



#### Article Modeling of the Modification Process of an Epoxy Basalt-Filled Oligomer in Traveling Wave Microwave Chambers

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Abstract: This paper presents modeling data to select the optimal industrial unit for the microwave modification of an epoxy basalt-filled oligomer (EBO) at electric field strength E of an electromagnetic wave equal to  $11.9 \times 10^3$  V/m and a uniform distribution of the temperature field over the entire volume of the modified object. A mathematical description of the electrodynamic and thermal processes occurring in the object under consideration subjected to microwave exposure includes the Helmholtz equation for the electric field strength vector and the heat conduction equation. The joint solution of this problem in a three-dimensional formulation is based on the use of the finite element method, which in this work was implemented in the COMSOL Multiphysics<sup>®</sup> 6.1 software environment. According to the modeling results, the use of microwave chambers with a traveling wave of a waveguide type is inefficient because the required value of the electric field strength E is not achieved, while the modeled microwave chamber with a traveling wave on a quasi-coaxial waveguide makes it possible to achieve the required value of the electric field strength E and uniform distribution of the temperature field over the entire volume of the modified object by reducing the generated power for the modification of an EBO from 400 W up to 300 W. Optimal parameters for modifying an epoxy basalt-filled oligomer in the microwave electromagnetic field in the working chamber with a traveling wave on a quasi-coaxial waveguide have been developed, which provide a uniform microwave modification of an EBO with a microwave installation capacity of 11.6 kg/h. A sketch of an industrial microwave working chamber has been developed, which provides a mode of the uniform modification of the oligomer at electric field strength  $E = 12.3 \times 10^3 \text{ V/m}$ . The proposed microwave chamber with a traveling wave on a quasi-coaxial waveguide can be replicated for the microwave modification of filled oligomers of various chemical compositions.

**Keywords:** epoxy oligomer; microwave modification; modeling; quasi-coaxial waveguide; electric field strength; generated power

#### 1. Introduction

Currently, the search for alternative technologies for polymer modification is one of the priorities for technical progress in various industries. To impart new functional properties to the material, various electro-physical processing methods are widely used, such as elastic vibrations of the ultrasonic frequency range [1,2], plasma treatment [3,4], corona electric



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). arc [5], radiation processing [6,7], and others [8]. Studies on the use of electro-physical methods for processing materials and products have shown high efficiency in using the energy of microwave electromagnetic oscillations for this purpose [9,10]. In Ref. [11], the preparation of polyionic liquid functionalized MXene particles was accompanied by processing with microwave radiation for 60 min. Materials based on carbon perceive the energy transmitted by microwave radiation quite well, which makes it possible to use them as a receptor for heterogeneous reactions [12]. Examples are reactions occurring with microwave radiation: Diels–Alder reactions, thermolysis of ethers, pyrolysis of carbamides, etc. [13]. A variant of carbon nanomaterials synthesis using microwave pyrolysis has become widespread, which allows for a reduction in the amount of harmful emissions, the production temperature, and also for the use of new renewable sources of raw materials [14]. Microwave radiation is often used to initiate the curing reaction of various polymers, examples of such usage being geopolymers [15], thermoplastics [16], lactones, lactides, etc. [17].

The volumetric processing of polymeric materials and products can significantly speed up the modification process compared to other processing methods, thus increasing the quality of finished products, reducing thermo-mechanical effects and the dimensions of the production unit, and improving the economic performance of the process [18–20].

In recent years, positive results have been obtained that prove the effectiveness of using a microwave electromagnetic field for modifying various polymeric materials [21–26], including filled epoxy polymers [27]. Therefore, the use of mathematical modeling methods both for the study of the processes occurring in polymers and for the development of microwave units for their modification is currently a promising area of research [28–30].

The mathematical description of the processes of the microwave heat treatment of dielectrics is based on the system of interrelated equations of electrodynamics and heat and mass transfer. Depending on the specific modification conditions, the mathematical model can be supplemented with the equations of thermo-mechanics, hydrodynamics, and equations describing chemical and biological processes, or simplified, for example, by transformation to a system of equations of electrodynamics and thermal conductivity.

To develop an industrial microwave installation that will provide the required electric field strength E and a uniform distribution of the temperature field throughout the volume of the modified object to obtain a composite with a given set of properties, it is necessary to determine the optimal parameters of electrical and thermal processes in the composite under microwave exposure, as well as to choose a microwave chamber design. Modeling in the COMSOL Multiphysics<sup>®</sup> 6.1 software environment allows us to predict, without laboratory studies, the required values of electrical and thermal processes in the material when choosing an optimal design of the microwave chamber.

In this work, the task of the study is to model an optimal industrial unit for the microwave modification of a previously developed epoxy basalt-filled oligomer (EBO) [31]. It has been proven that an electric field strength E of an electromagnetic wave equal to  $11.9 \times 10^3$  V/m has the greatest effect on the structure formation of an epoxy basalt-filled oligomer, which provides modification of the physicochemical and mechanical properties of epoxy basalt-filled polymer composite materials (PCMs). Using a laboratory unit, the required values of electric field strength E are achieved at a generated power of R<sub>mw</sub> = 400 W and exposure time of 24 s, while an epoxy basalt-filled oligomer should not be heated above  $220 \pm 10$  °C.

The novelty of the work consists in the developed method for modeling the process of modifying an epoxy basalt-filled oligomer in microwave chambers with a traveling wave, on the basis of which an optimal microwave chamber based on a quasi-coaxial waveguide has been developed, which makes it possible to provide the required electric field strength E and a uniform distribution of the temperature field throughout the volume of the modified object, which are necessary for obtaining a modified composite with a given set of properties.

#### 2. Mathematical Models of Electro-Dynamic and Thermal Processes during Microwave Modification of Oligomers

In this scientific work, the effect of a microwave electromagnetic field on an epoxy basalt-filled oligomer (EBO) and, as a result, on the properties of an epoxy basalt-filled polymer composite material (EB PCM), was studied.

Epoxy resin ED-20 manufactured by CHIMEX Limited (St. Petersburg, Russia) was used as a binder for obtaining polymer composite materials. Trichloroethyl phosphate (TCEP) manufactured by Xuancheng City Trooyawn Refined Chemical Industry Co. (Beijing, China) was used as a plasticizer and flame retardant. Trichloroethyl phosphatetris-(2-monochloroethyl) phosphate ( $C_6H_{12}Cl_3O_4P$ ) is a complete ester of phosphoric acid and ethylene chlorohydrin. It is an effective flame retardant that significantly improves the firefighting properties of materials. Trichloroethyl phosphate forms a homogeneous physical mixture with polymers and does not enter into a chemical reaction with them, which enhances the flame retardant effect. In addition, trichloroethyl phosphate is a good plasticizer. The presence of chlorine atoms in the composition of trichloroethyl phosphate does not reduce its compatibility with polymers. When trichloroethyl phosphate is added to the composition, a self-extinguishing material is obtained, which quickly goes out after the termination of an open flame. Crushed basalt rubble with a particle size of  $\leq$ 140  $\mu$ m was used as a filler for epoxy composites. Basalt is an igneous rock solidified in the upper layers of the earth crust. It has high strength and density as well as high chemical properties, fire resistance, strength, durability, and sound and heat insulation performance [31].

The mathematical description of the processes of the microwave heat treatment of dielectrics is based on a system of interrelated equations of electrodynamics and heat and mass transfer. Depending on the specific modification conditions, the mathematical model can be supplemented with the equations of thermo-mechanics, hydrodynamics, and equations describing chemical and biological processes, or simplified, for example, by transformation to a system of equations of electrodynamics and thermal conductivity (without taking into account mass transfer when modeling the thermal conductivity of modification objects).

The electro-dynamic part of the models, as a rule, is unchangeable and represents the system of Maxwell's equations, which, when considering wave processes, is converted to the system of Helmholtz wave equations. It is assumed that all fields (E, H, D, B) have harmonic time dependence with a known angular frequency and that all properties of the materials of the computational area (areas) are linear with respect to electric field strength E of the electromagnetic wave.

Modeling is limited by the Helmholtz equation with respect to the electric field strength vector E, since the remaining fields can be obtained from the field E according to the known relationships (boundary conditions and constitutive equations), and also due to the fact that the power of internal heat sources, because of dielectric losses  $q_v$ , (besides dielectric properties and frequency), is mainly determined by the distribution of the field E:

$$\mathbf{q}_{\mathbf{v}} = 0.5\omega\varepsilon_0\varepsilon_{\mathbf{r}}''\cdot|\mathbf{E}|^2\tag{1}$$

where  $\omega = 2\pi f$  is the angular frequency, f is the frequency of the electromagnetic field,  $\varepsilon_0$  is the electrical constant, and  $\varepsilon''_r$  is the loss factor (the imaginary part of the permeability).

Relation (1) describes the effect of heat release during dielectric heating and is used to set the relationship between thermal and electro-dynamic processes in modeling.

The Helmholtz equation for the electric field strength vector E and typical boundary conditions that are characteristic of describing the processes of the microwave heat treatment of dielectrics are given as:

$$\nabla \times \left(\mu_{\rm r}^{-1} \nabla \times E\right) - k_0^2 \left(\epsilon'_{\rm r} - \frac{j\sigma}{\omega \epsilon_0}\right) E = 0 \tag{2}$$

$$\mathbf{n} \times \mathbf{E} = \mathbf{0} \tag{3}$$

$$[H_2 - H_1, n] = 0; \ [n, E_2 - E_1] = 0; \ n(D_2 - D_1) = 0; \ n(B_2 - B_1) = 0, \tag{4}$$

where  $\mu_r$  is the relative magnetic permeability,  $k_0 = \omega \sqrt{\epsilon_0 \mu_0}$  is the wave number,  $\omega$  is the circular frequency,  $\epsilon_0$  is the electrical constant,  $\mu_0$  is the magnetic constant,  $\epsilon'_r$  is the relative permittivity (real part),  $\sigma = \omega \epsilon_0 \epsilon''_r$  is the electrical conductivity,  $\epsilon''_r$  is the loss factor,  $H_2$ ,  $H_1$ ,  $E_2$ ,  $E_1$  are the magnetic and electric field strength vectors,  $D_2$ ,  $D_1$ ,  $B_2$ ,  $B_1$  are the vectors of electric and magnetic induction for environments 2 and 1, respectively, and **n** is the unit vector of the normal to the surface.

Let us consider the formulation of the problem of modeling the processes of the microwave heating of dielectrics. When modeling microwave heating processes, in which mass transfer processes can be neglected, the equation of non-stationary heat conduction with boundary and initial conditions is added to the Equations of electrodynamics (2)–(4):

$$\rho c_{p} \frac{\partial T}{\partial \tau} + \rho c_{p} u \cdot \nabla T - \operatorname{div}(\lambda \cdot \operatorname{grad} T) = q_{v}$$
(5)

$$-\mathbf{n} \cdot \mathbf{q} = \mathbf{h} (\mathbf{T}_{\text{ext}} - \mathbf{T}_{\text{c}}) \tag{6}$$

$$-\mathbf{n} \cdot \mathbf{q} = \varepsilon \sigma_r \left( T_{\text{ext}}^4 - T_r^4 \right) \tag{7}$$

$$T_1 = T_2 \tag{8}$$

$$\lambda_1 \left(\frac{\partial T_1}{\partial n}\right)_{\rm S} = \lambda_2 \left(\frac{\partial T_2}{\partial n}\right)_{\rm S} \tag{9}$$

$$\Gamma(0) = T_0 \tag{10}$$

where  $\rho$  is the density,  $c_p$  is the specific heat, T is the temperature,  $\tau$  is the time,  $\lambda$  is the coefficient of thermal conductivity,  $q_v$  is the power of internal heat sources due to dielectric losses, h is the coefficient of heat transfer from the surface,  $T_{ext}$  is the ambient temperature,  $T_c$  is the temperature of the convective heat exchange surface,  $\varepsilon$  is the radiation coefficient,  $\sigma_r$  is the Stefan–Boltzmann constant, q is the heat flux density vector,  $T_r$  is the temperature of the radiative heat exchange surface,  $T_1$ ,  $T_2$  are the temperatures of the mating heat exchange surfaces of regions 1 and 2,  $\lambda_1$ ,  $\lambda_2$ , are the thermal conductivity coefficients of regions 1 and 2, n is the normal vector to the interface, S,  $T_0$  is the initial temperature of the object, and u is the velocity vector (for a moving composite material).

The boundary condition (6) characterizes the convective heat exchange with the environment according to the Newton–Richmann law. Boundary condition (7) characterizes radiative heat transfer. Boundary conditions (8) and (9) are set on the mating surfaces and represent the condition of equality of temperatures and heat fluxes on the contacting surfaces. The initial condition (10) sets the initial temperature of the heating process.

To model the installation for the microwave modification of an epoxy basalt-filled oligomer, the COMSOL Multiphysics<sup>®</sup> 6.1 software was used, which allows us to predict and optimize physical processes and devices using numerical modeling. With the help of COMSOL Multiphysics<sup>®</sup> 6.1, structures, devices and processes are modeled in all areas of engineering, manufacturing, and scientific research, and one can also analyze both individual and interconnected physical processes. The modeling environment allows one to go through all the stages, from constructing a geometric model, setting the properties of materials, and describing the physics of the problem to performing the calculation and analysis of the obtained simulation results.

The implementation of a general mathematical modeling algorithm In the COMSOL Multiphysics 6.1 program usually includes the following steps:

Constructing a geometric model;

- Setting equations that describe the process of microwave heat treatment under consideration, taking into account the corresponding relationship of these equations;
- Setting the boundary and initial conditions;
- Setting the properties of the model materials;
- Creating a finite element mesh;
- Developing the solution algorithm;
- Launching a solution or a series of solutions with varying parameters;
- Conclusions and analysis of modeling results.
- Initial data for modeling:
- Physical properties of EBO, its components, and fluoroplastic used as cuvettes and tubes for moving the oligomer in the microwave chambers are shown in Table 1.

Table 1. Physical properties of dielectric materials.

Physical Properties	EBO	Fluoroplastic
Thermal conductivity coefficient, W/(m K)	0.124	0.25
Specific heat capacity, J/(kg K)	580	1040
Density, kg/m <sup>3</sup>	1607	2200
Dynamic viscosity, Pa s	6.519	-
Relative permittivity $\varepsilon I_r$	4.921	2.1
Loss ratio $\varepsilon''_{r}$	1.55	0.000252

### 3. Modeling of the Process of Oligomer Modification in Microwave Chambers with a Traveling Wave of a Waveguide Type

The processing of polymers with a microwave electromagnetic field makes it possible (reducing the duration of the process) to achieve a uniform modification of the object in less time, while thermomechanical effects are reduced and the quality of finished products is increased. The reduction in the process time and energy/cost savings are usually in the focus of manufacturing process improvement. New technologies make it possible to achieve significant improvements in relevant performance. Therefore, new electrophysical methods for obtaining a modified epoxy basalt-filled polymer composite material with a given set of properties are an important area of research and development in the field of polymer matrix composite technology. The criteria for introducing changes are based on the scientific theory that the response of an electromagnetic field (EMF) to microwave exposure is observed only in polar polymers that have an unbalanced covalent bond due to polar groups [32].

There are three main microwave heating mechanisms: dipole polarization, ionic conduction, and interactive polarization. The mechanism is based on the fact that polarized molecules are subjected to a torque in an electric field, which makes the dipoles rearrange and become polarized. When an external electric field is applied, the molecules are polarized; that is, the symmetry of the arrangement of their charges breaks and they acquire a certain electric moment [15,19]. Epoxy oligomers are the most promising among other organic macromolecular substances and are of great interest as objects of the study of the effects of microwave electromagnetic fields due to their polarity [33,34]. However, there is no information in the literature on obtaining optimal parameters of electrical and thermal processes in the "epoxy oligomer—dispersed filler" system under microwave exposure, which confirms the relevance of solving the problem of choosing a microwave chamber design.

Figure 1 shows a block diagram of a microwave unit for heating EBO samples in a waveguide microwave chamber. To match the microwave generator with the load, in addition to the microwave chamber of waveguide type, in which the processed EBO is placed, an additional water load is applied, which absorbs part of the microwave energy that was not absorbed in the object.



**Figure 1.** Block diagram of a microwave unit for processing materials in a waveguide microwave chamber.

To select the optimal design of the microwave unit when modeling heating processes in microwave chambers with a traveling wave of a waveguide type at frequency of 2450 MHz with chamber dimensions of  $45 \times 90 \times 200$  mm, the following options for the location of the EBO were considered:

3.1. Option I. Microwave Modification of the Oligomer in a Fixed Cuvette 50  $\times$  40  $\times$  10 mm in Size

A fluoroplastic cuvette  $50 \times 40 \times 10$  mm in size with a wall thickness of 1 mm, filled with an oligomer, is placed on the symmetry axis of the waveguide parallel to the narrow part of the waveguide (to obtain the maximum electric field strength). The cuvette with the object does not move in the microwave chamber (Figure 2).



**Figure 2.** Geometric model of a waveguide microwave chamber with a fluoroplastic cuvette  $50 \times 40 \times 10$  mm in size and the object of modification: 1—waveguide microwave camera; 2—fluoroplastic cuvette with a sample; 3—conveyor belt.

The results of mathematical modeling at a power of 400 W and exposure time of 24 s of three-dimensional electric and temperature fields are shown in Figures 3–6.

Based on the analysis of the obtained simulation results, the following conclusions can be drawn:

The maximum electric field strength in the modified EBO is  $7.58 \times 10^3$  V/m (Figure 3), which is 36% less than E found during the experiment.

The distribution of the temperature field over the volume of the sample is uneven. For a heating time of 24 s, the temperature inside (in the middle section) is 160 °C, and on the outer surface of the oligomer it is 138 °C (Figure 5). The temperature in the middle of the outer surface of the sample at an instant of time 24 s is 130 °C (Figure 4b).



Figure 3. Change in electric field strength along the length sample (Ez component).



(b)

**Figure 4.** (a) Distribution of electric field strength in the xy plane in the microwave chamber; (b) temperature distribution in the zx plane of the sample at an instant of time 24 s (on the outer surface).



**Figure 5.** Temperature distribution in the yz plane of the sample at an instant of time 24 s (at the center of sample symmetry).



**Figure 6.** Change in temperature during microwave processing: 1—sample center; 2—outer surface of the sample.

3.2. Option II. Microwave Modification of the Oligomer in a Fixed Cuvette with a Cross Section of  $40 \times 10 \text{ mm}$ 

A long PTFE cuvette with a cross section of  $40 \times 10$  mm and a wall thickness of 1 mm, filled with an EBO, is located on the symmetry axis of the waveguide parallel to the narrow part of the waveguide (Figure 7a). The modeling results for a microwave power of 400 W and exposure time of 24 s for a fixed cuvette with an EBO are shown in Figures 7b, 8 and 9.

Based on the analysis of the obtained modeling results, the following conclusions can be drawn:

It has been stated that the maximum electric field strength E near the input of microwave energy into the chamber is  $8.5 \cdot 10^3$  V/m (Figure 7b), which is 28% less than the experimentally determined E.

The temperature in the oligomer at 24 s is distributed unevenly. By the thickness of the sample in the area of the electric field maximum, the temperature varies from 100 °C to 182 °C (Figure 8b). Along the length of the cuvette, the temperature in the material is also uneven: the temperature maximum is observed near the microwave energy input in the region that is about 3 cm wide (Figure 8a).



**Figure 7.** (a) Simplified geometric model of a waveguide microwave chamber with a fluoroplastic cuvette  $50 \times 40 \times 10$  mm in size and a modification object: 1—waveguide microwave camera; 2—fluoroplastic cuvette with a sample; 3—conveyor belt; (b) distribution of electric field strength in the xy plane.







**Figure 9.** Change in temperature during microwave processing (long cuvette  $40 \times 10$  mm): 1—sample center; 2—outer surface of the sample.

### 3.3. Option III. Microwave Modification of the Oligomer in a Moving Cuvette with a Cross Section of 40 $\times$ 10 mm

Let us carry out mathematical modeling of the modification of an EBO located in a long fluoroplastic cell moving at a speed of 0.5 cm/s at a microwave power of 400 W. The modeling results are presented in Figures 10 and 11. The above figures show the temperature fields in the longitudinal sections of the object in the middle part at an instant of time 50 s, as well as the dependence of the temperature change in the central part of the oligomer located in the microwave chamber and on its outer surface.



**Figure 10.** (a) Distribution of electric field strength in the xy plane; (b) temperature distribution at an instant of time 50 s and the cuvette movement speed 0.5 cm/s in the zx plane of the sample in a long cuvette  $40 \times 10$  mm (average longitudinal section).

Based on the analysis of the results of modeling the microwave modification of the oligomer located in a moving long cell  $40 \times 10$  mm in size in a waveguide-type microwave chamber, the following conclusions can be drawn:

The maximum electric field strength E near the input of microwave energy into the chamber is  $8.2 \times 10^3$  V/m (Figure 10a), which is 31% less than the experimentally determined E. For the cuvette movement speed v = 0.5 cm/s at microwave power P = 400 W, the EBO temperature increases during 50 s to T<sub>c</sub> = 265 °C in the middle section of the material and to T<sub>p</sub> = 235 °C on its surface, which is higher than the EBO destruction temperature. The temperature maximum in the object shifts in the direction of the cuvette movement along the microwave chamber. The time to reach the maximum temperature at the control points of the sample in the center of the microwave chamber is 30–35 s at a speed of v = 0.5 cm/s.



**Figure 11.** Change in temperature during microwave processing and the cuvette movement speed 0.5 cm/s (long cuvette  $40 \times 10 \text{ mm}$ ): 1—sample center; 2—outer surface.

## 3.4. Option IV. Microwave Modification of the Oligomer during Its Transportation through a Rectangular Tube

The oligomer was transported along a fluoroplastic tube of a rectangular cross section of  $40 \times 10$  mm with a wall thickness of 1 mm (Figure 12). The tube, like the cuvette, was located on the axis of symmetry of the waveguide parallel to the narrow part of the waveguide. The microwave chamber is located vertically to let the liquid oligomer flow through the tube under the action of gravity.



**Figure 12.** Simplified geometric model of a waveguide microwave chamber with a fluoroplastic tube  $40 \times 10$  mm in size and a modification object: 1—oligomer; 2—fluoroplastic tube; 3—microwave chamber.

The dimensions of the cuvette with the oligomer and the tube are limited by the fact that, at a standard frequency of 2450 MHz, the dimensions of the waveguide chamber in the cross section are  $45 \times 90$  mm.

The modeling results at a microwave processing power of 400 W for modifying the oligomer during its transportation through a rectangular tube are shown in Figures 13 and 14.



**Figure 13.** (a) Distribution of electric field strength in the xy plane; (b) temperature distribution at  $P_{MW} = 400$  W at an instant of time 50 s and the oligomer movement speed 0.5 cm/s along a tube of rectangular section  $40 \times 10$  mm in zx plane of the sample (average longitudinal section).



**Figure 14.** Temperature change over time at v = 0.5 cm/s,  $P_{mic} = 400$  W, tube rectangular section  $40 \times 10$  mm: 1—sample center; 2—outer surface.

Based on the analysis of the results of the modeling of the microwave processing of the oligomer, when it moves in a rectangular tube  $40 \times 10$  mm in size, located in a waveguide-type microwave chamber, the following conclusions can be drawn:

The maximum electric field strength E near the input of microwave energy into the chamber is an order of magnitude lower than the experimental E and is  $1.1 \times 10^3$  V/m (Figure 13a). For a motion velocity v = 0.5 cm/s at microwave power P = 400 W, the temperature of the sample rises during 50 s to Tc = 330 °C in the middle section of the material and to Tp = 190 °C on the material surface; at such temperatures in the middle section of the EBO, the oligomer is destroyed. The temperature maximum in the composite material shifts in the direction of the motion along the microwave chamber. The time taken to reach the

maximum temperature at the control points of the sample in the center of the microwave chamber is 40 s.

As a result of the mathematical modeling of the microwave processing of the oligomer in microwave chambers with a traveling wave of the waveguide type, it was established that regarding the microwave modification of the oligomer in a stationary cuvette (variants I and II), the maximum electric field strength in the modified EBO ranges from  $7.58 \times 10^3$  V/m up to  $8.5 \times 10^3$  V/m, and the maximum temperature difference in the middle and on the surface of the oligomer is from 22 °C to 82 °C, respectively. For the microwave modification of the oligomer in a moving cell (option III) and during its transportation through a rectangular tube, the maximum electric field strength in the modified EBO is from  $1.1 \times 10^3$  V/m to  $8.2 \times 10^3$  V/m, and the maximum temperature difference in the middle and on the surface of the oligomer is from 30 °C to 140 °C, the temperature values being higher than the destruction temperature of the epoxy oligomer. When modifying EBO in a rectangular tube, the voltage is  $1.1 \times 10^3$  V/m, the temperature ranging from 190 °C on the surface up to 330 °C in the middle section of the material.

Thus, as a result of modeling the EBO modification process, it has been established that, in microwave chambers with a traveling wave of the waveguide type, the required value of the electric field strength E is not achieved, while a large temperature difference is observed in the middle and on the surface of the epoxy basalt-filled oligomer (option IV) with the destruction of the oligomer (options III and IV).

# 3.5. Modeling of the Modification Process of an Epoxy Basalt-Filled Oligomer in a Microwave Chamber with a Traveling Wave on a Quasi-Coaxial Waveguide

Let us consider the modeling of heating processes in microwave chambers with a traveling wave on a quasi-coaxial waveguide at a frequency of 2450 MHz. The geometric model of the microwave chamber is shown in Figure 15. The main elements of the microwave chamber are: a segment of the waveguide  $45 \times 90 \times 200$  mm in size; a radio-transparent vertically located fluoroplastic tube along which the modified EBO moves; a matching transition and a screen for creating a uniformly distributed electric field in the modified EBO. Dimensions of the fluoroplastic tube are: outer diameter—20 mm, inner diameter—16 mm.



Figure 15. Geometric model of a microwave chamber on a quasi-coaxial waveguide.

Technological parameters varied in the following range: the microwave power was 200–400 W; the speed of movement of the oligomer in the fluoroplastic tube was 0.5–1.0 cm/s. The results of mathematical modeling for the EBO flow through a fluoroplastic tube with

an inner diameter of 16 mm led to the conclusion that the most optimal technological parameters of the microwave modification of the oligomer are microwave power—300 W and movement speed—1.0 cm/s because, under these modes, the required values of the electric field strength E are achieved, while the epoxy basalt-filled oligomer does not heat up above  $220 \pm 10$  °C (Figures 16–18).





**Figure 16.** (a) Distribution of the electric field strength in the xz plane; (b) the distribution of the electric field strength in the xy plane.



Figure 17. Temperature distribution in the zy plane of the sample (average longitudinal section).



**Figure 18.** Change in temperature during microwave processing of EBO: 1—the center of the sample; 2—outer surface.

Based on the analysis of the modeling results of an EBO moving along a vertically located fluoroplastic tube in a microwave chamber on a quasi-coaxial waveguide, the following conclusions can be drawn:

The dimensions of the microwave chamber on a quasi-coaxial waveguide and the internal diameter of the fluoroplastic tube, d = 16 mm, through which the EBO is transported, have been determined.

The maximum electric field strength is  $12.3 \times 10^3$  V/m, which is comparable with the experimental data.

At microwave power  $P_{mic} = 300$  W for a movement speed v = 1.0 cm/s, the temperature of the oligomer during 10 s increases to  $T_s = 202$  °C in the middle section of the object and to  $T_{surf} = 180$  °C on the EBO surface; that is, the material is not heated above  $220 \pm 10$  °C.

Thus, a microwave chamber on a quasi-coaxial waveguide, in contrast to microwave chambers of a waveguide type, allows us to obtain optimal modification parameters for an epoxy basalt-filled oligomer that correspond to a microwave power of 300 W and a movement speed of the object v = 1.0 cm/s. Modification in the working chamber on a quasi-coaxial waveguide makes it possible to obtain fairly uniform heating throughout the entire volume of the EBO, with a temperature gradient of 22 °C at an electric field strength E of  $12.3 \times 10^3 \text{ V/m}$ .

# 3.6. Design of the Working Chamber for Microwave Modification of an Epoxy Basalt-Filled Oligomer

With the selected parameters of the microwave modification, the performance of the microwave unit for EBO processing is:

$$W = \frac{\pi r^2 l\rho}{\tau}$$
(11)

where r = 0.8 cm is the inner radius of the PTFE tube;

l = 10 cm is the length of the active part of the microwave chamber, in which the microwave energy is absorbed by the composite material;

 $\rho = 1.607 \text{ kg/cm}^3$  is the density of the epoxy basalt-filled oligomer;

 $\tau = 10$  s is the exposure time.

$$W = \frac{3.14 \cdot 0.8^2 \cdot 10 \cdot 1.607 \cdot 10^{-3}}{10/3600} = 11.63 \text{ kg/h}$$



Based on mathematical modeling, a sketch of a microwave chamber for modifying the EBO was developed on a quasi-coaxial waveguide (Figure 19).

**Figure 19.** Working chamber for microwave modification of EBO: 1—flange; 2—rectangular waveguide; 3—matching screen; 4—ballast load with running water; 5—gateway; 6—radio-transparent tube; 7—matching element; 8—short-circuit plate; 9—gateway; 10—oligomer; 11—fluoroplastic tube; v—movement speed.

Using a working chamber on a quasi-coaxial waveguide at power of 300 W and the movement speed of the oligomer of 1.0 m/s, the productivity of a microwave installation for modifying an epoxy basalt-filled oligomer is 11.63 kg/h. The maximum electric field strength corresponds to the experimental value and is equal to  $12.3 \times 10^3$  V/m. Over a period of 10 s, the temperature in the material increases to 202 °C in the middle section of the material and to 180 °C on the surface of the EBO, which meets the technological requirements for maximum permissible temperatures and a uniform distribution of the temperature field and, as a result, has a modifying effect on a basalt-filled epoxy oligomer under microwave influence.

#### 4. Conclusions

Optimal parameters for modifying an epoxy basalt-filled oligomer in the microwave electromagnetic field in the working chamber with a traveling wave on a quasi-coaxial waveguide have been developed, which provide uniform microwave modification of the EBO in a methodical mode with a microwave unit capacity of 11.6 kg/h. The design parameters of an industrial microwave working chamber were calculated, which provides a mode of uniform modification of the oligomer at electric field strength  $E = 12.3 \times 10^3 \text{ V/m}$ . The developed microwave unit allows us to reduce the generated power and the duration of exposure for EBO modification while maintaining the required values of electric field strength E and a uniform distribution of the temperature field throughout the volume of the object being modified.

Modified basalt-filled PCM can be used in various industries to obtain the cast insulation of high-voltage devices, impregnation and sealing of capacitors, transistor windings, transformers, cellular structures formed from intersecting flat elements, insulation of electrical boards, industrial self-leveling floors, metal coatings, etc.

The proposed microwave chamber with a traveling wave on a quasi-coaxial waveguide can be replicated for the microwave modification of filled oligomers of various chemical compositions. Author Contributions: Conceptualization, A.B., E.V., Y.K., A.M., A.S., M.L. and N.Z.; data curation, A.B., E.V., Y.K., A.M. and A.S.; formal analysis, A.B., A.S., M.L. and N.Z.; funding acquisition, A.B.; investigation, E.V., S.T., Y.K. and A.M.; methodology, A.B., S.K., S.T., Y.K. and A.M.; resources, A.B.; software, E.V., S.T., A.M. and A.S.; supervision, S.K. and A.M.; validation, E.V., S.K., S.T., Y.K., A.M., A.S. and N.Z.; visualization, S.K., A.S. and M.L.; writing—original draft, A.B., E.V., S.K., S.T., Y.K., A.M. and A.S.; writing—review and editing, Y.K., A.M., M.L. and N.Z. All authors have read and agreed to the published version of the manuscript.

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#### References

- Ojogbo, E.; Ogunsona, E.O.; Mekonnen, T.H. Chemical and physical modifications of starch for renewable polymeric materials. *Mater. Today Sustain.* 2020, 7–8, 100028. [CrossRef]
- Studentsov, V.N.; Pyataev, I.V. Effect of vibration in processes of structure formation in polymers. *Russ. J. Appl. Chem.* 2014, 87, 352–354. [CrossRef]
- 3. Weltmann, K.-D.; Kolb, J.F.; Holub, M.; Uhrlandt, D.; Šimek, M.; Ostrikov, K.; Hamaguchi, S.; Cvelbar, U.; Černák, M.; Locke, B.; et al. The future for plasma science and technology. *Plasma Process. Polym.* **2019**, *16*, 1800118. [CrossRef]
- Singh, M.; Vajpayee, M.; Ledwani, L. Eco-friendly Surface Modification and Nanofinishing of Textile Polymers to Enhance Functionalisation. In *Nanotechnology for Energy and Environmental Engineering*; Ledwani, L., Sangwai, J., Eds.; Springer International Publishing: Cham, Switzerland, 2020; pp. 529–559; ISBN 978-3-030-33774-2.
- Leon-Garzon, A.R.; Dotelli, G.; Tommasini, M.; Bianchi, C.L.; Pirola, C.; Villa, A.; Lucotti, A.; Sacchi, B.; Barbieri, L. Experimental Characterization of Polymer Surfaces Subject to Corona Discharges in Controlled Atmospheres. *Polymers* 2019, 11, 1646. [CrossRef]
- Abdel-Rahman, H.A.; Awad, E.H.; Fathy, R.M. Effect of modified nano zinc oxide on physico-chemical and antimicrobial properties of gamma-irradiated sawdust/epoxy composites. J. Compos. Mater. 2020, 54, 331–343. [CrossRef]
- Kacem, I.; Daoudi, M.; Dridi, W.; Sellemi, H.; Harzli, K.; De Izzara, G.; Geslot, B.; Guermazi, H.; Blaise, P.; Hosni, F.; et al. Effects of neutron–gamma radiation on the free radical contents in epoxy resin: Upconversion luminescence and structural stabilization. *Appl. Phys. A* 2019, 125, 758. [CrossRef]
- Kolosov, A.E.; Sivetskii, V.I.; Kolosova, E.P.; Vanin, V.V.; Gondlyakh, A.V.; Sidorov, D.E.; Ivitskiy, I.I.; Symoniuk, V.P. Use of Physicochemical Modification Methods for Producing Traditional and Nanomodified Polymeric Composites with Improved Operational Properties. *Int. J. Polym. Sci.* 2019, 2019, 1258727. [CrossRef]
- 9. Zhang, J.; Duan, Y.; Wang, B.; Zhang, X. Interfacial enhancement for carbon fibre reinforced electron beam cured polymer composite by microwave irradiation. *Polymer* 2020, *192*, 122327. [CrossRef]
- Benega, M.A.G.; Silva, W.M.; Schnitzler, M.C.; Andrade, R.J.E.; Ribeiro, H. Improvements in thermal and mechanical properties of composites based on epoxy-carbon nanomaterials-A brief landscape. *Polym. Test.* 2021, 98, 107180. [CrossRef]
- Sun, S.; Sha, X.; Liang, J.; Yang, G.; Hu, X.; He, Z.; Liu, M.; Zhou, N.; Zhang, X.; Wei, Y. Rapid synthesis of polyimidazole functionalized MXene via microwave-irradiation assisted multi-component reaction and its iodine adsorption performance. *J. Hazard. Mater.* 2021, 420, 126580. [CrossRef]
- 12. Menéndez, J.A.; Arenillas, A.; Fidalgo, B.; Fernández, Y.; Zubizarreta, L.; Calvo, E.G.; Bermúdez, J.M. Microwave heating processes involving carbon materials. *Fuel Process. Technol.* **2010**, *91*, 1–8. [CrossRef]
- Laporterie, A.; Marquié, J.; Dubac, J. Microwave-Assisted Reactions on Graphite. In *Microwaves in Organic Synthesis*; John Wiley & Sons: Hoboken, NJ, USA, 2002; pp. 219–252; ISBN 978-3-527-60177-6.
- 14. Omoriyekomwan, J.E.; Tahmasebi, A.; Dou, J.; Wang, R.; Yu, J. A review on the recent advances in the production of carbon nanotubes and carbon nanofibers via microwave-assisted pyrolysis of biomass. *Fuel Process. Technol.* **2021**, *214*, 106686. [CrossRef]
- 15. Sun, Y.; Zhang, P.; Hu, J.; Liu, B.; Yang, J.; Liang, S.; Xiao, K.; Hou, H. A review on microwave irradiation to the properties of geopolymers: Mechanisms and challenges. *Constr. Build. Mater.* **2021**, *294*, 123491. [CrossRef]
- 16. Gao, C.; Li, M.; Zhu, C.; Hu, Y.; Shen, T.; Li, M.; Ji, X.; Lyu, G.; Zhuang, W. One-pot depolymerization, demethylation and phenolation of lignin catalyzed by HBr under microwave irradiation for phenolic foam preparation. *Compos. Part B Eng.* **2021**, 205, 108530. [CrossRef]
- 17. Kempe, K.; Becer, C.R.; Schubert, U.S. Microwave-Assisted Polymerizations: Recent Status and Future Perspectives. *Macro-molecules* **2011**, *44*, 5825–5842. [CrossRef]
- Abutalipova, E.M.; Bugai, D.E.; Avrenyuk, A.N.; Strel'tsov, O.B.; Sungatullin, I.R. Investigation of the Effect of Microwave-Radiation Energy Flux on the Structure and Properties of Polymeric Insulating Materials. *Chem. Pet. Eng.* 2016, 52, 212–216. [CrossRef]
- 19. Belkhir, K.; Riquet, G.; Becquart, F. Polymer Processing under Microwaves. Adv. Polym. Technol. 2022, 2022, 3961233. [CrossRef]

- 20. Kadykova, Y.A. A structural polymeric composite material reinforced with basalt fiber. *Russ. J. Appl. Chem.* **2012**, *85*, 1434–1438. [CrossRef]
- 21. Bogiatzidis, C.; Zoumpoulakis, L. Thermoset Polymer Matrix Composites of Epoxy, Unsaturated Polyester, and Novolac Resin Embedding Construction and Demolition Wastes powder: A Comparative Study. *Polymers* **2021**, *13*, 737. [CrossRef]
- Shcherbakov, A.; Mostovoy, A.; Bekeshev, A.; Burmistrov, I.; Arzamastsev, S.; Lopukhova, M. Effect of Microwave Irradiation at Different Stages of Manufacturing Unsaturated Polyester Nanocomposite. *Polymers* 2022, 14, 4594. [CrossRef]
- Englert, C.; Schwenke, A.M.; Hoeppener, S.; Weber, C.; Schubert, U.S. Microwave-Assisted Polymer Modifications. In *Microwave-Assisted Polymer Synthesis*; Hoogenboom, R., Schubert, U.S., Wiesbrock, F., Eds.; Springer International Publishing: Cham, Switzerland, 2016; pp. 209–240; ISBN 978-3-319-42241-1.
- 24. Galos, J. Microwave processing of carbon fibre polymer composites: A review. *Polym. Polym. Compos.* **2021**, *29*, 151–162. [CrossRef]
- 25. Bonab, V.S.; Karimkhani, V.; Manas-Zloczower, I. Ultra-Fast Microwave Assisted Self-Healing of Covalent Adaptive Polyurethane Networks with Carbon Nanotubes. *Macromol. Mater. Eng.* **2019**, *304*, 1800405. [CrossRef]
- Shcherbakov, A.S.; Mostovoy, A.S.; Yakovlev, N.A.; Arzamastsev, S.V. Effect of Carbon Nanotube Functionalization on the Physicochemical and Mechanical Properties of Modified Fiber-Reinforced Composites Based on an Epoxy Resin. *Russ. J. Appl. Chem.* 2021, 94, 1080–1087. [CrossRef]
- Bekeshev, A.; Mostovoy, A.; Tastanova, L.; Kadykova, Y.; Kalganova, S.; Lopukhova, M. Reinforcement of Epoxy Composites with Application of Finely-ground Ochre and Electrophysical Method of the Composition Modification. *Polymers* 2020, 12, 1437. [CrossRef] [PubMed]
- 28. Kondratov, D.V.; Barulina, M.A.; Ulitin, I.V.; Bekrenev, N.V.; Zlobina, I.V. Principles of constructing a mathematical model of thermal heating of a composite under microwave exposure. *AIP Conf. Proc.* **2023**, *2999*, 020044. [CrossRef]
- 29. Kosarev, A.V.; Studentsov, V.N. A Layered Model of the Curing Kinetics of Oligomer Resins. *Int. Polym. Sci. Technol.* **2014**, *41*, 49–54. [CrossRef]
- Hidalgo, P.; Echeverria, A.; Romero, L.; Navia, R.; Hunter, R. Microwave-assisted epoxidized oil production from the wet microalga Nannochloropsis gaditana to obtain environmentally friendly epoxy resins. *Chem. Eng. Process. Process. Intensif.* 2023, 183, 109215. [CrossRef]
- Bekeshev, A.; Vasinkina, E.; Kalganova, S.; Kadykova, Y.; Mostovoy, A.; Shcherbakov, A.; Lopukhova, M.; Aimaganbetova, Z. Microwave Modification of an Epoxy Basalt-Filled Oligomer to Improve the Functional Properties of a Composite Based on It. *Polymers* 2023, 15, 2024. [CrossRef]
- 32. Lu, H.; Zhang, A.; Zhang, Y.; Ding, L.; Zheng, Y. The effect of polymer polarity on the microwave absorbing properties of MWNTs. *RSC Adv.* **2015**, *5*, 64925–64931. [CrossRef]
- Haider, I.; Gul, I.H.; Umer, M.A.; Baig, M.M. Silica-Fiber-Reinforced Composites for Microelectronic Applications: Effects of Curing Routes. *Materials* 2023, 16, 1790. [CrossRef]
- Tominaga, Y.; Shimamoto, D.; Hotta, Y. Curing Effects on Interfacial Adhesion between Recycled Carbon Fiber and Epoxy Resin Heated by Microwave Irradiation. *Materials* 2018, 11, 493. [CrossRef] [PubMed]

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