Phase transitions in polymers under influence of microwave electromagnetic field

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Abstract. The performance of the microwave installation in a periodic mode during realization of the technological process with a phase transition without the expressed mass transfer is considered. The mathematical model of heat and mass transfer, describing phase transitions in polymers under the influence of a microwave electromagnetic field, is received. Determining experimental values, included in the ratios for the processing time of the polymeric material, it is possible to investigate the phase transitions in the object and the ways of energy supply, e.g. convective, radiant, on the phase transitions in the object.

1. Introduction

Phase transitions theories are applied in various fields of natural, technical sciences and even humanities. Phase transitions theories are of special importance for the reception technology of composite and polymeric materials with the given operational properties. The modern direction of technology of polymer materials modification is the use of electrophysical methods of influence on the structure. Acoustic methods, high-frequency impact, plasma and laser treatment, infrared impact on polymer materials, etc. are widely used [1, 2].

The possibility of non-thermal influence of the microwave electromagnetic field on the process of solidification of thermosetting polymers is established. As a result of this there is a modification of their physical and mechanical properties [3]. This characterizes the polymers with increased stiffness of macromolecular chains, which are of great practical importance as heat-resistant materials that do not lose their physical and chemical properties up to high temperatures (more than 350 °C).

To understand many technological processes of polymer processing and physic and chemical processes occurring during the operation of thermosetting polymer products, it is necessary to consider modern views on the phase states of polymers. Thus, the development of a mathematical model of heat and mass transfer at the phase transitions in polymers, describing the influence of the parameters of the microwave electromagnetic field, is an important component of the scientific research.

2. Materials and methods

As an object of the mathematical model, the authors used a thermosoftening polymer material, e.g. an epoxy compound based on epoxy-diane resin (epoxy group 20) and polyethylenepolyamine solidifier. The solution of the mathematical model for the study of the phase transitions during the microwave impact is based on the scientific foundations of electrodynamics, microwave dielectric heating, physical chemistry of polymers. Experimental methods are based on the application of modern high-
precision technical means such as an automated microwave installation based on the chamber with a running wave with adjustable processing power and time of microwave exposure [4]. The authenticity of the results is confirmed by the correctness and adequacy of the developed mathematical model, the convergence of theoretical results with the experimental data, as well as the studies performed by other authors.

3. Results
When talking about/discussing the phase transitions in polymers, one should have in mind phase transitions of the first-order, when the density, thermodynamic potentials and entropy of a substance change abruptly, heat of the phase transition is soaked out or absorbed [5,6].

To study the phase transitions in polymers, it is required to have the ratios establishing the influence of the microwave electromagnetic field parameters.

In the microwave installation operating in a discontinuous mode, the process with the phase transition was implemented. The processing time of the volume unit of compound \( \tau_{pr} \) was found from the solution of equations:

\[
\left( \alpha_{\text{conv}} S_{\text{conv}} + \alpha_{\text{ph}} V \right) \Theta + c \rho V \frac{d \Theta}{d \tau} = P, \tag{1}
\]

\[
\frac{dm}{d \tau} = \frac{\alpha_{\text{ph}} V}{r} \Theta,
\]

where \( \alpha_{\text{conv}} \) – the heat transfer coefficient (solidification process occurs in the temperature range where the radiation heat exchange can be neglected); \( \alpha_{\text{ph}} \) – the coefficient that takes into account the effect of heat dissipation per volume unit \( V \) on the temperature growth; \( S_{\text{conv}} \) – the surface of the heat-transfer object; \( c, \rho \) – the specific heat capacity and density of the object; \( r \) – the coefficient, which takes into account the energy costs for the phase transition; \( m \) – the mass of the solidified object; \( P \) – power absorbed from the external source; \( \Theta = T - T_0 \), \( T, T_0 \) – the temperatures of the object after and before the microwave processing, respectively.

From equation (1) it follows:

\[
\Theta = \frac{P}{\alpha_{\text{conv}} S_{\text{conv}} + \alpha_{\text{ph}} V \left[ 1 - \exp \left( - \frac{\left( \alpha_{\text{conv}} S_{\text{conv}} + \alpha_{\text{ph}} V \right) \tau}{c \rho V} \right) \right]} , \tag{2}
\]

and considering equation (2):

\[
\Delta m = \frac{\alpha_{\text{ph}} VP}{r \left( \alpha_{\text{conv}} S_{\text{conv}} + \alpha_{\text{ph}} V \right) \left[ 1 - \exp \left( - \frac{\alpha_{\text{ph}} \tau}{c \rho} \right) \right]}, \tag{3}
\]

where \( \Delta m = m_{\text{fin}} - m_{\text{beg}} \), \( m_{\text{fin}} \) – the mass of the object unit in the modified state after the phase transition; \( m_{\text{beg}} \) – the mass of the object unit in the modified state at the beginning of the phase transition.

It was experimentally determined that the acceleration of the solidification process was possible at low levels of power \( P \), when the temperature of epoxy compound as a result of microwave impact increased slightly by 2–5 °C [3,7]. Hence, \( \alpha_{\text{conv}} S_{\text{conv}} = 0 \), and then:

\[
\Theta = \frac{P}{\alpha_{\text{ph}} V \left[ 1 - \exp \left( - \frac{\alpha_{\text{ph}} \tau}{c \rho} \right) \right]} , \tag{4}
\]
In this case:

$$\tau_{pr} = \frac{mr + cP V \Theta}{P}.$$  \hfill (6)

During microwave processing of the epoxy compound, the phase transition occurred. When a certain temperature drop was achieved [8], the total processing time $\tau_{pr}$ was composed from the heating time of the epoxy compound up to the set temperature $\tau_{heat}$ and the time required for the phase transition $\tau_{ph}$, i.e.:

$$\tau_{pr} = \tau_{heat} + \tau_{ph}.$$  

At the heating stage, the heating rate is usually maximal, so the following equation was obtained from (4):

$$\tau_{heat} = \frac{cP}{\alpha_{ph}} \ln \left(1 - \frac{\alpha_{ph} V \Theta_{ph}}{P}\right) ,$$  \hfill (7)

where $\Theta_{ph}$ – the temperature drop of the phase transition.

When the heating time $\tau_{narp}$ was reduced, the microwave power was chosen as follows:

$$\frac{\alpha_{ph} V \Theta_{ph}}{P} \ll 1,$$

then:

$$\tau_{heat} = \frac{cP V \Theta_{ph}}{P} .$$  \hfill (8)

The time spent on the phase transition $\tau_{ph}$ was found from (1) [3,7]:

$$mr = \int_{0}^{\tau_{ph}} \alpha_{ph} V \Theta_{ph} d\tau = \alpha_{ph} V \Theta_{ph} \tau_{ph},$$

whence:

$$\tau_{ph} = \frac{mr}{\alpha_{ph} V \Theta_{ph}} .$$

So:

$$\tau_{pr} = \frac{cP V \Theta_{ph}}{P} + \frac{mr}{\alpha_{ph} V \Theta_{ph}} .$$  \hfill (9)

If during the microwave processing the phase transition started, the temperature drop, to which the epoxy compound was heated during the phase transition, was calculated according to the equation:

$$mr + cP \frac{d\Theta}{d\tau} = Q.$$
When $\tau = \tau_{\text{heat}}$, that is:

$$\Theta = \Theta_{\text{ph}} + \frac{Q - m r}{c p V} (\tau - \tau_{\text{heat}}),$$

(10)

where $Q = Q_{\text{MW}} + Q_{\text{own}}$, $Q_{\text{MW}}$, $Q_{\text{own}}$ - heat dissipated per volume unit of the object under the influence of the microwave electromagnetic field and heat of the phase transition [8,9]. It should be noted that $Q_{\text{own}} = \pm |Q_{\text{own}}|$, where «+» and «−» are referred to the phase transition with emission and absorption of the heat, respectively.

When $\tau = \tau_{\text{ph}}$, the following condition must be true:

$$\Theta(\tau = \tau_{\text{heat}}) \leq \Theta_{\text{perm}},$$

where $\Theta_{\text{perm}}$ – permissible temperature drop of the epoxy compound.

In the above formulas when the object was affected by the microwave electromagnetic oscillations [10]:

$$P = \left(1 - |\Gamma|^2 \right) P_{\text{MW}},$$

where $\Gamma$ – the reflection coefficient of the working chamber, in which the phase transition occurred; $P_{\text{MW}}$ – the power of the microwave installation generator.

4. Conclusions

A mathematical model of heat and mass transfer with phase transitions in thermosetting polymers was developed. When determining experimental values included in ratios for the processing time of polymeric material $\tau_{\mu}$, it is possible to study the influence of the microwave field on phase transitions in the object and the ways of energy supply (convective and radiant).

References

[1] Galbrajh I 2005 Polymers and polymeric materials: synthesis, structure, properties (Moscow: Moscow state textile University named after A. N. Kosygin)
[2] Plakunova E V, Tatarintseva E A, Mostovoy A S and Panova L G 2013 Structure and properties of epoxy thermosets Perspective materials 3 57-62
[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 Prof Egbert Baake, Prof Bernard Nacke (Hannover: UIE-2017) pp 333-337
[4] Arkhangelskiy Yu S, Kalganova S G, Yafarov R K 2018 Measurement in microwave electrotechnological installations (Saratov: JSC «Amerit»)
[5] Garipov R M, Derbedeev T R and Zagitullin A I 2003 Influence functionality of mesh point on the solidification process of epoxyamine compositions Plastics 7 pp 21–24
[6] Tretyakov Yu D 1978 Solid-phase reactions (Moscow: Chemistry)
[7] Vasinkina E Yu, Kalganova S G, Lavrentyev V A, Trigorly S V, Alekseev V S 2018 Phase transitions in polymers under the impact of microwave electromagnetic fields Innovations and Perspectives Development of Mining Engineering and Electromechanics: IPDME-2018 Prof V Maxarov (St. Petersburg: Saint-Petersburg Mining University) p 49
[8] Tarutina L I, Pozdnyakova F O 1986 Spectral analysis of polymers (Leningrad: Chemistry)
[9] Kiperman S L 1979 Fundamentals of chemical kinetics in heterogeneous catalysis (Moscow: Chemistry)
[10] Arkhangelsky Y S 2011 Reference book on microwave electrothermics: Handbook (Saratov: Scientific book)