STUDY OF HYDROGEL MATERIALS THERMOPHYSICAL PROPERTIES

by

Boris POKUSAEV[a,b]*, ***Nikolay ZAKHAROV***[a,b], ***Andrey VYAZMIN***[a,b],
Dmitry NEKRASOV[a], ***Elena VOLKOVA***[a,b], ***and Andrey MOSHIN***[a,b]

[a] Moscow Polytechnic University, Moscow, Russia
[b] RTU MIREA – Russian Technological University, Moscow, Russia

Original scientific paper
https://doi.org/10.2298/TSCI221126071P

Based on the optical holography method, heating studies of the wall area in various hydrogels have been carried out applied to 3-D bioprinting technologies. For quantitative measurement of temperature fields, the method of optical holography was used in combination with the method of gradient thermometry, based on the refractive index dependence on the properties of hydrogel systems of different concentrations and temperatures. Under the conditions of the thermophysical properties changes of hydrogels, as well as the magnitude of the supplied heat flow, the heating features are studied in order to determine the coefficients of thermal conductivity and heat capacity, as well as the thermal conditions for the occurrence of convective flows near the wall heated from below in such systems.

Key words: *hydrogels, 3-D bioprinting, thermophysical properties of hydrogels, optical methods*

Introduction

The 3-D bioprinting is a promising technology for various biomedical applications, with the potential to create complex structures with tunable characteristics [1-3]. The applied and promising hydrogel systems consisting of materials such as agarose, gelatin, collagen, hyaluronic acid, alginate, and polyethylene glycol are widely used as the basis of bioinks for 3-D bioprinting [4]. However, since most hydrogel-based bioinks do not provide rapid stabilization of the created object immediately after 3-D bioprinting, achieving high resolution and accuracy in accordance with the proposed architecture is a common problem when implementing 3-D bioprinting technologies with hydrogel materials [5, 6].

Hydrogels are 3-D networks of hydrophilic polymers that can retain a large amount of water in a swollen state [7-10]. Also hydrogels with special characteristics, such as tunable physical and biochemical properties with the ability to control their structure, multi-network crosslinking and bioresorbability, are used with the aid of innovative technologies such as photolithography, the formation of interpenetrating polymer grids, coacervation and assembly of micro-structures for other different applications [11-15]. However, due to the lack of detailed information on the thermophysical properties dependence on various factors, it is difficult to use them to create precisely controlled complex structures and complex 3-D architectures that copy those ones in tissues and organisms [16]. At the same time, the stability of the 3-D archi-

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[*] Corresponding author, e-mail: pokusaev2005@yandex.ru

tectures and constructions play an important role in providing cells with biomechanical signals that regulate their behavior and allow implantation in vivo [17].

In Xu *et al.* [18], molecular dynamics (MD) models of randomly crosslinked polyacrylamide hydrogels with different volume fractions of water are constructed using the reaction method. Based on these models, the thermal conductivity of hydrogels is investigated by the non-equilibrium MD method. It is shown that in some cases the thermal conductivity of the studied gels with a relatively low moisture content may be higher than that of pure water.

Similar studies were carried out in [19], in which it was found that the thermal conductivity of polyacrylamide hydrogel is insensitive to temperature in the range of 25-40 °C, which is an interesting feature, since this range is critical from the point of view of cell culture survival.

Zaragoza *et al.* [20] presents the experimental studies results of the nanoparticles presence effect on the hydrogel material properties. The model system consisting of pAAM hydrogels containing silica nanoparticles was evaluated by measuring three different properties of the polymer: elastic modulus, swelling, and thermal conductivity. The experimental analyses results have shown that both the mechanical and thermal properties of the hydrogel largely depend on the size and concentration of silica nanoparticles. The data obtained demonstrate that the addition of nanoparticles can lead to a higher crosslinking density of the hydrogel. It is also shown that an abnormal increase in thermal conductivity with the addition of nanoparticles exceeds the values predicted by the effective medium theory, which indicates that improvements in the polymer structure mediated by the nanofiller can also lead to an improvement in its thermal properties.

Thus, the issue of determining the thermophysical properties of hydrogel materials, as well as the creation of reliable calculation methods for modelling heat and mass transfer processes in such systems is extremely relevant.

This work is devoted to the creation of a combined technique for determining the transfer coefficients in hydrogel materials based on the method of holographic interferometry, which allows obtaining detailed visualization of temperature fields in such materials, as well as a method for solving inverse problems of thermal conductivity.

The experimental part

To visualize and study the features of the temperature distribution fields in hydrogel materials, the optical method of holographic interferometry, previously worked out on the study of heat transfer in such materials, was used [21], which significantly improved the accuracy of temperature measurement relative to the method implemented in [22].

The essence of the method is to obtain a series of interference patterns (interferograms) of the process under study both in near-wall layer area and in the entire volume of the studied optically transparent samples.

For the full implementation of the optical holography method in order to obtain quantitative values of temperature fields in gels, a necessary condition is the presence of a dependence of the refractive index of the medium under study on temperature. For this purpose, the base of the experimental measuring complex was improved (modernized) by adding a refractometric method for studying hydrogel materials with the possibility of connecting radiation sources with different wavelengths.

The dependence of refractive indices on the gels temperature was determined using an IRF-23 refractometer, the principle of which is based on the study of phenomena occurring when light passes through the interface of two media with different refractive indices. The use of this method makes it possible to determine the refractive indices for transparent media in the liquid solution form, and for the investigated translucent gels.

Figure 1 shows a diagram of an experimental set-up, the main elements of which are: a 20 MW helium-neon laser (He-Ne) with a wavelength of 0.63 μ – 1 an optical polarizing filter – 2, and a Pulfrich refractometer – 3, which includes a set of measuring prisms, a visual tube, a counting device and the lighting system, as well as a DC power source connected to it – 5, and a water thermostat with adjustable temperature control of the heating modes of the studied samples – 6.

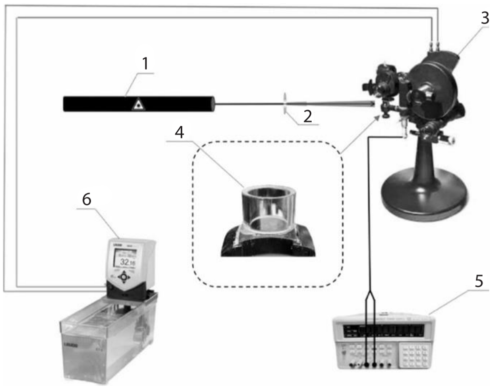

Figure 1. Experimental set-up diagram: *1 – helium-neon laser, 2 – polarizing filter, 3 – IRF-23 Pulfrich refractometer, 4 – gel cuvette, 5 – DC power source, 6 – thermostat*

To ensure the accuracy of measurements, the test sample must be optically homogeneous. Both pure and mixed gels were used in the experiment. The content of agarose in the samples varied in the range of 0.1-0.4% by weight, and gelatin 4.0% by weight. The gel sample was loaded into a cylindrical cuvette and set on a refractometer prism. The light beam from the source passed through the gel sample and was refracted and displayed in the instrument's telescope. According to the angle of refraction of the ocular micrometer correlated with the scale of the microscope, the dependences of the gels refractive index of on temperature were determined. The temperature range of the gel study was from 20-40 °C. Such a temperature range of gel research was determined by the choice of favorable for the development of a wide range of microbioobjects (cells), including stem (human) cells.

Results

As a result of experiments, temperature dependences of refractive indices for various gel samples were obtained. Figure 2 shows the characteristic dependences of the refractive index for two individual gels and one mixed gel.

As can be seen in the figure, the refractive indices for the samples under study vary quite significantly in a small temperature range, which has a significant effect on improving the accuracy of determining the temperature difference between neighboring isolines and minimizes the error in solving the inverse problem of thermal conductivity. Among the three samples, Sample 1 has the maximum value, compared to Samples 2 and 3.

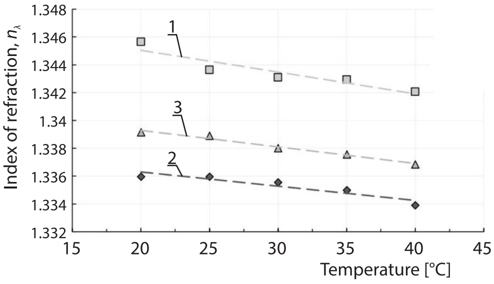

Figure 2. Dependence of the refractive index for different gels on the temperature at the wavelength – 632.8 nm: *1 – gelatin gel 4.0% by weight, 2 – agarose gel 0.4% by weight, 3 – mixed gel of agarose and gelatin*, *respectively 0.1% and 4.0% by weight; points are experimental data, lines are calculated values*

The technique of visualization of temperature fields used in this study, based on interferometric measurements, made it possible to visualize and determine the temperature distribution in the entire volume of the cuvette.

Based on high speed video recording of unsteady heating of hydrogels, interference patterns of the process under study were obtained. Interference patterns are images on which lines of equal temperatures – isotherms – were recorded. To determine and decipher isotherms it is necessary to know the temperature at least at one point of the liquid volume under study and the gradient of the change in the refractive index of the medium from temperature. In the experiments, the initial gel temperature was measured by contact method using thermocouples and it was 20 °C. Using the obtained new data on the dependence of refractive indices on temperature, the values of temperature gradients were calculated for both individuals and mixed gel samples.

As an example, fig. 3 shows video frames of measuring temperature fields after 30 seconds from the start of heating. Here is also a scale with determined temperature values for agarose, gelatin and mixed gel. The thermal load set on the current source was $N = 1.5$ W. The isotherms shown in fig. 3, parallel to the heating surface, characterize the mode of classical unsteady thermal conductivity.

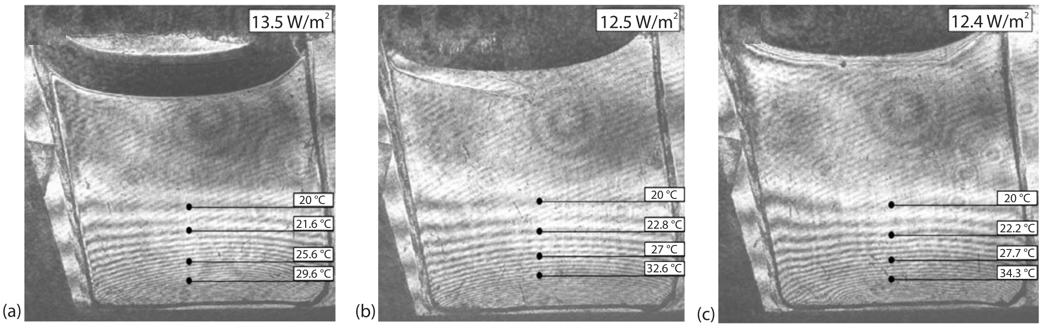

Figure 3. Video frames of temperature fields for different hydrogel samples at the same time $t = 30$ seconds from the start of heating at $N = 1.5$ W; (a) gelatin gel 4.0% by weight, (b) agarose gel 0.4% by weight, and (c) mixed gel of agarose and gelatin, respectively 0.1% and 4.0% by weight

For the first time, quantitative values of the temperature difference between two interference lines of the studied samples of gel materials were obtained. Using the implemented technique, characteristic values of temperature differences were obtained for gelatin, agarose and mixed hydrogels, which amounted to $\Delta T = 0.8$ °C, 1.4 °C, and 1.1 °C, respectively. These data make it possible to obtain temperature values at any point of the sample under study in time, which are necessary to solve the inverse problem of thermal conductivity and determine the calculated values of heat transfer coefficients.

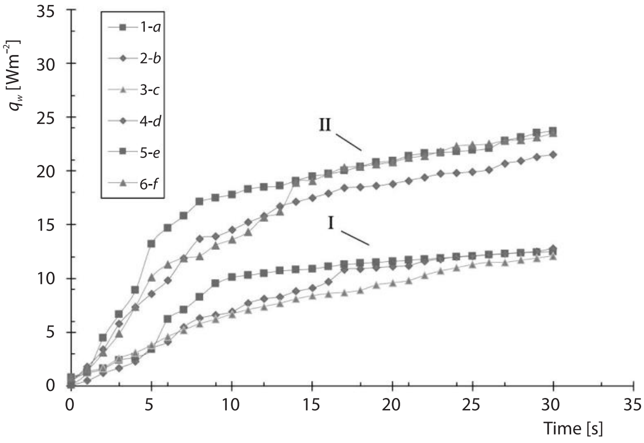

Figure 4. Changes in the heat flow density q_w (W/m^2) from time under different modes of heat load in the heater, I – at 1.5 W; (a) gelatin gel 4.0% by weight, (b) agarose gel 0.4% by weight, (c) agarose mixed gel 0.1% by weight and gelatin 4.0% by weight, II – at 3.5 W, (d) agarose gel 0.4% by weight, (e) gelatin gel 4.0% by weight, and (f) mixed gel of agarose 0.1% by weight and gelatin 4.0% by weight

A special feature of experimental studies of unsteady heat transfer in inhomogeneous micro-structured hydrogels was the combination of optical and thermometric techniques. The use of a gradient heat flow sensor made it possible to record the dynamics of changes in the magnitude of the surface heat flow over time and synchronize it with the results of high speed video recording of the process of unsteady heating of hydrogel samples.

For comparison, fig. 4 shows experimental results of measuring the density of the surface heat flow in the lower wall area of the cuvette at different set heat dissipation power $N = 1.5$ and 3.5 W, respectively. The graph shows that the values of the surface heat flow at $N = 3.5$ W are significantly higher compared to $N = 1.5$ W.

The presented dependences reflect heat transfer in an inhomogeneous dispersed medium in the mode of unsteady thermal conductivity, characterized, as is known, by molecular heat transfer. The graphs show that in gelatin gel, the heat flow values have higher values compared to agarose and mixed gel samples. The obtained data are important for the creation and verification of computational methods for the numerical solution of the problem of the spatial-temporal distribution of temperature fields in gels with anisotropic properties, including the possibility of predicting the onset of melting and the occurrence of microconvective flows in soft gel materials. At the same time, as in previous studies, this method allows you to clearly determine the moment of the beginning of melting of the material under study and the moment of the beginning of free convection.

Numerical modelling

Based on new experimental data obtained by optical visualization of temperature fields, which significantly improve the processing accuracy, a computational method for calculating the coefficients of thermal conductivity and heat capacity of the studied gels during their heating has been developed.

At the same time, in contrast to the previously conducted experiments [22], both with natural cooling of cylindrical gel samples and with their heating, in which the dynamics of temperature field changes were monitored using thermocouples and the actual inability to control the change in heat flow over the entire surface of the sample, the implemented method of thermal diagnostics of gels allowed to significantly reduce the influence of external factors and control the level of heat exposure in real time.

The use of a heater built into the working area with a control system and control of the supplied power allowed experiments to be carried out with the same sample at different levels of the supplied heat flow, including minimum level, which additionally improves the accuracy of the determined values, and the absence of foreign objects in the working area allowed diagnostics of the thermal state of gel samples with bioobjects without their influence on the studied environment.

In addition, in contrast to the previously implemented calculation method [22], where the inverse problem was solved in a cylindrical formulation, in order to determine the thermophysical properties, a physical and mathematical formulation of the 1-D thermal conductivity problem in a Cartesian co-ordinate system was formulated in this work:

$$C\frac{\partial T}{\partial t}=\frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right),\ t>0, 0<x<X \tag{1}$$

$$t=0: T\left(x,0\right)=T_0 \tag{2}$$

$$x=0: -\lambda\frac{\partial T}{\partial x}=q\left(t\right) \tag{3}$$

$$x = X : \frac{\partial T}{\partial x} = 0 \tag{4}$$

where x is the co-ordinate, t – the time, X – the boundary of the outer sample surface, T_0 – the initial temperature, C – the volumetric heat capacity coefficient, λ – the thermal conductivity coefficient, and $q(t)$ – the heat flow density. The determination of the coefficients C and λ from the known experimental values of temperature $T'(x_m, t_n)$ at the time point t_n at the points of the sample material x_m is the essence of the coefficient inverse problem of thermal conductivity, the solution of which is associated with minimizing the functional sum of squared deviations of the experimental temperature values $T'(x_m, t_n)$ from the calculated ones $T(r_m, t_n)$ for all selected time points N and sensors M:

$$J\left(C, \lambda\right) = \sum_{m=1}^{M}\sum_{n=1}^{N}\left[T'\left(x_m, t_n\right) - T\left(x_m, t_n\right)\right]^2 \rightarrow \min \tag{5}$$

The direct problem of thermal conductivity was solved by the finite-difference method using an implicit difference scheme. The solution of a system of difference equations with a tridiagonal matrix of coefficients is obtained by the run-through method. The task of minimizing the functional was solved by the method of co-ordinate descent.

Numerical solutions of direct and inverse problems, as before, were carried out using the VISUAL FORTAN software environment. The results of the calculations are the values of the coefficients of thermal conductivity and volumetric heat capacity, some of which are given in tab. 1.

Table 1. Calculated values of thermal conductivity and heat capacity of hydrogel materials

Substance type	λ [Wm^{-1}K^{-1}]	C [kJm^{-3} K^{-1}]
Gelatin gel 4%	0.474	2059
Agarose gel 0.4 %	0.495	2075

Thus, the computational and experimental complex makes it possible to determine the thermophysical properties of hydrogel materials with high accuracy, including those with various modifying components, which makes it possible to apply the described methods, for example, for express analysis of the properties of promising bioinks based on them in a wide range of concentrations.

Conclusions

An experimental study of the temperature fields distribution under unsteady heating of hydrogels was carried out using optical holography and gradient thermometry. The obtained dependences of the refractive index and high speed video frames were used to determine the quantitative values of the temperature difference between the two interference lines of the gel samples. As a result, new data of the determined temperature fields values of hydrogels of various nature and concentration were obtained, which were used to solve the inverse problem of thermal conductivity and determine the transfer coefficients. The use of the gradient thermometry method made it possible to determine the dynamics of changes in the value of the surface heat flow over time and synchronize it with the results of high speed video recording of the process of unsteady heating of hydrogel samples. It was found that at the same time and comparable thickness of the heated layer for different hydrogel samples, the heating temperature of the mixed sample has the maximum value compared to individual hydrogels.

The computational method for solving the inverse problem of thermal conductivity has been modified and the accuracy of determining the thermal conductivity and heat capacity of hydrogel materials has been significantly increased, which, along with the contactless diagnostic method, allows creating a complex for express diagnostics of the properties of such materials.

This study provides a fundamental understanding of heat transfer in soft materials, which in its turn will make it possible to design printing devices based on hydrogels more efficiently.

Acknowledgment

The work was prepared as part of the implementation of the basic part of the state task of the Moscow Polytechnic University (state registration No. AAAAA20-120092190052-9).

The measurements have been performed partially using the equipment of the Joint Center of Collective Usage of RTU MIREA.

Nomenclature

C – heat capacity coefficient, [kJm^{-3}K^{-1}]
M – sensor
N – power, [W]
N – point
$q(t)$ – heat flow density, [Wm^2]
T_0 – initial temperature, [°C]
ΔT – characteristic values of temperature differences were obtained for gelatin, agarose and mixed hydrogels, [°C]
t – time, [s]
X – boundary of the outer sample surface
x – co-ordinate, [m]

Greek symbols

λ – thermal conductivity coefficient, [Wm^{-1}K^{-1}]

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Paper submitted: November 26, 2022
Paper revised: January 16, 2023
Paper accepted: February 27, 2023