Mathematical model of solidification kinetics of epoxy compound

S G Kalganova, V S Alekseev, E Y Vasinkina, Yu A Kadykova, S V Arzamastsev, V V Kovalenko

Yuri Gagarin Saratov State Technical University, 7, Politechnicheskaya Street, Saratov, Russia, 410054

E-mail: s.kalganova2016@yandex.ru

Abstract. A mathematical model of the solidification kinetics of an epoxy compound reflecting the effect of the technological modes of microwave treatment on its structure, physical and mechanical properties was developed. The equation of the crystalline phase growth for the case of microwave solidification of an epoxy compound, which allows the description of the mechanism of the non-thermal effect of the microwave electromagnetic field on the compound, was obtained.

1. Introduction
Treatment with high-frequency and ultrahigh-frequency (microwave) electromagnetic field (EMF) is used in the processing of metallic materials, particularly when modifying the surface of small-sized titanium products [1, 2], and non-metallic materials, in particular for the epoxy compound solidification [3, 4]. However, the information on the mechanism of the modifying effect of the microwave electromagnetic field on polymeric materials is fragmentary. In the opinion of the authors, the explanation of the nature of the non-thermal microwave modification of polymers can be found in polarization effects, their specific features at ultrahigh frequencies.

Due to the effect of an external microwave electromagnetic field, without disruption of chemical bonds, conformational changes occur in the polymer macromolecules. They are related to a change in the density of the molecular packing of interdomain regions, as a result of which the crystallinity degree of the polymer changes and, as a consequence, the properties are modified. The development of a mathematical model of the solidification kinetics of an epoxy compound reflecting the effect of technological modes of microwave treatment on its structure, physical and mechanical properties is an actual and important component of scientific research.

2. Materials and methods
The object of the study was a compound (EC) based on ED-20 epoxy resin and polyethylene polyamine (PEPA) was used as a solidifier. The effect of the microwave electromagnetic field on the process of EC solidification was studied on a specialized microwave equipment at a frequency of 2450 MHz. The equipment allows the adjustment of the microwave power from 130 to 3000 W and processing in a uniform microwave electromagnetic field [5].

The solution of the research problems is based on the application of the scientific fundamentals of electrodynamics, microwave dielectric heating, physical chemistry of polymers. IR spectroscopy was used to study the kinetics of polymerization, since it has a large set of absorption bands corresponding to the vibrations of almost all functional groups (from 12500 to 10 cm⁻¹). The main condition for the application of IR spectroscopy to study the kinetic regularities is the presence of spectrally separated characteristic absorption bands of the resin and solidifier.
3. Results
Let us consider the factors that affect the structural-phase state of solidified EC. Diane epoxy resins have the following general chemical formula [4]:

![Chemical formula of epoxy resin](image)

where \( x = n \) is the number of monomer units in the polymer chain. According to the results of infrared spectroscopy (IRS), the degree of conversion \( \gamma \) DGEBA can be determined, hence the degree of polymerization is [3]:

\[
p = \frac{1}{1 - \gamma}
\]

Solidification of EC is accompanied by reaction of the solidifier with resin molecules and the polymerization of monomer units \( x \). The maximum value \( x_{\text{max}} \) can be found using the Stirling formula [4]. The calculated dependence in the coordinates \((x_{\text{max}}, \gamma)\) is shown in Figure 1. It follows that after \( \gamma \geq 0.7 \), it should be \( x_{\text{max}} \approx p \), and with \( \gamma = 0.1 - 0.7 \) the value \( x_{\text{max}} = 2-4 \) was obtained.

These results show that the polymerization of DGEBA is realized according to two mechanisms: a slow topokinetic one when EC crystalline phase is formed on the nuclei of crystallization corresponding to either a di- or tetrameric polymer and the rapid formation of an amorphous phase at polymerization degrees of the order \( p = 6-100 \). Moreover the globules of EC crystalline phase when solidified with polyamine have a diameter of 0.85 \( \mu \text{m} \) [6,7].

![Graph showing dependence of number of monomeric DGEBA molecules](image)

**Figure 1.** The calculated dependence of the number of monomeric DGEBA molecules as a function of the degree of conversion of the epoxy resin during the solidification process.

It is established that the non-thermal effect of microwave EMF can change the crystallinity degree of the polymer, and, consequently, its properties. Therefore, let us consider the growth patterns of the crystalline phase in the solidification process, which obey the Erofeev-Avrami-Kolmogorov equation [8]:

\[
\alpha = 1 - e^{b \tau^{n}}.
\]  

(1)

where \( \alpha \leq 1 \) is the degree of crystallinity of solidified EC, \( n > 0 \) and \( b = n K^{n}, \tau \) is the solidification time of EC; \( K = B e^{-A/RT_{0}} \) is the crystallization rate constant, \( B \) - Arrhenius pre-exponential, \( A \) - activation energy, \( R = 8.314 \text{ kJ/mol} \) and \( T_{0} = 298 \text{ K} \) is the ambient temperature (at the solidification time of 660–900 min EC heating is insignificant) [3]. After substituting the values \( b \) and \( K \), and double logarithm equation (1) takes the form:

\[
\ln\left[\ln\left(1 - \alpha\right)\right] = \ln n + n \ln B - \frac{n A}{R T_{0}} + n \ln \tau.
\]  

(2)
The expression, according to which by the angular coefficient of the line in the double logarithmic coordinates \((\ln(-\ln(1-\alpha)), \ln(\tau))\) the value can be determined as:

\[
n = \frac{\partial \ln(-\ln(1-\alpha))}{\partial \ln(\tau)}.
\]

And with a known activation energy \(A\), the Arrhenius pre-exponent \(B\) can be calculated. The rate of crystalline solidification can be found from the relation below:

\[
u = \frac{\partial \alpha}{\partial \tau} = n^2 \tau^{n-1} B^n e^{-\frac{n A}{RT_0}} e^{-\frac{n A}{RT_0} \tau^n}.
\]

(3)

From Eq. (3) it follows that with a short duration of EC solidification, the crystallization rate increases, whereas with large values of \(\tau\) it decreases, i.e. it passes through its maximum, which is determined from the condition \(\frac{\partial^2 \alpha}{\partial \tau^2} = 0\) at \(\tau = \tau_{\text{max}}\). Let \(\beta < 1\) be the degree of the amorphous phase of the solidified EC, and \(\beta / \alpha = \xi\) be some constant determined by X-ray diffraction analysis of solidified EC. If \(\gamma \leq 1\) is the degree of DGEBA conversion, which can be determined from the analysis of the infrared spectroscopy (IRS), then it can be written as:

\[
\alpha + \beta = \gamma = \alpha(1 + \xi)
\]

(4)

or

\[
\alpha = \frac{\gamma}{1 + \xi}.
\]

(5)

This implies the following:

\[
\ln \left( - \ln \left(1 - \frac{\gamma}{1 + \xi}\right) \right) = \ln n + n \ln B - \frac{n A}{RT_0} + n \ln \tau.
\]

(6)

Therefore, from the IRS data, by constructing in double logarithmic coordinates:

\[
(\ln \left( - \ln \left(1 - \frac{\gamma}{1 + \xi}\right) \right), \ln \tau)
\]

(7)

It is possible to determine the value \(n\) from the angular coefficient of the obtained lines and, if is \(A\) known, to calculate the Arrhenius pre-exponential \(B\).

Indeed, within the range of solidification time \(\tau \leq 3-4\) hrs, based on the results of IRS and calculating the epoxy number [3], there is rectification of experimental data in theoretical coordinates (7) (Figure 2). In Figure 2, the arrows on the curves show the effect of additional heating of the compound to 65, 100, 150 and 200 °C, respectively. Moreover, the value \(n = 1, 2\) indicates an increase in the distance between the globules of EC crystalline phase, which exceeds their dimensions [7]. The value \(B\) decreases linearly with an increasing ratio of resin volume to the volume of solidifier, while \(n\) and compound temperature \(t\) are independent of this ratio (Figure 3).

It is known if the medium does not have magnetic properties, i.e. \(\mu'_a = 1, \mu''_a = 0\), then the specific power of thermal losses of microwave energy in a heated medium is determined by the relation:

\[
P_{sp} = 0.5 \omega \varepsilon_0 E^2 |E| = 0.278 \omega^{-12} f \varepsilon' \varepsilon'' |E|^2,
\]

(8)

where \(P_{sp}\), W/cm\(^3\); \(\omega\) – circular frequency; \(\varepsilon_0 = 10^{-9}/36\ \pi\), F/m; \(f\) - frequency, Hz.; \(E\) – electric field strength, V/cm; \(\varepsilon_0 = 10^{-9}/36\pi\), F/m; \(\varepsilon', \varepsilon''\) – real and imaginary parts of the absolute permittivity of the medium; \(\varepsilon'_0\) – dielectric losses [8]. If EC solidification occurs as a result of a non-thermal effect of microwave EMF, the absorbed microwave power per 1 mole of DGEBA with allowance for (8) is equal to:
\[ W = \frac{P \tau_{\text{СВЧ}} M}{\rho} = 2.78 \cdot 10^{-13} f e^' i g \delta E_0^2 \tau_{\text{СВЧ}} M \]  

(9)

where \( \tau_{\text{micro}} \) is the time of microwave EMF effect on EC.

Then the equation of the crystalline phase growth for the case of microwave solidification of EC will have the form:

\[ \ln \left[ -\ln \left( 1 - \frac{\lambda}{1 + \xi} \right) \right] = \ln n + n \ln B - \frac{n(A - W)}{RT} + n \ln \tau, \]  

(10)

where \( T \) is the temperature of the reaction mixture (epoxy resin and the solidifier).

It follows from Eq. (10) that the non-thermal effect of microwave EMF on EC leads to a decrease in the energy barrier of the solidification reaction \( A \) with the formation of a crystalline phase by an amount \( W \) due to the increase in the rotation angle \( \varphi \) of DGEBA polar groups and the solidifier, which adds possibilities to their interaction and the formation of more transverse "cross-links" accompanied by the decrease in the viscosity of the compound [4,9].

After substituting (9) into (10), we obtain:

\[ \ln \left[ -\ln \left( 1 - \frac{\gamma}{1 + \xi} \right) \right] = \ln n + n \ln B - \frac{nA}{RT} + n \ln \tau + 2.78 \cdot 10^{-13} \frac{n f e^' i g \delta E_0^2 M}{\rho RT} \tau_{\text{micro}}. \]  

(11)

The expression, according to which the degree of crystalline solidification should increase linearly with the increase in the microwave time \( \tau_{\text{micro}} \) and the square of the amplitude of the electric field strength \( E_0^2 \) of the electromagnetic wave [3,10].

Indeed, a series of experiments performed to determine the degree of conversion \( \gamma \) from the reduction of the epoxy resin number from the IRS data [3,11] showed that for all volume ratios of the resin to the solidifier, the uniform character of topokinetic straight lines in the coordinates (7) is observed under the strong influence of the time of the microwave EMF effect, the increase in which leads to the accelerated EC solidification.

The expression for the coefficient of acceleration of the solidification process of the microwave EC EMF can be written as:

\[ K_a = \frac{\tau}{\tau_{\text{hard.micro}}} \]  

(12)

where \( \tau_{\text{hard.micro}} \) is the time of EC solidification with microwave effect.

Based on kinetic equation (11) and expression (12), we obtain:

\[ \ln K_a = \frac{nA}{RT_0} + \frac{nA}{RT} + 2.78 \cdot 10^{-13} \frac{n f e^' i g \delta E_0^2 M}{\rho RT} \tau_{\text{micro}}. \]  

(13)
There is an expression, according to which $\ln K_a$ should increase linearly with the growing time of microwave effect $\tau_{\text{micro}}$ on the process of EC solidification.

4. Conclusions

A mathematical model of the microwave EMF effect on the kinetics of EC solidification, which describes the effect of the electric field strength of an electromagnetic wave and the duration of microwave effect on the compound structure, was obtained.

Since the main functional properties of EC, e.g. strength, are due precisely to the crystalline phase, it is necessary to conduct the microwave solidification process in the topokinetic mode at $\tau_{\text{micro}} \leq 20–30$ s, which provides the values $K_a = 4–7$ as they are practically sufficient.

The effect of microwave acceleration of the EC solidification process is not solely caused by the thermal effect of the microwave EMF, since by Eq. (8) for $E_0 \approx 25–30$ W/cm, the amount of power absorbed by the compound does not exceed several W/cm$^2$, which is insufficient for microwave heating. The experimentally observed increase in the compound temperature is related to its heating due to a quite high heat of the reaction of solidification by polyethylene polyamine EC $Q = 92–105$ kJ/mol.

References

[1] Fomin A., Fomina M., Koshuro V., Rodionov I., Zakharevich A. and Skaptsov A. 2017 Structure and mechanical properties of hydroxyapatite coatings produced on titanium using plasma spraying with induction preheating Ceramics International 43(14) 11197-204

[2] Fomin A., Dorozhkin S., Fomina M., Koshuro V., Rodionov I., Zakharevich A., Petrova N., Skaptsov A. 2016 Composition, structure and mechanical properties of the titanium surface after induction heat treatment followed by modification with hydroxyapatite nanoparticles, Ceramics International, 42(9) 10838-10846

[3] Kalganova S, Arkhangelskiy Yu, Lavrentyev V, Trigorly S, Artyukhov I and Stepanov S 2017 Electrotechnology of non-thermal modification of polymeric materials in a microwave electromagnetic field XVIII Int. UIE-Congress on Electrotechnologies for Material Processing, (Hannover) pp 333-337

[4] Vasinkina E Yu, Kalganova S G, Lavrentyev V A, Trigorly S V and Alekseev V S 2018 Phase transitions in polymers under the impact of microwave electromagnetic fields Int. Conf. on Innovations and Perspectives Development of Mining Engineering and Electromechanics: IPDME-2018 (St. Petersburg, Russia)

[5] Arkhangelskiy Yu S, Kalganova S G and Yafarov R K 2018 Measurement in microwave electrotechnological installations (Saratov: JSC «Amerit»)

[6] Plakunova E V, Tatarintseva E A, Mostovoy A S and Panova L G 2013 Structure and properties of epoxy thermosters Perspective materials 3 57-62

[7] Stromberg A G and Semchenko D P 2009 Physical chemistry (Moscow: High school)

[8] Arkhangelsky Y S 2011 Reference book on microwave electrothermics: Handbook (Saratov: Scientific book)

[9] Tretyakov Yu D 1978 Solid-phase reactions (Moscow: Chemistry)

[10] Tarutina L I and Pozdnyakova F O 1986 Spectral analysis of polymers (Leningrad: Chemistry)

[11] Kiperman S L 1979 Fundamentals of chemical kinetics in heterogeneous catalysis (Moscow: Chemistry)