two adjacent aromatic rings and by a steric hindrance for the attack of amines exhibited by the methyl groups.

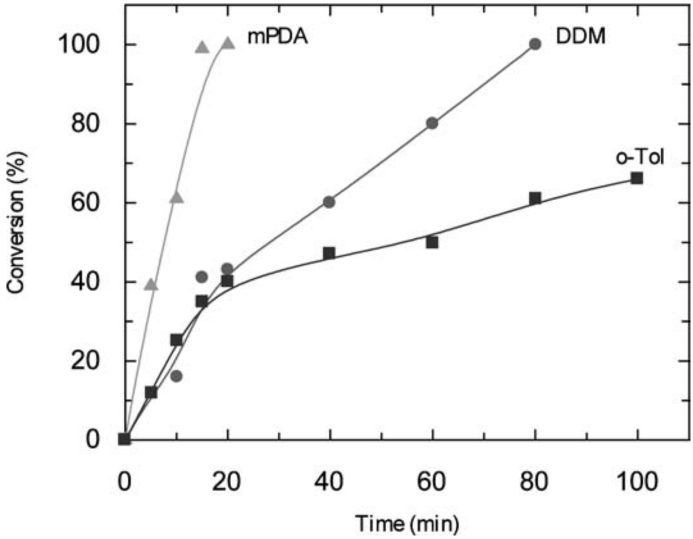


FIGURE 8 The dependence of conversion against time for the thermal curing process of DGEBA with three different amines. [Amine] = 14.5%; t = 130°C.

TABLE 1 The Conditions for Curing Tests of DGEBA with Different Amines under MW

Sample symbol	Article II. amine type	Amine concentration % wt.	Microwave power (W)
A	mPDA	14,5	220
B	mPDA	14,5	400
C	DDM	26,6	220
D	DDM	14,5	220
E	DDM	14,5	400
F	o-TOL	15	220
G	o-TOL	15	400
H	o-TOL	15	600

The curing tests of DGEBA with mPDA, DDM and o-TOL were carried on under microwave field in the conditions presented in Table 1.

Figure 9 shows a comparison between the curing curves for the thermal curing process and microwave curing process of DGEBA with mPDA.

One may notice that the curing process of DGEBA with mPDA in the microwave field goes on with a much higher rate than for a thermal process, thus after 8 minutes the epoxy groups entirely disappeared.

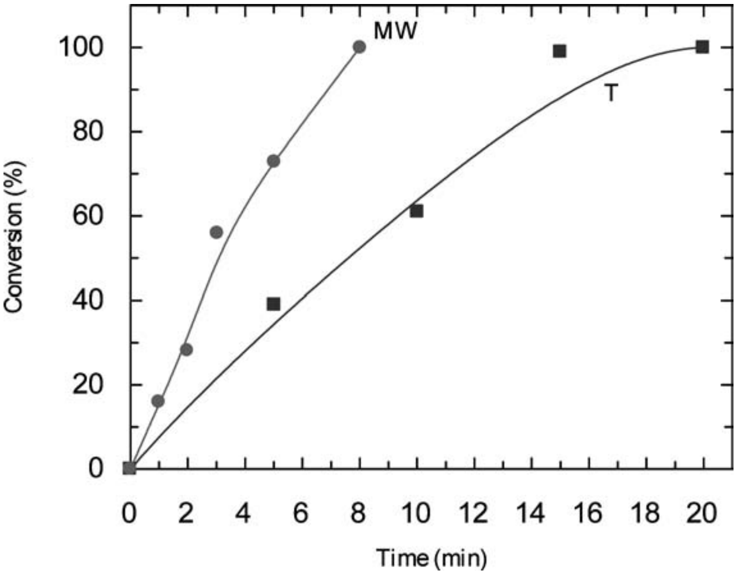


FIGURE 9 The dependence of conversion against time for the thermal curing process (T) and under microwave (MW) of DGEBA with mPDA. Reaction conditions: [mPDA] = 14.5%.

Similar results are obtained in the case of DGEBA with DDM curing under microwave (Fig. 10). Also it may be observed a higher reaction rate in the microwave field.

The influence of the microwave field power on the curing process of DGEBA was put in evidence for o-TOL. The data obtained for three different values of the microwave field power (220, 400, 600 W) are shown in Figure 11.

As it was expected, when the power of the microwave field increases, the corresponding conversion increases.

The difference in reactivity under microwave of the three curing agents (mPDA, DDM, o-TOL) is shown in Figure 12.

It is observed that even in the case of microwave curing the following order of reactivity is maintained:

o-TOL ⟨ DDM ⟨ mPDA

This fact represents an argument for a similar reaction mechanism both in microwave and thermal curing. For all tests the curing processes occur with much higher reaction rate in microwave compared to the thermal methods. This may be explained by the higher temperature reached during

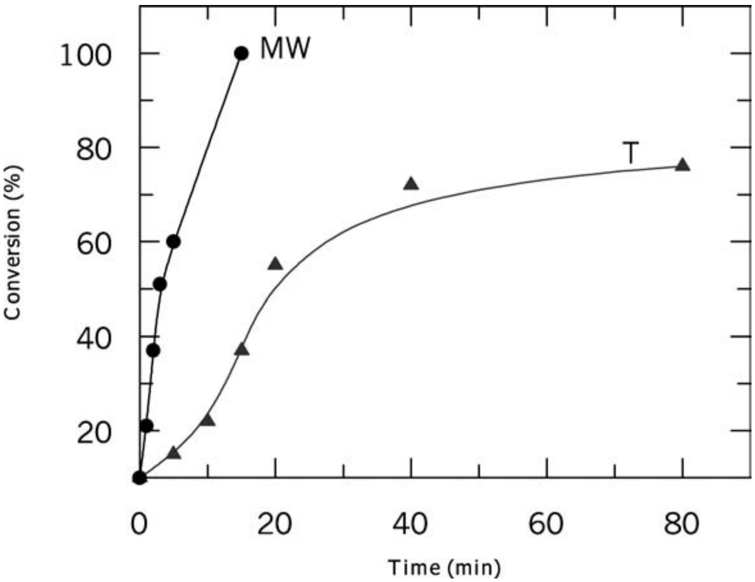


FIGURE 10 The influence of the curing method (thermal T and under microwave MW) on the conversion-time dependence for the curing process of DGEBA with DDM. Reaction conditions: [DDM] = 26.6%.

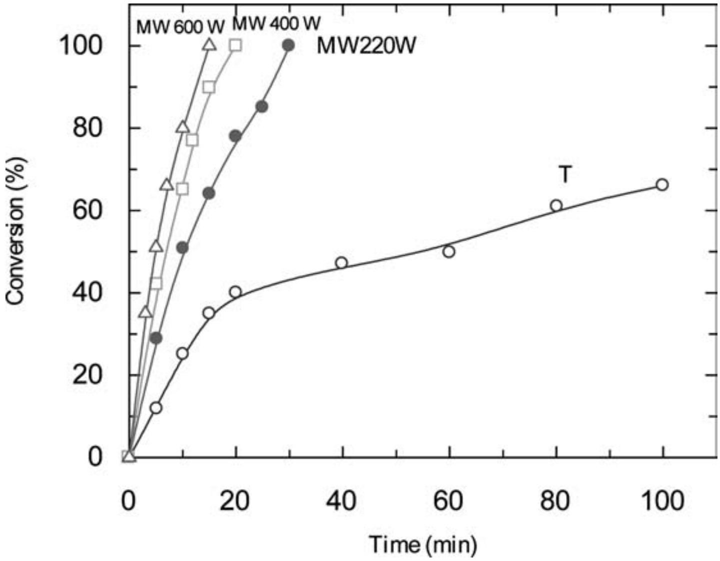


FIGURE 11 The influence of the curing method (thermal T and under microwave MW) and the microwave power against the conversion vs. time dependence for the curing process of DGEBA with o-TOL. Reaction conditions: [o-TOL] = 15%.

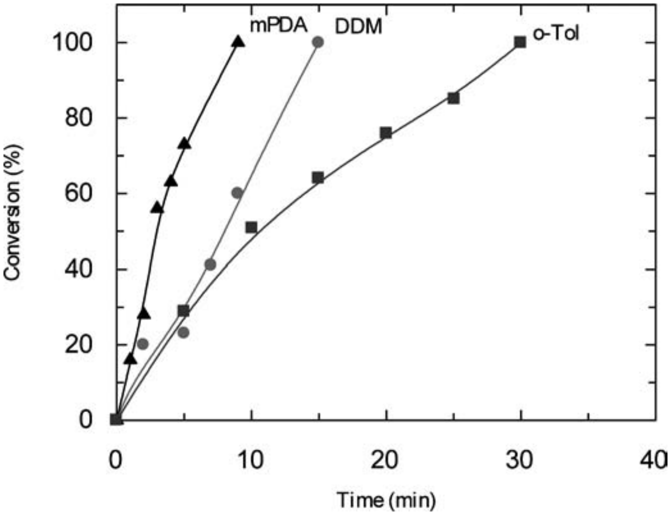


FIGURE 12 The influence of the curing agent type against the conversion vs. time dependence for the curing process of DGEBA under microwave. [Amine] = 14.5%.

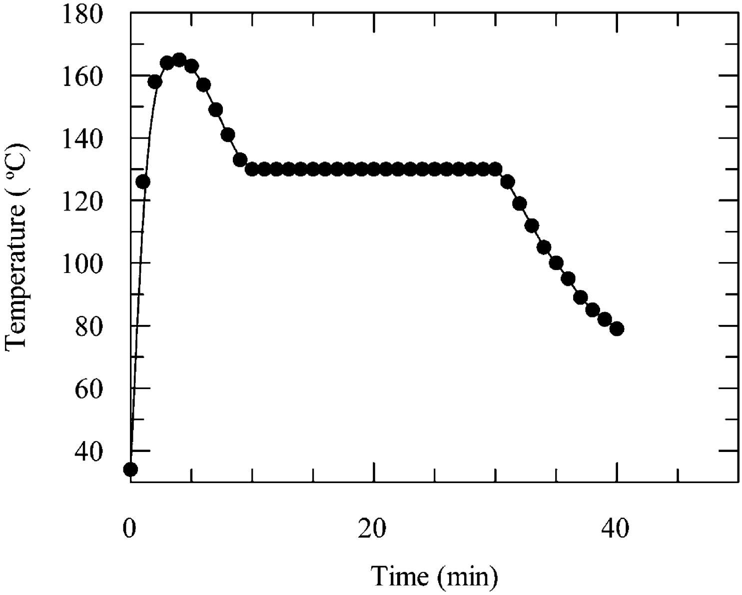


FIGURE 13 The dependence of temperature against time for the microwave curing process of DGEBA with o-TOL. Reaction conditions: [o-TOL] = 15%.

the microwave curing, as it is shown in Figure 13. Even if the temperature was set at 130°C inside the microwave reactor (as it was for the thermal curing process) one may observe that the real temperature is higher, especially during the crosslinking reaction when it reached a maximum value of 165°C.

One may take into account also the formation of hydroxil groups during the curing process, groups that will selectivelly absorbe the microwave energy and will lead to the autoacceleration of the curing reaction.

CONCLUSIONS

The curing process of DGEBA with three different amines namely mPDA, DDM and o-TOL occurs with a higher reaction rate under microwave field than for a thermal classical process. This is due to the higher temperature reached and the selective activation of the polar groups from DGEBA by the microwave field. Therefore the required curing time significantly decreases.

The kinetics of the curing process is influenced by the type and concentration of the amine used as well as by the microwave field power. As the microwave power increases the reaction rate is higher but there is a limitation in the increase of the microwave power which may lead to the degradation of the epoxy resin.

The differences observed in the behavior of the three amines studied, mPDA, DDM and o-TOL, may be explained considering the structure of each amine. Both under thermal and microwave the amines reactivity is as follows:

o-TOL $\langle$ DDM $\langle$ mPDA

The curing process of DGEBA under microwave represents an alternative method to the thermal classical procedure, offering the possibility of a "green chemistry" method for producing composite materials based on epoxy resins due to the low energy consumption, a reduced quantity of catalyst and low curing times.

REFERENCES

[1] Boey, F., Yap, B. F., & Chia, L. (1999). Microwave curing of a DGEBA-amine epoxy system: effect of curing agent on the curing rate enhancement. *Polym Testing*, *18*, 93–109.

[2] Jayanthi, J., Boey, F., & Chia, L. H. L. (1997). Rate enhancement in microwave curing. *Am Ceram Soc Trans.*, *57*, 23–28.

[3] Boey, F. (1997). Application of microwave curing for structural fiber reinforced composite components using a high pressure autoclave. *Am Ceram Soc Ceram Trans.*, *57*, 88–98.

[4] Jacob, J., Chia, L. H. L., & Boey, F. (1997). Microwave curing of polymethylacrylate: conversion at variable power. *J Appl Polym Sci.*, *63*, 787–797.

[5] Chia, L. H. L., Boey, F., & Jacobs, J. (1996). Microwave radiation effect on the polymerization of styrene. *J Polym Sci.*, *34*, 2087–2094.

[6] Boey, F. Y. C. & Yap, B. H. (2001). Microwave curing of an epoxy-amine system: effect of curing agent on the glass-transition temperature. *Polymer Testing*, *20*, 837–845.

[7] Wei, J. B., Shidaker, T., & Hawley, M. C. (1996). Recent progress in microwave processing of polymers and composites. *Trends in Polymer Science*, *4*, 18–24.