Theoretical and experimental studies of laser heating of low-molecular polymer Styrosil

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Abstract. The present article is devoted to the theoretical and experimental research on the decomposition processes of the modified low-molecular polymer Styrosil in the field of continuous laser radiation. The radiance temperature of the surface and the temperature of the rear surface of the modified low-molecular polymer Styrosil were obtained as a function of the power density of the radiation. To describe the processes of decomposition and the mass loss there was developed the computational model for the interaction of the continuous laser radiation with the modified low-molecular polymer Styrosil, which was then verified using the experimental data.

1. Introduction
Laser technologies are widely used now for processing of polymer materials [1–5]. So, optimum operation modes for laser treatment can be different depending on the materials being treated. The specific feature of engineering plastics lies in the presence of incorporations that impede their laser processing. Low-molecular polymer Styrosil is often used as a binder in such materials [1]. So, the problem of the research on the processes of interaction of continuous laser radiation (LR) with engineering plastics coated with modified low-molecular polymer (MLMP) Styrosil is quite urgent.

The goal of this work was to study the processes of decomposition and the loss of engineering plastics coated with Styrosil MLMP in the region of continuous intensive LR and finding the consistent patterns of physical processes that take place.

2. The experimental facility
Optical lay-out of the experiments is shown in figure 1. The output laser beam of the fiber laser passed through the telescopic system of lenses expanded up to the necessary sizes impacting the sample under the analysis. The research was carried out in two stages. In the experiments of the first stage (experiments 1–14) the effective radius of the laser beam with the distribution according to the Gaussian law on the sample was \( r_{\text{eff}} = 0.6 \text{ cm} \) at the level of 0.1. In experiments...
15–18 of the second stage the optical arrangement additionally incorporated a limiting membrane to form a laser beam with a uniform intensity distribution in the spot in the plane of the sample ($r_{\text{eff}} = 0.7$).

The energy of laser radiation was measured with Ophir, the measuring device for energy. The scheme adjustment was realized by the radiation of a pilot laser build in the fiber laser.

The temperature of the front surface of the sample in the region of the LR effect was measured with two radiance pyrometers, and in the operation zone on the rear surface of the sample it was measured with thermocouples. Amplification of the analogue electric signals from thermocouples, their conversion into the digital code followed up with the registration of the output signals was done with the help of digital recorder. The produced experimental data were registered and stored in the memory of the computer workstation with the help of the automated data acquisition system.

Space distribution of the intensity in the laser beam was measured by the results of video recording the affected spot on the scattering screen with the help of a video camera. The measuring circuit is shown in figure 2. Then the image from the camera was processed with a special code as a part of the software package. This code allowed us to record the LR profile in the given cross section, to plot intensities as a function of space coordinates $X$ and $Y$ and to do approximation with the Gaussian function. The measurement error for the LR intensity distribution was not more than 13%. The plots of the LR intensity distribution in the contact spot are given in figure 3.

Power density at the sample was calculated by formula

$$q_{av} = \frac{P}{S},$$

where $P$ is laser radiation power on the sample at the level of 0.1; $S$ is the laser radiation spot area corresponding to the power level of 0.1.

3. Experimental data on the effect of the continuous LR on the Styrosil MLMP

Experimental results on the effect of continuous LR on Styrosil MLMP are given in table 1.
Table 1 introduces the following symbols: \( q_{\text{eff}} \) is the power of the laser radiation at the sample at the level of 0.9; \( t_{\text{LR}} \) is the time of irradiation; \( T_{\text{max}} \) is the maximum temperature at the rear surface of the sample; \( t_{\text{max}} \) is the time to reach the maximum temperature at the rear surface of the sample; \( T_{\text{face}} \) is the maximum radiance temperature of the surface of the sample.

As pyrometers measured the radiance temperature in the center of the affected spot, then this value of the radiance temperature corresponds not to the mean value of the LR power density in the affected spot, but to the value of the higher density of LR power in the center of the affected spot (\( q_{\text{eff}} \approx 2.2q_{\text{av}} \)). Using the obtained experimental data we plotted the radiance temperature on the surface of the Styrosil MLMP as a function of laser power in the center of the affected spot; it is shown in figure 4.

4. Computational model of the laser effect on Styrosil MLMP
Computational model for the effect of the continuous LR on Styrosil MLMP, which is used to describe thermal effect of the laser on the Styrosil LMP, is based on the known equations of
Table 1. Experimental results.

| Experiment | $q_{eff}$, W/cm$^2$ | $t_{LR}$, s | $T_{max}$, °C | $t_{max}$, s | $T_{face}$, °C |
|------------|---------------------|-------------|--------------|--------------|--------------|
| 1          | 70                  | 15          | —            | —            | —            |
| 2          | 4400                | 15          | 1138         | 15.2         | —            |
| 3          | 755                 | 10          | 862          | 7.1          | 3050         |
| 4          | 250                 | 20          | 160          | 44.0         | 2505         |
| 5          | 100                 | 5           | 36           | 45.0         | 1847         |
| 6          | 250                 | 5           | 55           | 44.0         | 2541         |
| 7          | 400                 | 5           | 64           | 89.2         | 2637         |
| 8          | 755                 | 5           | 191          | 7.5          | 3131         |
| 9          | 100                 | 15          | 91           | 57.6         | 1978         |
| 10         | 1000                | 5           | 1195         | 5.0          | 3156         |
| 11         | 40                  | 5           | 14           | 41.2         | 820          |
| 12         | 400                 | 5           | 1231         | 4.55         | 3123         |
| 13         | 400                 | 5           | 150          | 6.2          | 2937         |
| 14         | 161                 | 5           | 72           | 57.5         | 2813         |
| 15         | 300                 | 5           | 99           | 37.0         | 1800         |
| 16         | 460                 | 5           | 115          | 35.0         | 2070         |
| 17         | 460                 | 13          | 319          | 25.0         | 2060         |

Figure 4. Radiance temperature on the surface of the Styrosil MLMP plotted as a function of the laser power in the center of the affected spot.

conservation in multi-material media [6]. The computational model accounts for the following processes: volume absorption of the composite material; pyrolysis of the binder; convection cooling of the surface layers of the material with gaseous pyrolysis products; chemical reactions between the glass filler and coke (carbon) residue; radiative heat conductivity; absorption of the laser radiation in the products of thermal destruction of the material; dependence of thermal and physical characteristics of the material on the temperature and the rate of heating.
The composite heating by laser radiation including all the processes mentioned is described with the nonstationary thermal conductivity equation:

\[ \rho(T, n_i) c(T, n_i) \frac{\partial T}{\partial t} = \partial \left( \lambda(T, n_i) \frac{\partial T}{\partial x} - c g \lambda(T, n_i) \right) + W_{\text{chem}}(T) + W_{\text{LR}}(T), \]

where \( \rho(T, n_i) \), \( c(T, n_i) \), \( \lambda(T, n_i) \) are the density, the heat capacity and the thermal conductivity of the material respectively; \( n_i \) is the mass fraction of carbon, filler and binder; \( i \) corresponds to the name of material (carbon, filler or binder); \( c_g \) is the gas heat capacity; \( \lambda(T, n_i) \) is the sum of the heat conductivity factor which is the sum of the heat conductivity factor of the gaseous products of thermal decomposition; \( W_{\text{chem}}(T) \) is the energy consumed for the chemical reactions; \( W_{\text{LR}}(T) \) is the absorbed laser radiation energy determined by the Bouguer law considering the radiation reflection and absorption in the products of thermal destruction of the material:

\[ W_{\text{LR}}(T) = q_0 [1 - R_0(T)] [1 - \Theta(T)] \exp \left( -\frac{x}{\delta} \right), \]

where \( q_0 \) is the power density of incident laser radiation; \( R_0(T) \) is the coefficient of laser radiation reflection from the material surface; \( \Theta(T) \) is the coefficient taking into account the attenuation of laser radiation in the products of thermal destruction of the composite and depending on the mass loss rate of the material; \( \delta \) is the depth of laser radiation penetration.

The thermal conductivity factor \( \lambda(T, n_i) \) in (4) is a function of temperature and material composition changing during the chemical reactions. At high temperatures it is necessary to consider not only the variation of the rigid structure thermal conductivity with temperature but also the heat transport by the radiation [7]. Here, the effective heat conductivity factor \( \lambda(T, n_i) \) is the sum of the heat conductivity factor \( \lambda_h(T, n_i) \) and of the radiative heat conductivity factor \( \lambda_R(T, n_i) \) [6]:

\[ \lambda(T, n_i) = [1 - \Pi(T)] \lambda_h(T, n_i) + \Pi(T) \lambda_R(T, n_i), \]

where \( \Pi(T) \) is the material porosity; \( \lambda_R = 2 \varepsilon \sigma T^3 h; \varepsilon \) is the emissivity factor; \( \sigma \) is Stefan–Boltzmann constant; \( h \) is the typical pore size [8, 9].

Gaseous products consumption \( G(T) \) is determined from the continuity equation according to the generally accepted assumptions [10]:

\[ \frac{\partial}{\partial t} \left( \Pi(T) \rho_g \right) + \frac{\partial}{\partial x} \left( \Pi(T) \rho_g v_g \right) = - \frac{\partial}{\partial x} \left( \Pi(T) j_g(T) \right) + \omega_g(T), \]

where \( j_g(T) \) is the diffusion gas flux; \( \omega_g(T) \) is the mass rate of the chemical components formation as a result of reactions per unit volume of the porous medium.

The first assumption in the model is that flow resistance of the porous structure and the possibility of gas accumulation inside the pores are neglected: \( \partial(\Pi(T) \rho_g) / \partial t = 0 \).

The second assumption is that the diffusion process is not taken into account because the diffusion flux rate is significantly smaller than the gas rate in direction towards the external surface.

Taking into account the accepted assumptions and the expression \( \omega_g(T) = \partial \rho / \partial t \), and by integrating (5) we get

\[ G(T) = \Pi(T) \rho_g v_g = - \int_L^x \frac{\partial \rho}{\partial x} \, dx. \]

The change in the density of decomposing substance with regard for pyrolysis and chemical reactions, used in the calculation model, is described by the equation

\[ \frac{\partial \rho}{\partial t} = (\rho_k - \rho) B \exp \left( \frac{E_a}{RT} \right), \]
where $B$ is the chemical reaction rate; $E_a$ is the activation energy; $R$ is the universal gas constant; $\rho_k$ is the coke density.

When the temperature of the start of the loss $T_{loss}$ is reached then the loss from the surface of the material begins. To find the mass loss rate we use the Knudsen–Langmuir equation [11]:

$$G(T)_i = \alpha \frac{P_s^i - P\nu}{\sqrt{2\pi RT/M}},$$  \hspace{1cm} (8)

where $\alpha$ is the accommodation coefficient (the physical sense of which is the portion of the inhibitory collisions of gas molecules with a solid surface); $M$ is the molecular mass of vapors; $P_s^i$ is the pressure of the saturated vapor; $P\nu$ is the partial pressure of the evaporating components.

The pressure of the saturated vapor is found by the Clapeyron–Clausius equation [11]:

$$P_s^i = 101300 \exp\left(\frac{P_i - Q_i}{T}\right);$$  \hspace{1cm} (9)

$P_C = -85717 \text{ K}$, $P_{C_2} = -98363 \text{ K}$, $P_{C_3} = -93227 \text{ K}$, $Q_C = 18.69$, $Q_{C_2} = 22.2$, $Q_{C_3} = 23.93$.

Total sublimation rate of carbon is found as a sum of sublimation speeds of different carbon compounds ($C$, $C_2$, $C_3$) calculated by Knudsen–Langmuir equation (8). And the accommodation coefficients here should be set for each of the compounds. The values of the accommodation coefficients in the computations were taken as $\alpha_C = 0.14$, $\alpha_{C_2} = 0.26$, $\alpha_{C_3} = 0.03$ [11–13].

Boundary conditions for the front and back surfaces were calculated by the formula

$$-\lambda(T, n_i) \frac{\partial T}{\partial x} = \varepsilon \sigma T^4.$$  \hspace{1cm} (10)

5. Computation results and verification of the computational model for the continuous effect of LR on Styrosil MLMP

Realization of the developed model and the computations were done both in 1D setup in our own software product and in the software suite LOGOS [14] designed for three-dimensional engineering simulations. Calculation results are the same but LOGOS makes it faster 5 orders of magnitude. As a result of computations we got the dependencies of the radiance temperature of the front surface of Styrosil MLMP, the mass loss rate of Styrosil MLMP and the depth of the coke (carbon residue) formation, the loss of the material as a function of the LR power density, and the temperature at the rear surface of the sample as a function of time. The experimental data on the mass loss rate, the depth of the coke (carbon residue) formation and the loss of the material are taken from [15, 16]. Figure 5 shows the plot of the loss rate of Styrosil MLMP per unit of the surface area as a function of average LR power density in the affected spot, where the preliminary obtained experimental data are marked [16].

As it comes from the analysis of the plot in figure 5, the mass loss rate of Styrosil MLMP per unit of the surface area under the continuous LR grows with the increase of the power density of the incident LR. It was found out that the start of the carbon residue loss has a significant effect on the material loss rate, as the lost layers do not shield the initial material from the LR that causes the process of pyrolysis of new layers. Figure 6 shows the calculated values of the depth of the coke formation and the loss of Styrosil MLMP as a function of the LR power density at the irradiation time $t_{LR} = 5$ s in comparison with earlier obtained experimental data [15].

Figure 7 shows the calculated radiance temperature of Styrosil MLMP as a function of the LR power density compared with the experimentally obtained data. Figure 8 shows the calculated temperatures at the rear surface of the polymer sample with Styrosil MLMP as a function of time after the start of the irradiation with LR of different intensity compared with analogous functions obtained in the experiments. Sample thickness was 5 mm.

After the analysis of the plots in figures 5–8 we see that the developed computational model for the effect of continuous LR on Styrosil MLMP is adequate as there is a good convergence...
Figure 5. The plot of the loss rate for LM Styrosil per unit of the surface area as a function of average LR power density in the affected spot of Styrosil MLMP at the irradiation time of 5 s.

Figure 6. The calculated values of the depth of the coke (carbon residue) formation and the loss of Styrosil MLMP as a function of the LR power density at the irradiation time of 5 s.

of theoretical and experimental research. Maximum relative errors for the loss rate of Styrosil MLMP per unit surface, the depth of the coke formation, the loss of the MLMP and the radiance temperature as a function of the LR power density, as well as the temperature at the rear surface
Figure 7. The radiance temperature of Styrosil MLMP as a function of the LR power density.

Figure 8. The calculated temperatures at the rear surface of Styrosil MLMP as a function of time after the start of irradiation with LR in different modes at a depth of 5 mm from the surface: (a) $q = 300 \text{ W/cm}^2$, $t_{LR} = 5 \text{ s}$; (b) $q = 460 \text{ W/cm}^2$, $t_{LR} = 5 \text{ s}$; (c) $q = 460 \text{ W/cm}^2$, $t_{LR} = 13 \text{ s}$.

of Styrosil MLMP as a function of time after the start of irradiation at different modes are not higher than 10%.

6. Conclusions
So, the task of theoretical and experimental studies of the Styrosil MLMP decomposition in the continuous laser radiation field was set for this work and solved. The dependences of the mass loss for Styrosil MLMP per unit of the surface area, of the depth of the coke formation and the loss of MLMP, of the radiance temperature on the laser radiation power density, as well as the dependency of the temperature on the rear surface of Styrosil MLMP on the time from the start of irradiation at different modes were found. The calculation model of continuous laser radiation effect on the Styrosil MLMP was developed and verified. The agreement between theoretical and experimental results was good.

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