Graphical user interface for optimization of starch modified by electron beam irradiation

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Experimental investigation of electron beam induced graft copolymerization of starch (corn and potato), using electron beam generated by a linear accelerator with energy of 5.5 MeV and 6.23 MeV is performed. The modification of starch is realized by acrylamide grafting and water-soluble copolymers having flocculation abilities are synthesized. The influence of the variation of the the following parameters: acrylamide/starch weight ratio, electron beam irradiation dose, dose rate and in some of the cases - the presence or absence of metallic silver nanoparticles is investigated. Characterization of graft copolymers is carried out by the monomer conversion coefficient; residual monomer concentration; apparent viscosity; intrinsic viscosity and Huggins' constant. Robust engineering design in the case of replicated observations is implemented in order to estimate models of the dependencies of the means and the variances of the quality characteristics from the process parameters. Multi-criteria optimization, involving requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process and good solubility in water, is also made. Graphical user interface aiming investigation of the graft copolymer characteristics and process parameter optimization, which can be used for supporting the operator's choice of appropriate work regimes, obtaining the required quality standards, education and investigations is developed and presented.

Графичен потребителски интерфейс за оптимизация на модифициране на нишесте, индуцирано с електронен лъч (Елена Г. Колева, Лиляна Ст. Колева, Мирела Брасовеану, Моника Р. Немтану, Тони Панева, Венцислав Цочев). *Проведени са експериментални изследвания на модифицирането на нишесте (царевично и картофено), чрез кополимеризация, индуцирана с електронен лъч, генериран от линеен ускорител с енергии 5.5 MeV и 6.23 MeV. Модификацията на нишесте се реализира чрез присъединяване на акриламид, и се получават водоразтворими кополимери с флуколантни свойства. Изследвано е влиянието на изменението на параметрите: тегловното съотношение акриламид/нишесте;доза на облъчване с електронен лъч; скорост на облъчване с електронният лъч и в някои случаи – присъствието или отсъствието на сребърни наночастици. Характеристиките на присъединения кополимер са представени чрез коефициента на преобразуване на мономера, остатъчна концентрация на мономера, външен и вътрешен вискозитет и константа на Хъгинс. На базата на повторни опити са изведени модели за робастно инжинерно управление, описващи зависимостите на средните стойности и дисперсиите на качествените характеристики от параметрите на процеса. Направена е многокритериална оптимизация, която обединява изискванията за икономическа ефективност, осигуряване на ниска токсичност, висока ефективност на кополимера във флуколантните процеси и добра разтворимост във вода. Разработен и представен е графически потребителски интерфейс, целящ изследване на характеристиките на модифицирано нишесте и параметрична оптимизация на процеса, който може да бъде приложен за подпомагане на избора на оператора на подходящ работен режим, за достигане на зададени стандарти за качество, за обучение и изследвания.*

Introduction

Electron beam (EB) grafting is an important process for creation of new functional materials with different applications. The current environmental requirements are connected with the minimization of the impact of wastes on the environment. Consequently, there is a strong demand to develop economically viable and eco-friendly replacements of conventional synthetic flocculants, which are renewable organic materials with low cost [1]. Grafting is the most effective way to produce high efficient graft copolymers [2], with required properties and having application as flocculating agents for treatment of different wastewaters.

Electron beam (EB) modification of polymer substrates using electron beam induced graft copolymerization (irradiation grafting) is used to develop a wide variety of ion exchangers, polymer-ligand exchangers, chelating copolymers, hydrogels, affinity graft copolymers and polymer electrolytes, having various applications in water treatment, chemical industry, biotechnology, biomedicine, etc. [3, 4].

Robust or not sensitive to noises and errors engineering approach [5, 6] can be implemented when analyzing experiments, during which the variance is non-homogeneous over the factor (process parameters') space and when the noise factors cannot be identified nor an experiment to study them can be conducted. The observations in this case are called heteroscedastic (variance varies with the factor levels). The performance characteristic can depend on both quantitative and qualitative factors. Models for the mean and the variance of the quality characteristics of the product, based on repeated observations and taking into account the influence of the qualitative and the qualitative factors can be estimated. Parameter optimization in terms of obtaining repeatability of the product parameters and quality improvement by minimization of variations in the quality characteristics can be performed.

In all observed cases multi-criteria optimization, involving requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process and good solubility in water is presented. Models, describing the dependencies of the means and the variances of the quality characteristics: monomer conversion coefficient (%), residual monomer concentration (%), intrinsic viscosity (dL/g) and Huggins' constant on the variation of the process parameters: EB irradiation dose, dose rate, acrylamide/starch (AMD/St) weight ratio and in some case one qualitative factor – the presence or absence of metallic silver nanoparticles (nAg), are estimated.

Monomer conversion coefficient, residual monomer concentration, apparent viscosity, intrinsic viscosity and Huggins' constant were estimated using three measurements and the following equations:

$$\bar{y}_u = \frac{1}{n}\sum_{i=1}^{n} y_{ui} \qquad s_u^2 = \frac{1}{n-1}\sum_{i=1}^{n}\left(y_{ui} - \bar{y}_u\right)^2 \qquad u = 1, 2, ..., N,$$

where n is the number of replications, N is the number of experimental sets.

Experimental conditions

Four series of experiments for the modification of starch by grafting acrylamide using electron beam irradiation were performed in order to synthesize water-soluble copolymers having flocculation abilities. The synthesis of graft copolymers was performed by two steps: (1) preparation of starch aqueous solutions with added acrylamide monomer in various acrylamide/starch (AMD/St) weight ratios; (2) irradiation of solutions by electron beam at ambient temperature and pressure by using linear electron accelerator of mean energy of 6.23or 5.5 MeV with different irradiation doses and dose rates.

A. Corn starch modified by electron beam irradiation of 6.23 MeV

The synthesized graft copolymers were characterized by monomer conversion coefficient, *Conv* [%]; residual monomer concentration, M_r [%]; apparent viscosity, η_a [mPa·s] and intrinsic viscosity, [η] [dL/g]; and Huggings' constant, k_H. The variation regions [z_{min}-z_{max}] of the process parameters were: for EB irradiation dose (z_1) - [0.65-5.50 kGy]; the dose rate (z_2) – [0.41-1.50 kGy/min] and the concentration of AMD (z_3) – [9.8-19.6 %]. The concentration of St for this experiment was constant and is 1.8%. The AMD/St weight ratio varies from 5.56 to 11.11 [7].

B. Corn starch modified by electron beam irradiation of 5.5 MeV

During these experiments the irradiations were carried out at ambient temperature and pressure by using linear electron accelerator with mean energy of 5.5 MeV.

The synthesized graft copolymers were characterized by the following performance quality parameters: y_1 [%] - residual monomer concentration, y_2 [%] - monomer conversion coefficient, y_3 [dL/g] - intrinsic viscosity and y_4 - Huggins' constant. The variation regions [z_{min}-z_{max}] of the process parameters were: for EB irradiation dose (z_1) – [0.64-1.44 kGy]; the EB irradiation dose rate (z_2) – [0.45-1.40 kGy/min] and the (AMD/St) weight ratio (z_3) – [5.00-10.02]. The concentration of St for these experiments varies from 2.00% to 6.15% and the concentration of AMD varies from 10.00% to 33.67%. [8]

C. Corn starch modified by electron beam irradiation of 5.5 MeV and qualitative factor (nAg)

The synthesized graft copolymers were

characterized by the same quality parameters, used in previous case, but the variation regions [z_{min}-z_{max}] of the process parameters were: for EB irradiation dose (z_1) – [0.67-1.37 kGy]; the dose rate (z_2) – [0.55-0.81 kGy/min] and the (AMD/St) weight ratio (z_3) – [4.98-9.97 %]. The influence of one qualitative factor is also investigated: (v) – presence of nAg – experiments were held both with certain addition and no addition of nAg to the aqueous solutions before irradiations. The concentration of St for these experiments was constant and is 3.33% and the concentration of AMD varies from 16.6% to 33.2% [9].

D. Potato starch modified by electron beam irradiation of 6.23 MeV

In this case was investigated modified potato starch. The synthesized graft copolymers were characterized by the following performance quality parameters: y_1 [%] - residual monomer concentration, y_2 [%] - monomer conversion coefficient and y_3 [dL/g] - apparent viscosity. The variation regions [z_{min}-z_{max}] of the process parameters were: for EB irradiation dose (z_1) – [0.3 - 2.7 kGy]; the EB irradiation dose rate (z_2) – [0.7 – 2.1 kGy/min] and the AMD/St weight ratio (z_3) – [6 - 17]. The concentration of St for these experiments was constant and is 1.7% and the concentration of AMD varies from 9.9% to 29.4%

Table 1

Models for the means of the product quality characteristics

	Models for the means of the product quality characteristics	R
$\tilde{\bar{y}}_1(\vec{x})$	$7.6301301 - 10.511391x_1 + 3.6634437x_2 + 3.7076966x_3 + 5.3440613x_1^2 + 2.6928483x_2x_3 - 5.7559852x_1x_3$	0.94
$\tilde{\bar{y}}_2(\vec{x})$	$50.135158 + 63.825498x_1 + 7.2695758x_3 - 30.821651x_1^2 + 20.728795x_2^2 + 46.570908x_1x_2 - 6.2559946x_2x_3 + 7.1792709x_1x_3$	0.94
$\tilde{\bar{y}}_3(\vec{x})$	$4.9863614 + 0.79876942x_3 - 1.8164872x_1^2 - 2.4291323x_2^2 + 0.28578303x_3^2 + 2.8628548x_1^2x_2 - 0.36988326x_1^2x_3 - 6.5866358x_1x_2^2$	0.77

The dependencies of the means and the variances of the product quality characteristics: y_1 (%), y_2 (%) and y_3 (dL/g) on the variation of the process parameters: x_1 – electron beam irradiation dose, x_2 – electron beam irradiation dose rate and x_3 – AMD/St weight ratio are estimated. The obtained regression models are presented in Table 2 and Table 3, together with the values of the corresponding multiple correlation coefficients R. These coefficients are tested for significance and their values are measures of the accuracy of the estimated models. The closer to 1 the value of R is, the better the model describes the variations of the quality characteristics as a function of the process parameters. All models have enough high and significant values of their multiple correlation coefficients and consequently the models are good for prediction and optimization of the considered quality characteristics.

Table 2

Models for the variance of the product quality characteristics

	Models for the variance of the product quality characteristics	R
$\ln\left(\tilde{s}_1^2(\vec{x})\right)$	$-2.4798878 - 4.0003851x_1 - 0.57765525x_2 + 4.1711416x_1^2 - 1.0759422x_3^2 - 3.9161133x_1x_2 + 0.65013091x_2^2x_3 + 1.2773211x_1x_3 - 1.8572702x_1^2x_3 + 6.0599373x_1x_2^2 + 0.62670214x_1x_3^2 + 1.0690743x_1x_2x_3$	0.83
$\ln\left(\tilde{s}_2^2(\vec{x})\right)$	$0.8216977 + 2.1896934x_1 - 1.8923076x_1^2 - 0.58333338x_3^2 - 1.793822x_1x_3 - 1.8912097x_2^2x_3 - 2.7704084x_1x_2^2 - 0.38270749x_2x_3^2 - 1.8676796x_1x_2x_3 - 2.2114287x_1^2x_2$	0.91
$\ln\left(\tilde{s}_3^2(\vec{x})\right)$	$-2.6596544 - 2.8045736x_1 + 0.80422168x_3 - 1.8970163x_1^2 + 0.72143614x_3^2 + 1.1522243x_1x_3 - 1.6532444x_1^2x_3 + 2.3354389x_1x_3^2$	0.94

Models of the mean and the variance of the quality characteristics

The estimated values of the means $\bar{y}_u$ and the variances s_u^2 can be considered as two responses at the design points and ordinary least squares method can be used to fit regression models for the mean value and for the variance for each quality characteristic [5]:

$$\tilde{\bar{y}}(\vec{x},w)=\sum_{i=1}^{k_y}\hat{\theta}_{yi}\,f_{yi}(\vec{x},w)$$

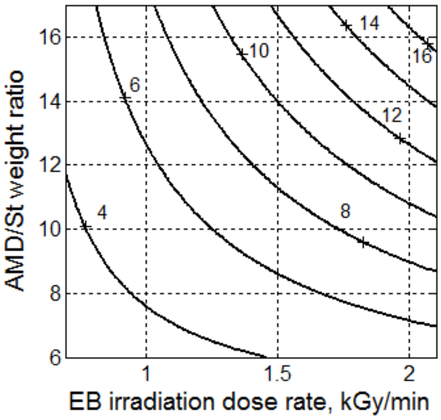
$$\ln\left(\tilde{s}^2(\vec{x},w)\right)=\sum_{i=1}^{k_\sigma}\hat{\theta}_{\sigma i}\,f_{\sigma i}(\vec{x},w),$$

where $\hat{\theta}_{yi}$ and $\hat{\theta}_{\sigma i}$ are estimates of the regression coefficients, and f_{yi} and $f_{\sigma i}$ are known functions of the process parameters x_i and the qualitative factor w. The variance of normally distributed observations has a χ^2- distribution. The use of the logarithm transformation of the variance function makes it approximately normally distributed, which improves the efficiency of the estimates of the regression coefficients.

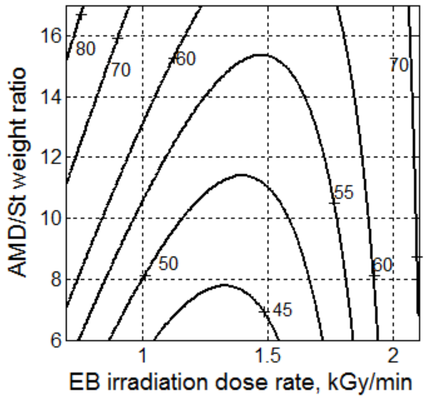
The models are estimated for coded in the region [-1÷1] values of the process parameters, using the following equation:

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

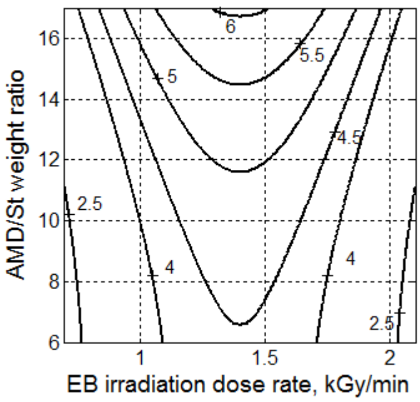
where x_i and z_i are the coded and the natural values of the process parameter, correspondingly, $z_{i,min}$ and $z_{i,max}$ are the minimal and the maximal values of the parameter experimental region.



a) y_1



b) y_2

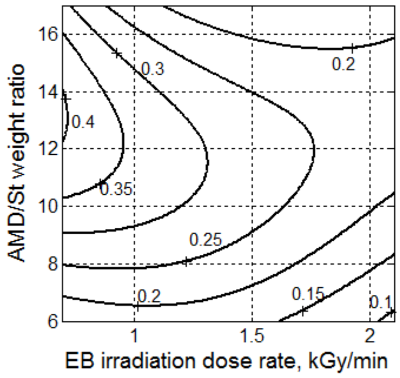


c) y_3

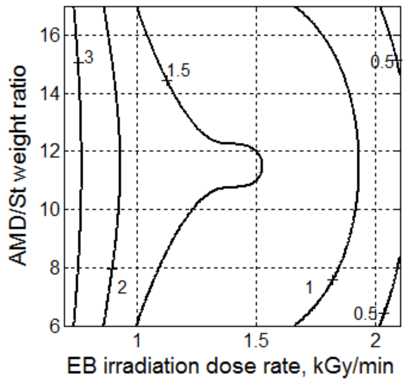
Fig. 1 . Potato starch experiments contour plots of the mean values of the product quality characteristics for constant EB irradiation doses z_1= 1.5 kGy.

.The dependencies of the means and the variances of the product quality characteristics of the presented experiments are estimated.

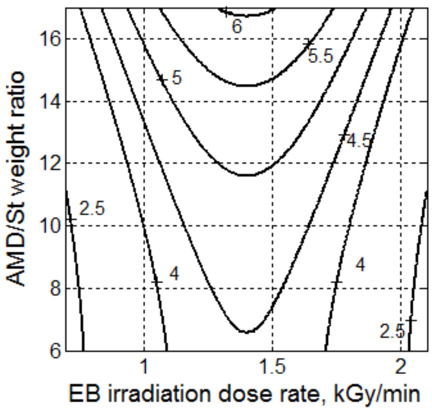
For the potato starch experiments in Fig. 1 the contour plots of the variation of the residual monomer concentration (y_1), monomer conversion coefficient (y_2) and apparent viscosity (y_3) depending on the EB dose rate (x_2) and AMD/St weight ratio (x_3) are presented.



a)



b)



c)

Fig. 2. Contour plots of the standard deviations of product characteristics depending on EB irradiation dose rate (x_2) and the AMD/ST ratio (x_3) at constant EB irradiation dose z_1= 1.5 kGy: a) $\tilde{s}_1(x)$; b) $\tilde{s}_2(x)$; c) $\tilde{s}_3(x)$;

Fig. 2 shows the contour plots of the variations of the three investigated quality characteristics, depending on the EB dose rate (x_2) and AMD/St weight ratio (x_3) and constant EB irradiation dose $z_1 = 1.5$ kGy.

Optimization

Multi-criteria optimization unifying requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process, good solubility in water, as well as the repeatability of the obtained results is performed. Methods based on graphical optimization and on Pareto-optimization are implemented for solving this task. The set of requirements is the following:

- residual monomer concentration: < 5% => assurance of low toxicity
- monomer conversion coefficient: > 90% => economic efficiency
- apparent viscosity: > 3 mPa·s => copolymer efficiency in flocculation process
- intrinsic viscosity: > 6 dL/g => copolymer efficiency in flocculation process
- Huggings' constant: 0.3 ÷ 1 (or -1.20397 ÷ 0) => good solubility in water

Graphical optimization is a method for multi-criteria optimization, applicable in cases with formulated one- or two-sided constrains for the product quality characteristics. It is conducted in order to find the regions of the process parameters, working at which the requirements for the quality characteristics are fulfilled simultaneously. The optimal regions are obtained by superimposing the contour plots of the calculated limit values of the characteristics, thus finding the section of all the admissible values of the process parameters.

Expert system

All the described features (investigation, prediction, optimization), the possibility to upgrade with new data and estimate new models are integrated into an integrated user interface that is applicable for education, operator's advise, prognostication, optimization and quality improvement of the process starch modified by electron beam irradiation.

The structure of the interface for the analysis of each of the described four series experiments involves the following possibilities:

- Calculator – calculates the mean and variance of the product quality characteristics (Fig. 3).
- Optimization - Graphical optimization is conducted in order to find the regions of the process parameters where the requirements for the quality characteristics are fulfilled simultaneously. Graphical user interface display for the optimization is presented on Fig. 4.

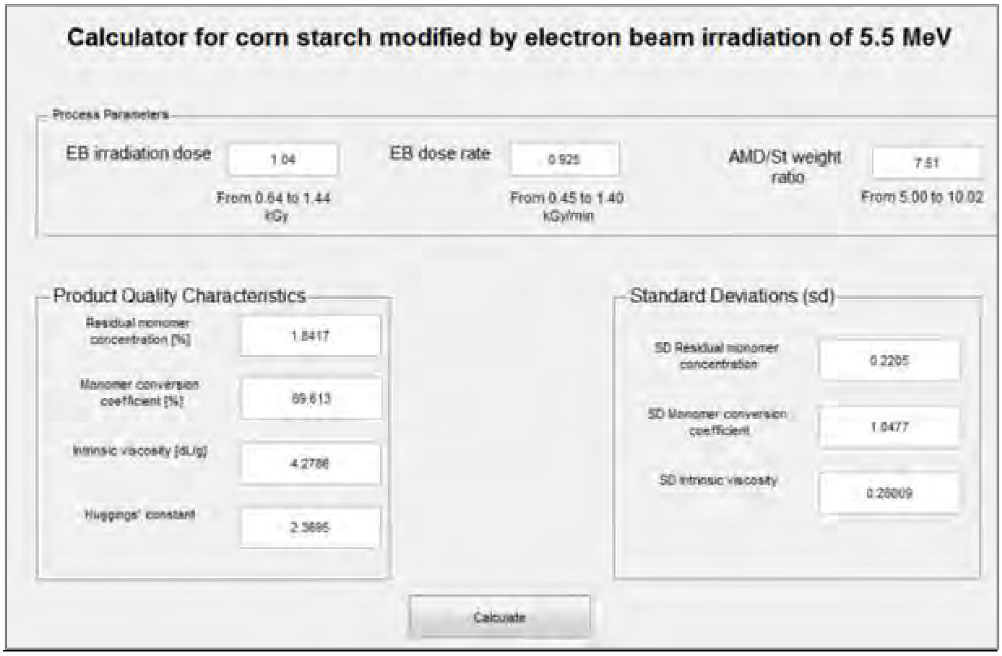


Fig. 3. Calculator window

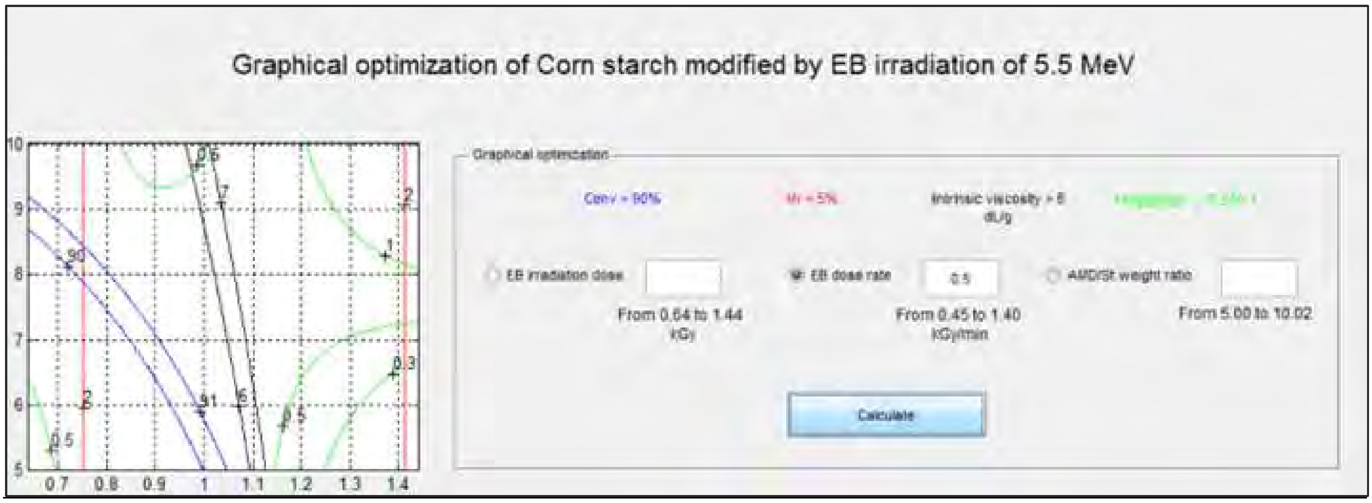


Fig. 4. Graphical optimization window

Conclusions

The developed graphical user interface aiming investigation of the graft copolymer characteristics and process parameter optimization, which can be used for supporting the operator's choice of appropriate work regimes, obtaining the required quality standards, education and investigations is presented. The additional requirement for robustness (insensitivity) in respect of variations in input parameters and noise factors of the process leads to better reproducibility of the results, together with the implementation of the requirements for economic efficiency, low toxicity, efficient copolymer in flocculation processes and good water solubility.

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