Modelling of E-beam crosslinking of composite hydrogels

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Response Surface Methodology and robust engineering approach were applied for the investigation of preliminary experimental data related to the synthesis of composite biopolymer-based hydrogels via electron beam (e-beam) radiation cross-linking. Two different biopolymers – xanthan gum (XG) and carboxymethylcellulose (CMC) were used for hydrogel preparation in the presence of sodium salts of acrylic acid and a water-soluble cross-linking agent (CA). The influence of various concentrations of XG, CMC, and CA as well as the effect of the irradiation doses up to 15 kGy on several parameters of the synthesized hydrogels as: gel fraction, G [%]; swelling degree, SD [%]; elastic modulus, G' [Pa] and viscous modulus, G" [Pa] were investigated.

Keywords – Biopolymers, composites hydrogels, electron beam radiation crosslinking, modelling.

Моделиране на комбинирани хидрогелове получени чрез електронно-лъчево индуцирано свързване (Мариа Деметер, Ион Калин, Каталина Ванцеа, Тони П. Панева, Елена Г. Колева, Лиляна Ст. Колева). *Методологията на повърхнината на изходните параметри, както и робастно инженерно проектиране са използвани за изследването на предварителни експериментални данни, свързани със синтезирането на комбинирани биополимери – на основа хидрогел, получени чрез електронно-лъчево индуцирано свързване. Два различни биополимера – xanthan gum (XG) и carboxymethylcellulose (CMC) са използвани за приготвянето на хидрогел в присъствието на натриеви соли на акрил ацид и водоразтворим свързващ агент (CA). Изследвано и представено е влиянието на различна концентрация на XG, CMC и CA, влиянието на дозата на облъчване – до 15 kGy, върху параметрите на синтезираният хидрогел, които са: фракция на гела, G [%]; степен на набъбване, SD [%]; модул на еластичност , G' [Pa] и вискозен модул, G" [Pa].*

Introduction

Hydrogels manufactured from natural polymers such as polysaccharides and filled with graphene oxide have demonstrated important performances in various fields as energy storage, wastewater treatment, and biomedicine compared with traditional hydrogels [1].

Radiation cross-linking is a very convenient technique for the preparation of hydrogels. This method has many advantages comparing with classical synthesis routes, such as easy process control, simultaneous cross-linking of polymer to hydrogel formation and is environmentally friendly because it leaves no residue or environmental pollutants [2]. E-beam cross-linking occurs when the macroradicals extracted from the initial polymer chains recombine with each other, resulting in a three-dimensional network [3].

In order to optimize the production process of such composites hydrogels based on biopolymers and graphene oxide using e-beam cross-linking, we applied comprehensive statistical procedures for developing of a complete experimental design, aiming to reduce the final number of experimental trials and shortens the time frame for obtaining valid experimental results.

Response surface methodology and robust engineering approach

Response surface methodology (RSM) is a group of mathematical and statistical procedures used in fitting an empirical model to the experimental data obtained in relation to an experimental design [4, 5]. The RSM implements the regression analysis as a powerful method for model building, providing relationship model estimation between the product performance characteristics and factors. The estimated models, which are considered here and which are a matter of the linear regression analysis, are polynomial, linear with respect to the parameters models. Polynomial models can describe any continuous steady-state relationship and are most frequently used. Regression models (polynomial models of some order), giving an adequate functional relationship between a response of interest y (performance characteristic) and a number of associated control (or input) variables (process parameters) $x_1, x_2, \ldots x_m$, are estimated:

$$(1)\quad \hat{y}(\vec{x}) = \sum_{i=1}^{k} \hat{\theta}_i f_i(\vec{x}) + \varepsilon$$

ε is a random experimental error, assumed to have a zero mean, $\hat{\theta}_i$ are the estimates of the model coefficients.

The natural values of the factors (z_i) in the regression models are coded in the region [-1÷1] and the relation between the coded (x_i) and the natural values (z_i) is given by:

$$(2)\quad x_i = (2z_i - z_{i,max} - z_{i,min})/(z_{i,max} - z_{i,min}),$$

where $z_{i,min}$ and $z_{i,max}$ are the corresponding values of the minimum and the maximum of the process parameters during the experiment.

Robust design [5] implies the theories and methodologies that make quality performance measures (responses, time, energy, etc.) invariant to uncertainties in design variables (manufacturing processes, material dimensions and properties, etc.) and the noise factors (environmental variation during the product's usage, manufacturing variation, and component deterioration). In some cases, when there are repeated observations and there are errors due to process parameter uncertainties and noises, two models are estimated for the mean value and the variance of each quality characteristic. The process quality can be improved by increasing the repeatability of the performance characteristics through minimization of its variance while keeping its target value.

In this paper models describing the dependencies of the gel fraction, y_1 (%), the swelling degree, y_2 (%), the elastic modulus, y_3 (Pa) and the viscous modulus, y_4 (Pa) on the variation of the process parameters as: irradiation dose (kGy), concentration of CA (%), concentration of XG (%) and concentration of CMC (%) are estimated.

1. Experimental

Food grade xanthan gum (XG) sample (Jungbunzlauer, Austria) in powder form having molecular weight of M_w~1.6×10^6g/mol was used without further purifications. Concentrated aqueous solution of GO (6.2g/L) was purchased from Graphene Laboratory Inc., USA. Sodium carboxymethylcelullose (CMC) with molecular weight $M_w = 2.5\times10^5$ g/mol, acrylic acid (AA) anhydrous 99% with M_w=72.06 g/mol, N'N-methylene-bis-acrylamide (MBA) 99% with Mw = 154.17 g/mol and NaOH were purchased from Aldrich Co., respectively Sigma-Aldrich (USA).

In order to prepare XG-CMC aqueous solutions, stock solutions of 5% XG and 2% CMC were used. Different volumes of these stock solutions were mixed and stirred at room temperature until complete homogenization resulting in XG-CMC aqueous solutions with different concentrations. The same concentration of graphene oxide (GO) was added to the final polymeric blends. In order to initiate the cross-linking reaction, different amounts of cross-linking agent (CA) were added.

The e-beam irradiation was performed using ALID-7, a 5.5 MeV linear electron accelerator owned by INFLPR-National Institute for Laser, Plasma and Radiation Physics (Magurele, Romania). Irradiation was carried out at an average beam current of 10 µA, pulse length of 3.75 µs and pulse repetition rate of 53 Hz [6]. The dosimetry was performed using a graphite calorimeter (according to ISO/ASTM 51631:2013 [7]. The applied irradiation doses were up to 15 kGy at the same dose rate.

Model estimation

The robust engineering approach and response surface methodology are used for the estimation of prediction models for the variation of the investigated quality characteristics: the mean value and the variance of the gel fraction, y_1 (%), the swelling degree, y_2 (%), the elastic modulus, y_3 (Pa) and the viscous modulus, y_4 (Pa), depending on the variation of the process parameters: irradiation dose (x_1), concentration of CA (x_2), concentration of XG (x_3) and concentration of CMC (x_4). They are presented in Table 1, together with the square of the multiple correlation coefficients (R^2) and the square of the adjusted multiple correlation coefficients (R^2_{adj}).

The values of both coefficients are high (close to 1 or 100%) and consequently the estimated models for the gel fraction; the swelling degree, the elastic modulus and the viscous modulus can be considered as good enough for prediction and parameter optimization.

Fig. 1 shows the experiment contour plots of the variance of the gel fraction (s_1^2) depending on the EB irradiation dose (x_1) and concentration of the crosslink agent (CA) (x_2).

Table 1

Regression models for the quality characteristics and the dispersion of the product

	Models	R^2	R^2_{adj}
$\tilde{\tilde{y}}_1$	$59.939 - 8.959x_1 + 10.678x_2 + 9.149x_3 + 1.074x_1^2 - 0.900x_1x_2 - 7.098x_1x_4$	0.9992	0.9980
$\ln(s_1^2)$	$1.3625397 + 1.3014971x_2 - 1.6940564x_1^2 + 0.45154512x_1x_2$	0.7656	0.6651
$\hat{y}_2$	$3948.5881+651.47997x_1-2240.114x_4^2-1297.1441x_1x_2-322.26061x_1x_3$	0.9104	0.8507
$\hat{y}_3$	$802.38997-93.218139x_1 + 40.437702x_2 + 255.33628x_3 - 157.34779x_1x_4$	0.8951	0.8251
$\hat{y}_4$	$164.55436-4.7947041x_2-22.198708x_4+13.766544x_1x_3-5.8143704x_1x_2^2+7.871501x_1^2x_4$	0.8462	0.6925

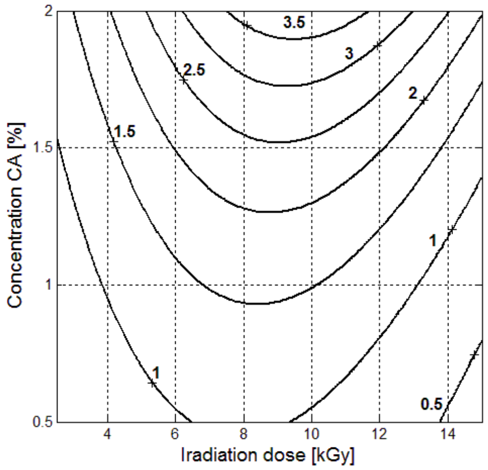
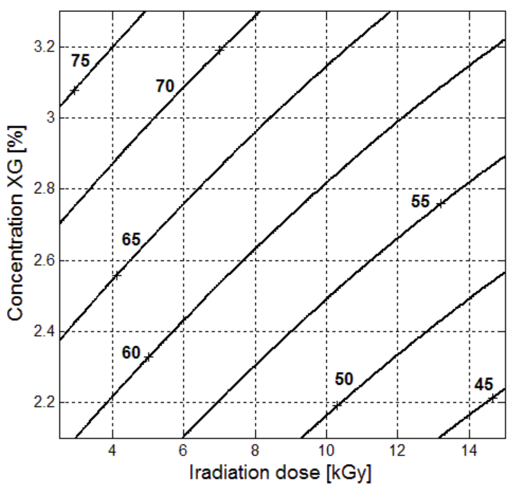
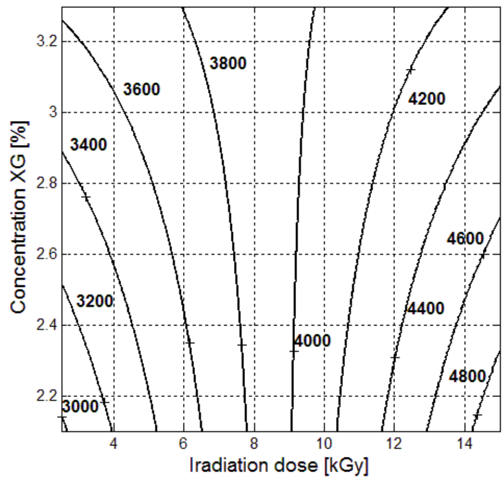


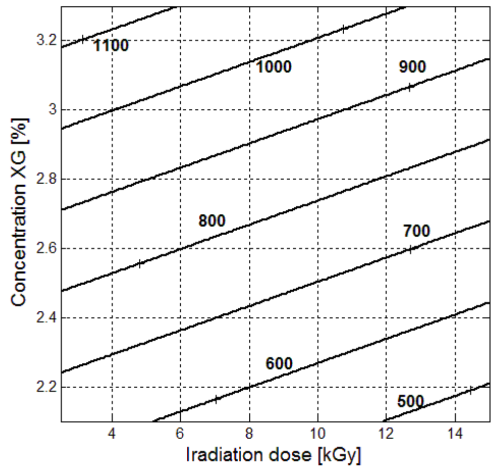
Fig. 1. Contour plot of the variance of the gel fraction s_1^2



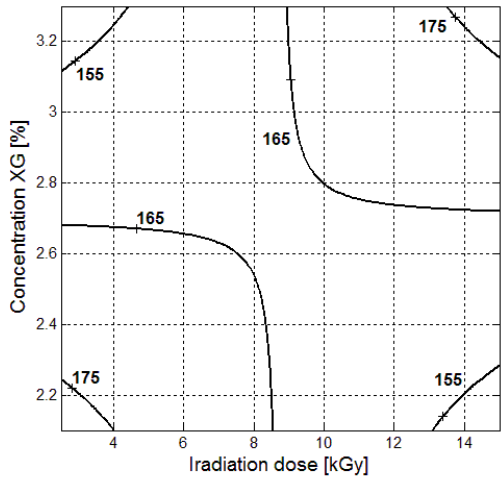
a) $\tilde{\tilde{y}}_1$



b) $\hat{y}_2$



c) $\hat{y}_3$



d) $\hat{y}_4$

Fig. 2. Contour plots of the variation of a) gel fraction; b) swelling degree; c) elastic modulus and d) viscous modulus for constants: concentration of crosslinking agent z_2 = 1.25 % and concentration of CMC z_4 = 2.7 %

It can be seen that the dispersion has minimum when the concentration CA is under 1 % and irradiation dose is more than 12 kGy.

In Fig. 2 the contour plots for the mean values of the gel fraction ($\tilde{\tilde{y}}_1$), the swelling degree ($\hat{y}_2$), the elastic modulus ($\hat{y}_3$) and the viscous modulus ($\hat{y}_4$) depending on the EB irradiation dose (x_1) and XG concentration (x_3) are presented. Contour plots show that the gel fraction (Fig. 2a) and concentration of the crosslinking agent (Fig. 2c) has maximal value when the concentration of XG is high and the irradiation dose is lower.

The highest viscous modulus (Fig. 2d) is obtained when the irradiation dose and the concentration of XG are minimum or at their maximum values. The highest swelling degree (Fig. 2b) will be obtained with the lowest concentration of XG and irradiation dose higher than 13 kGy.

Conclusions

Response Surface Methodology and robust engineering design approach were used for the investigation of preliminary experimental data related to the synthesis of composite biopolymer. Prediction models for the mean values of the gel fraction (%), the swelling degree (%), the elastic modulus G' [Pa] and the viscous modulus G" [Pa] as well as the variance of the gel fraction (s_1^2) are estimated in dependence on the process parameters: EB irradiation dose, concentration of CA, concentration of XG and concentration of CMC.

The obtained regression models can be used for future investigation and optimization of the e-beam synthesis of XGGOCMC hydrogels.

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