INVESTIGATION AND OPTIMIZATION OF ELECTRON BEAM GRAFTING OF CORN STARCH

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Abstract: *Experimental investigation of the modification of starch by grafting acrylamide using electron beam irradiation in order to synthesize water-soluble copolymers having flocculation abilities is performed. The influence of the variation of the parameters acrylamide/starch (AMD/St) weight ratio, electron beam irradiation dose and dose rate, as well as the presence or absence of metallic silver nanoparticles is investigated. The characterization of graft copolymers was carried out by monomer conversion coefficient, residual monomer concentration, intrinsic viscosity and Huggins' constant. Models, describing the dependencies of the quality characteristics (their means and variances) from the process parameters, are estimated by implementation of the robust engineering approach in the case of qualitative and quantitative factors. 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 presented.*

Keywords: GRAFT COPOLYMERIZATION, ELECTRON BEAM IRRADIATION, WATER-SOLUBLE COPOLYMERS, STARCH, ACRYLAMIDE, FLOCCULATION PROPERTIES, RESPONSE SURFACE METHODOLOGY, DUMMY VARIABLES

1. Introduction

The current environmental considerations impose rigorous protection rules and sustainable progress that minimize the impact of wastes on the environment. Accordingly, there is a strong demand to develop economically viable and eco-friendly replacements of conventional synthetic flocculants, based upon the renewable organic materials that are low cost and degrade naturally when are released in the environment [1]. Grafting is the most effective way of regulating the properties of natural polysaccharides, which can be 'tailor-made' according to the needs and produce high efficient graft copolymers [2], having application as flocculating agents for treatment of different wastewaters.

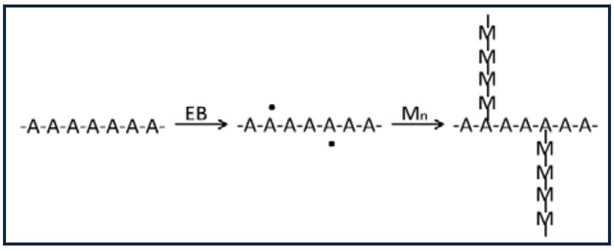


Fig. 1 *Electron beam induced grafting process*

Electron beam (EB) irradiation grafting (modification of polymer substrates using electron beam induced graft copolymerization – see Fig. 1) 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 (not sensitive to noises and errors) engineering approach 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). On the other hand, many performance characteristics depend on both quantitative and qualitative factors. In this case 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 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 this paper 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: y_1 - monomer conversion coefficient (%), y_2 - residual monomer concentration (%), y_3 - intrinsic viscosity (dL/g) and y_4 - Huggins' constant on the variation of the process parameters: EB irradiation dose, dose rate, acrylamide/starch (AMD/St) weight ratio and one qualitative factor – the presence or absence of metallic silver nanoparticles (nAg), are estimated.

2. Experimental conditions

Experimental investigation of the modification of starch by grafting acrylamide using electron beam irradiation in order to synthesize water-soluble copolymers having flocculation abilities is performed. Acrylamide monomer gives a polar graft side chain resulting in hydrophilic copolymer. The prepared homogenous aqueous solutions containing starch and acrylamide were exposed to electron beam irradiation. The irradiations were carried out at ambient temperature and pressure by using linear electron accelerator of 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) – [0.67-1.37 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%.

The conducted experimental design with 13 experimental process parameter sets for coded values in the region [-1÷1] is presented in Table 1. The coding of the process parameter values is done, using the following equation:

$$(1) \quad x_i = (2z_i - z_{i,\max} - z_{i,\min})/(z_{i,\max} - z_{i,\min})$$

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 variation region.

Table 1: *Experimental design with one dummy variable*

	x_1	x_2	x_3	w
1	-0.315	-1	-1	1
2	-0.257	-1	-0.999	0
3	-0.915	-0.769	-0.999	1
4	-0.857	-0.769	-1	0
5	-0.000	0.539	-0.999	0
6	0.914	1	-0.999	1
7	1	1	-0.999	0
8	-0.257	-0.846	1	1
9	-0.171	-0.846	0.997	0
10	0.400	0.154	0.997	1
11	0.457	0.154	0.997	0
12	-1	1	0.997	1
13	-0.943	1	0.997	0

The qualitative factor (nAg) has two levels being presented by a dummy variable (w) in the experimental design. The dummy variable has value 1, if the nAg is used and value 0 when nAg is not used.

For each set of the process parameters (Table 1) three replicated measurements are used for estimation of the means $\bar{y}_{ui}$ and the variances s_{ui}^2 of the quality characteristics of the graft copolymers:

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

where n is the number of replications (n=3), N is the number of experimental sets (N=13).

The observed variations are due to unmeasured and uncontrolled factors and internal and external noises, as well as errors in the controlled process parameters, and depend on the values of the process parameters.

3. Models of the mean and 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]:

$$(3) \qquad \tilde{\bar{y}}(\vec{x}, w) = \sum_{i=1}^{k_y} \hat{\theta}_{yi} f_{yi}(\vec{x}, w)$$

$$(4) \qquad \ln\left(\tilde{s}^2(\vec{x}, w)\right) = \sum_{i=1}^{k_\sigma} \hat{\theta}_{\sigma i} f_{\sigma i}(\vec{x}, w),$$

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 dependencies of the means and the variances of the product quality characteristics: y_1 – residual monomer concentration (%), y_2 – monomer conversion coefficient (%), y_3 – intrinsic viscosity (dL/g) and y_4 – Huggins' constant on the variation of the process parameters: x_1 – electron beam irradiation dose, x_2 – electron beam irradiation dose rate, x_3 – AMD/St weight ratio and w – dummy variable for the metallic silver nanoparticles (nAg) 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 means of the product quality characteristics*

	Models for the means of the product quality characteristics	R
$\tilde{\bar{y}}_1(\vec{x})$	$1.9448-1.2606x_1+0.7151x_2-0.3670x_2^2+0.1647x_2x_3$	0.9879
$\tilde{\bar{y}}_2(\vec{x})$	$90.7891+5.3299x_1+2.8949x_3-4.4823x_1^2+5.0562x_2^2$	0.9656
$\tilde{\bar{y}}_3(\vec{x})$	$4.1080638+2.6314569x_3+2.7220436x_2^2+1.9317618x_1x_3$	0.9838
$\ln\left(\tilde{\bar{y}}_4(\vec{x}, w)\right)$	$-0.03086538+1.2538333x_2-0.85624927x_3$ $+0.86750972x_1x_3-0.91415941x_2x_3-0.92492186x_2w$	0.8894

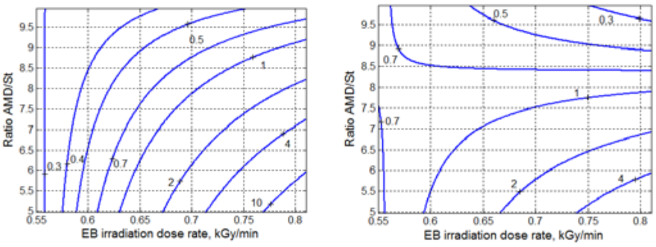
Table 3: *Models for the variance of the product quality characteristics*

	Models for the variance of the product quality characteristics	R
$\ln\left(\tilde{s}_1^2(\vec{x}, w)\right)$	$-4.5364234+0.12292116x_3+0.79212581x_1w$ $+0.43349994x_2x_3-0.47428125x_2w$	0.7397
$\ln\left(\tilde{s}_2^2(\vec{x}, w)\right)$	$-1.5511989-0.34467508x_3+0.63124098x_1w$ $+0.43211686x_2x_3-0.59623974x_3w-0.52122579x_2w$	0.9390
$\ln\left(\tilde{s}_3^2(\vec{x}, w)\right)$	$-3.4516581+1.0785755x_1+1.0385076x_2$ $+1.2911789x_3+1.78367x_1w+1.4572152x_2x_3-$ $0.68503696x_3w-2.2585183x_2w+1.3509026x_1x_2$	0.9818

The models are estimated for coded in the region [-1÷1] values of the process parameters (see eq. (1)). The AMD/St weight ratio and the concentration of AMD, when coded, have equal levels, since St concentration was constant during the experiment. Their influence on the variation of the quality characteristics cannot be distinguished in this case.

One can see that the qualitative factor w (the presence of nAg) has an effect only on the model of the mean of the Huggins' constant y_4, while it takes place in all models of variances in Table 2.

In Fig. 2 contour plots of the mean values of the Huggins' constant $\tilde{\bar{y}}_4(x)$, depending on the variation of EB irradiation dose rates (z_2) and the AMD/St ratios (z_3) for constant EB irradiation doses z_1= 1.02 kGy and in absence or presence of metallic silver nanoparticles nAg are presented.



a) without nAg *b) with nAg*

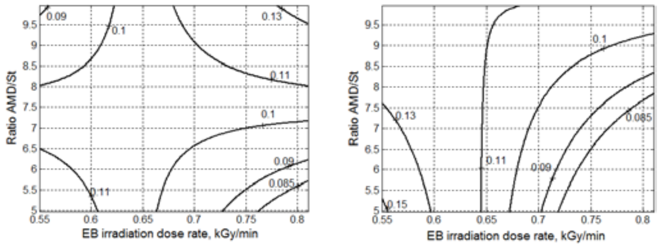
Fig. 2 *Contour plots of the mean values of the Huggins' constant* $\tilde{\bar{y}}_4(x)$ *, depending on the variation of EB irradiation dose rates* (z_2) *and the AMD/St ratios* (z_3) *for constant EB irradiation doses* z_1= *1.02 kGy and a) in absence or b) presence of metallic silver nanoparticles nAg*

It can be seen that at the chosen EB irradiation dose (z_1= 1.02 kGy), the presence of nAg leads to a decrease of the values of the Huggins' constant in the region of higher irradiation dose rates (z_2 > 0.7 kGy/min), while at smaller irradiation dose rates (z_2 < 0.5 kGy/min) the absence of nAg leads to the same effect.

The standard deviations of the product characteristics are calculated by the equation:

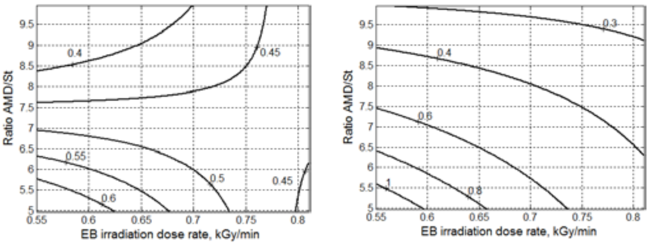
$$(5) \qquad \tilde{s}_i(x) = \sqrt{e^{\ln(\tilde{s}_i^2)}} .$$

Contour plots of the standard deviations $\tilde{s}_i(x)$ of the product characteristics, depending on the EB irradiation dose rate (z_2) and the AMD/St ratios (z_3) for constant EB irradiation dose z_1= 1.02 kGy and in absence or presence of metallic silver nanoparticles nAg are presented in Figs. 3-5.



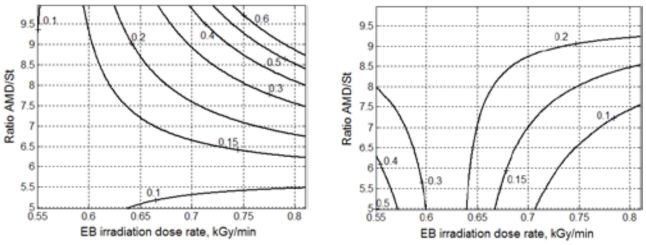
a) without nAg b) with nAg

Fig. 3 *Contour plots of the standard deviation* $\tilde{s}_1(x)$ *of the residual monomer concentration (y_1, %), depending on EB irradiation dose rate (z_2) and the AMD/St ratio (z_3) for EB irradiation dose z_1= 1.02 kGy and a) in absence or b) in presence of metallic silver nanoparticles nAg*



a) without nAg b) with nAg

Fig. 4 *Contour plots of the standard deviation* $\tilde{s}_2(x)$ *of the monomer conversion coefficient (y_2, %), depending on EB irradiation dose rate (z_2) and the AMD/St ratio (z_3) for EB irradiation dose z_1= 1.02 kGy and a) in absence or b) in presence of metallic silver nanoparticles nAg*



a) without nAg b) with nAg

Fig. 5 *Contour plots of the standard deviation* $\tilde{s}_3(x)$ *of the intrinsic viscosity (y_3, dL/g), depending on EB irradiation dose rate (z_2) and the AMD/St ratio (z_3) for EB irradiation dose z_1= 1.02 kGy and a) in absence or b) in presence of metallic silver nanoparticles nAg*

4. Optimization

Multi-criteria graphical optimization unifying requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process, good solubility in water is performed. The set of performance characteristics' requirements is the following:

- $\tilde{y}_1(\vec{x}) < 5\%$ - residual monomer concentration in this region ensures low toxicity;
- $\tilde{y}_2(\vec{x}) > 90\%$ - monomer conversion coefficient values are related to the economic efficiency;
- $\tilde{y}_3(x) > 6$ dL/g - intrinsic viscosity copolymer values are related to the efficiency in the flocculation process
- $0.3 \le \tilde{y}_4(x) \le 1$ (or $-1.20397 \le \ln(\tilde{y}_4(x)) \le 0$) => good solubility in water is achieved with Huggins' constant in this region.

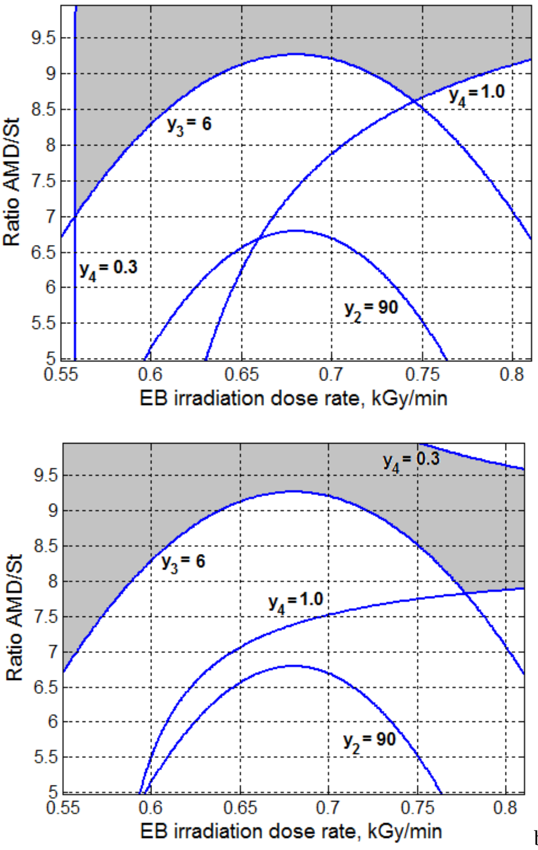


Fig. 6 *Graphical optimization – optimal regions of EB irradiation dose rates (z_2) and the AMD/St ratios (z_3) for EB irradiation dose z_1= 1.02 kGy and a) in absence or b) in presence of metallic silver nanoparticles nAg*

Graphical optimization is conducted in order to find the regions of the process parameters where 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. The optimal regions of the process parameters values EB irradiation dose rate (z_2) and concentration of AMD (z_3) for constant EB irradiation dose z_1= 1.02 kGy and in absence or presence of metallic silver nanoparticles nAg are presented shaded in Fig. 6. The contour lines represent the formulated constraints for the means of y_2 – monomer conversion coefficient (%), y_3 – intrinsic viscosity (dL/g) and y_4 – Huggins' constant. All the values of the mean of the residual monomer concentration y_1 under these conditions are in the required region.

Although the obtained optimal regions for the process parameters differ due to the dependence of the mean of the Huggins' constant y_4 on the qualitative factor w - the presence of nAg, there are many possible process parameter sets, fulfilling the defined requirements. The choice between them can be done by adding supplementary requirements or criteria. Such criteria can be, for example, the minimization of the standard deviations of the product characteristics.

Simultaneous optimization of the standard deviations of the product characteristics is performed for the cases presented in Fig. 6, for EB irradiation dose z_1=1.02 kGy, when the defined requirements of the performance characteristics are fulfilled. The obtained regime conditions with minimal standard deviations are presented in Table 4, in case of absence and presence of metallic silver nanoparticles nAg.

For improving the reproducibility of the obtained results the variations of the product quality characteristics should be minimized.

Table 4: *Optimization of the standard deviations of the product characteristics for EB irradiation dose z_1= 1.02 kGy*

	z_2	z_3	$\tilde{\bar{y}}_1$	$\tilde{\bar{y}}_2$	$\tilde{\bar{y}}_3$	$\tilde{\bar{y}}_4$	$\tilde{s}_1$	$\tilde{s}_2$	$\tilde{s}_3$
With nAg	0.81	9.35	2.42	98.02	8.80	0.36	0.10	0.29	0.21
Without nAg	0.56	9.97	0.81	98.06	9.10	0.30	0.09	0.32	0.11

Table 5: *Pareto-optimization – optimal process parameters, values of the means $\tilde{\bar{y}}_i(x)$ and the standard deviation $\tilde{s}_i(x)$ of the product characteristics*

	№	z_1	z_2	z_3	$\tilde{\bar{y}}_1$	$\tilde{\bar{y}}_2$	$\tilde{\bar{y}}_3$	$\tilde{\bar{y}}_4$	$\tilde{s}_1$	$\tilde{s}_2$	$\tilde{s}_3$
Without nAg	1	1.14	0.55	9.97	0.29	100	10.09	0.39	0.0886	0.3122	0.0933
With nAg	2	0.75	0.81	8.44	3.35	90.01	7.26	0.52	0.0666	0.2512	0.0276
With nAg	3	0.74	0.81	8.75	3.40	90.03	7.37	0.38	0.0683	0.2411	0.0297
With nAg	4	0.76	0.81	8.17	3.28	90.13	7.15	0.69	0.0656	0.2612	0.0266
With nAg	5	0.74	0.81	8.82	3.40	90.13	7.40	0.36	0.0688	0.2395	0.0306
With nAg	6	0.77	0.81	7.96	3.23	90.20	7.07	0.85	0.0647	0.2689	0.0257

This puts additional requirements for the solutions that are obtained through graphical optimization. In order to minimize the variances of the product parameters, multi-criterion optimization is performed and compromise Pareto-optimal solutions are obtained. Some of the estimated results are presented in Table 5. If these compromise solutions are compared two by two, one can note the property of these solutions – some of the obtained optimal values are better but at least one value is worse than that in another compromise solution. In the case of absence of metallic silver nanoparticles nAg only one solution is obtained, while when nAg is present, the choice is between several possible solutions. This compromise choice should be made according additional criteria or requirements or estimated weight coefficients, giving the relative importance of the optimized performance characteristics.

5. Conclusions

Investigation of the modification of starch by grafting acrylamide using electron beam irradiation in order to synthesize water-soluble copolymers having flocculation properties is performed. Models for the mean values and the variances of the investigated product quality characteristics depending on the variations of the process parameters were estimated.

It was shown that the investigated qualitative factor (presence of of metallic silver nanoparticles nAg) during the EB induced grafting had significant effect only on one of the performance quality characteristics - the mean of the Huggins' constant y_4, as well as on the variances of the residual monomer concentration (y_1, %), of the monomer conversion coefficient (y_2, %) and of the intrinsic viscosity (y_3, dL/g). Only the interactions between the qualitative and the quantitative factors are significant.

In order to meet simultaneously the requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process, good solubility in water, the EB irradiation doses (z_1) should be higher than 0.8 kGy.

Parameter optimization in terms of obtaining repeatability of the product parameters and quality improvement by minimization of variations in the quality characteristics is performed. Compromise Pareto-optimal solutions within the investigated experimental region of the process parameters in case of absence and presence of metallic silver nanoparticles nAg are obtained.

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