ROBUST DESIGN AND MULTIPLE CRITERIA OPTIMIZATION OF ELECTRON BEAM GRAFTING OF CORN STARCH

Assoc. Prof. M.Sc. Eng. Koleva E. PhD.[1,2], M.Sc. Eng. Koleva L. [2], M.Sc. Eng. Nemțanu M.R. PhD.[3], M.Sc. Brașoveanu M. PhD.[3]
Institute of Electronics, Bulgarian Academy of Sciences, Bulgaria [1]
University of Chemical Technology and Metallurgy, Bulgaria [2]
National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, Romania [3]

eligeorg@abv.bg

Abstract: *Electron beam (EB) irradiation has the ability to modify polymer substrates by process of graft copolymerization to synthesize water-soluble copolymers having flocculating potential. Models - depicting the dependencies of the described quality characteristics (their means and variances) from process parameters - are estimated by implementation of the robust engineering methodology for quality improvement. Multiple criteria optimization based on the desirability function approach, involving requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process, good solubility in water, bias, robustness, quality of prediction and the relative importance of responses, is presented.*

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

1. Introduction

The model-based robust approach for improving the quality of the process [1, 2] can be successfully applied to different industrial processes. For each of the quality performance characteristics, using their regression models, two other models are estimated - for their mean values and variances. The quality improvement is performed using some overall criterion or simply by the performance characteristics variances minimization, while keeping their mean values close to their target values. The Robust Parameter Design (RPD) is an issue of numerous papers in the literature since 1990 [3, 4], but there are much less of them in the area of application of RPD [1, 5] for multiple responses. Some of these articles consider the multi-response case, when replicated observations are available [6], while others are focused on formulation of appropriate optimization criteria. A systematic procedure implementing response surface methodology and desirability function for optimization of multiple response surface (MRS) problems that accommodates all of bias, robustness and quality of prediction besides relative importance of responses in a single framework is developed in [7] and compared with other multiple response techniques.

Electron beam (EB) grafting is a process of modification of polymer substrates implementing radiation-induced graft copolymerization in order to yield water-soluble copolymers having flocculation abilities [8]. The irradiation was performed with linear electron accelerator of mean energy of 5.5 MeV, and the influence of the variation of the following parameters: acrylamide/starch (AMD/St) weight ratio, electron beam irradiation dose and dose rate was investigated. The characterization of graft copolymers was carried out by monomer conversion coefficient, %; residual monomer concentration, %; intrinsic viscosity, dL/g; and Huggins' constant.

In this paper the robust parameter design methodology is applied for estimation of models, describing the dependencies of the means and the variances of the investigated quality characteristics. Multiple criteria optimization based on the desirability function approach, involving requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process, good solubility in water, bias, robustness, quality of prediction and the relative importance of responses, is presented.

2. Robust parameter design

EB modification of polymer substrates through radiation-induced graft copolymerization is generally 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. [9, 10].

The synthesized graft copolymers were characterized [8] 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: 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%.

The conducted experimental design consisted in 20 experimental process parameter sets [8]. For each set of the process parameters three replicated measurements were used for estimation of the means and the variances of the quality characteristics of the graft copolymers. 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 [1]:

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

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

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. 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 response surfaces models for the mean and standard deviation of the quality characteristic are estimated and presented in Table 1 for coded values of the process parameters in the region [-1÷1]. The coding of the process parameter values is done, 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 variation region.

Table 1: *Models for the means and variances of the product quality characteristics*

Parameter	Models	R^2	w'
$\tilde{\bar{y}}_1(\vec{x})$	$1.8416958 - 1.4711672x_1 + 0.39465799x_2 + 0.76523861x_1^2 - 1.4618933x_1x_2$	0.8172	0.1652
$\tilde{\bar{y}}_2(\vec{x})$	$89.612983 + 6.1859389x_1 + 2.921934x_3 + 5.2145372x_2^2 - 2.1297402x_1x_3$	0.7415	0.1499
$\tilde{\bar{y}}_3(\vec{x})$	$4.2786392 - 0.95051438x_2 + 2.2118238x_3 + 1.2412826x_2^2 - 7.0991376x_1^2x_2 + 0.721455x_2x_3 - 1.2935142x_1^2x_3$	0.7921	0.1602
$\ln\left(\tilde{\bar{y}}_4(\vec{x})\right)$	$0.86268086 + 1.5188592x_2 - 1.6109201x_3 + 0.87526587x_1x_3 - 1.6469938x_2x_3 + 1.4461714x_1^2x_3$	0.6191	0.1252
$\ln\left(\tilde{s}_1^2(\vec{x})\right)$	$-3.0237265 - 0.60469566x_2 - 1.0612263x_3 - 4.3482641x_1^2 - 4.2402799x_2^2 + 5.604919x_1x_2 - 2.2657548x_2x_3$	0.7179	0.1451
$\ln\left(\tilde{s}_2^2(\vec{x})\right)$	$0.09316988 - 1.0210062x_2 - 1.7785371x_3 - 4.6387008x_1^2 - 4.9999832x_2^2 + 6.047145x_1x_2 - 2.242544x_2x_3$	0.7550	0.1527
$\ln\left(\tilde{s}_3^2(\vec{x})\right)$	$-2.5452688 - 0.67825221x_3 - 2.7034767x_1^2 - 2.1048188x_2^2 + 3.2229606x_1x_2 + 0.88934159x_2^2x_3$	0.5028	0.1017

Table 2: *Specification regions and target values for the mean values and the standard deviation of response variables*

Bounds	$\tilde{\bar{y}}_1(\vec{x})$	$\tilde{\bar{y}}_2(\vec{x})$	$\tilde{\bar{y}}_3(\vec{x})$	$\tilde{\bar{y}}_4(\vec{x})$	$\tilde{s}_1^2(\vec{x})$	$\tilde{s}_2^2(\vec{x})$	$\tilde{s}_3^2(\vec{x})$
lb	0	90	6	0.3	0	0	0
ub	5	100	9	1	0.2	1.8	0.6
τ	smaller	larger	larger	0.6	smaller	smaller	smaller

In Table 1 the estimated response model's quality of prediction is measured by the squared multiple correlation coefficient R^2.

3. Desirability function approach

An approach for optimization of multiple responses simultaneously is combining them into a single function. The desirability technique analysis is presented by Derringer and Suich [11]. This approach includes systematic transform of the quality characteristic $\tilde{\bar{y}}_j(\vec{x})$ into individual desirability function $d_j(\vec{x})$, calculated depending on the optimization tasks:

- cases with defined target values:

$$d_j(\vec{x}) = \begin{cases} \dfrac{\tilde{\bar{y}}_j(\vec{x}) - lb_j}{\tau_j - lb_j}; & lb_j \le \tilde{\bar{y}}_j(\vec{x}) \le \tau_j \\ \dfrac{\tilde{\bar{y}}_j(\vec{x}) - ub_j}{\tau_j - ub_j}; & \tau_j < \tilde{\bar{y}}_j(\vec{x}) \le ub_j \\ 0; \quad \tilde{\bar{y}}_j(\vec{x}) < lb_j \;\; or \;\; \tilde{\bar{y}}_j(\vec{x}) > ub_j \end{cases}$$

- cases the larger the better:

$$d_j(\vec{x}) = \begin{cases} 0; & \tilde{\bar{y}}_j(\vec{x}) \le lb_j \\ \dfrac{\tilde{\bar{y}}_j(\vec{x}) - lb_j}{ub_j - lb_j}; & lb_j < \tilde{\bar{y}}_j(\vec{x}) \le ub_j \\ 1; & \tilde{\bar{y}}_j(\vec{x}) \ge ub_j \end{cases}$$

- cases the smaller the better:

$$d_j(\vec{x}) = \begin{cases} 1; & \tilde{\bar{y}}_j(\vec{x}) \le lb_j \\ \dfrac{ub_j - \tilde{\bar{y}}_j(\vec{x})}{ub_j - lb_j}; & lb_j < \tilde{\bar{y}}_j(\vec{x}) < ub_j \\ 0; & \tilde{\bar{y}}_j(\vec{x}) \ge ub_j \end{cases}$$

In this way the individual optimization desirability functions of the mean values of each response (d_{oj}) scaled in the region between 0 and 1 can be calculated, together with the individual robustness desirability functions (d_{rj}) [7]. Here lb_j and ub_j are the minimal and the maximal acceptable levels for the mean responses and the standard deviations, τ_j is the target or the desirable value of the j-th quality characteristic (Table 2). The robustness here refers to the low sensitivity of the quality characteristics to the noise factors. This can be achieved by a proper selection of values for the controllable process parameters, and can lead to a reduction for variance of the response in production conditions.

For the consideration of robustness in multiple response optimization problems, the following measures are defined [7]:

- Optimization desirability function D_{opt}, defined as the weighted geometric average of the individual optimization desirability functions:

$$D_{opt}(\vec{x}) = d_{o1}(\vec{x})^{w_{1\mu}} \; d_{o2}(\vec{x})^{w_{2\mu}} \ldots d_{om}(\vec{x})^{w_{m\mu}};$$

- Robustness desirability function D_{rob}, defined as the weighted geometric average of the individual robustness desirability functions:

$$D_{rob}(\vec{x}) = d_{r1}(\vec{x})^{w_{1\sigma}} \; d_{r2}(\vec{x})^{w_{2\sigma}} \ldots d_{rm}(\vec{x})^{w_{m\sigma}};$$

A multi-response optimization problem requires an overall optimization, i.e. simultaneous satisfaction with respect to the mean and standard deviation of all of the quality characteristics by using a combined desirability function between optimization and robustness. The overall desirability function can be defined as follows:

$$D_{overall}(\vec{x}) = D_{opt}(\vec{x})^{w_{opt}} \; D_{rob}(\vec{x})^{w_{rob}}.$$

In order to formulate weights for a given magnitude of predictive capability, a relationship between the weights and a predictive capability index (squared multiple correlation coefficient, R^2) is needed (see Table 1):

$$w'_j = \frac{R_j^2}{\sum R_j^2}.$$

4. Optimization results and discussion

The overall desirability function in the considered EB induced synthesis of graft copolymers is calculated by:

$$D_{overall}(\vec{x}) = d_{o1}(\vec{x})^{w_{1\mu}} \; d_{o2}(\vec{x})^{w_{2\mu}} \; d_{o3}(\vec{x})^{w_{3\mu}} \; d_{o4}(\vec{x})^{w_{4\mu}} \; d_{r1}(\vec{x})^{w_{1\sigma}} \; d_{r2}(\vec{x})^{w_{2\sigma}} \; d_{r3}(\vec{x})^{w_{3\sigma}}$$

The acceptable specification regions and the type of the case for the individual desirability functions (target value, the larger the better, the smaller the better) are presented in Table 2.

Desirability functions are formulated for several cases:

Case 1: Without consideration of the models predictive capabilities, the weights w_j are their optimization and robustness geometric average degrees:

$w_{o1} = w_{o2} = w_{o3} = w_{o4} = 1/4$ and $w_{r1} = w_{r2} = w_{r3} = 1/3$; $w_{opt} = w_{rob} = ½$.

Case 2: With consideration of the models predictive capabilities, the weights w_j' are calculated in Table 1.

Case 3: Without consideration of the models predictive capabilities the weights w_j are calculated, considering the mean and variances as equivalent functions by their geometric average degrees:

$w_{o1} = w_{o2} = w_{o3} = w_{o4} = w_{r1} = w_{r2} = w_{r3} = 1/7$;

Case 4: Without consideration of the models predictive capabilities, the weights w_j are equal [7]:

$w_{o1} = w_{o2} = w_{o3} = w_{o4} = w_{r1} = w_{r2} = w_{r3} = 1$, $w_{opt} = w_{rob} = 1$.

Table 3: *Optimal individual and overall desirability functions*

Case	z_1	z_2	z_3	d_{o1}	d_{o2}	d_{o3}	d_{o4}	d_{r1}	d_{r2}	d_{r3}	$D_{overall}$
1	1.3800	0.45	7.7108	0.6016	1	1	0.9990	0.9964	0.9988	0.9843	0.9351
2	1.3560	0.45	7.7359	0.6165	0.9826	1	0.9980	0.9947	0.9982	0.9802	0.9176
3	1.3760	0.45	7.7108	0.6042	1	1	0.9960	0.9962	0.9988	0.9836	0.9271
4	1.3760	0.45	7.7108	0.6042	1	1	0.9960	0.9962	0.9988	0.9836	0.5889

Table 4: *Optimal values of the means and variances of the product quality characteristics*

Case	$\tilde{y}_1(\vec{x})$	$\tilde{y}_2(\vec{x})$	$\tilde{y}_3(\vec{x})$	$\tilde{y}_4(\vec{x})$	$\tilde{s}_1^2(\vec{x})$	$\tilde{s}_2^2(\vec{x})$	$\tilde{s}_3^2(\vec{x})$
1	1.9920	100.00	21.9203	0.6004	0.00072	0.0024	0.0094
2	1.9173	99.83	20.5134	0.6008	0.0011	0.0032	0.0119
3	1.9792	100.00	21.6812	0.5988	0.00077	0.0022	0.0098
4	1.9792	100.00	21.6812	0.5988	0.00077	0.0022	0.0098

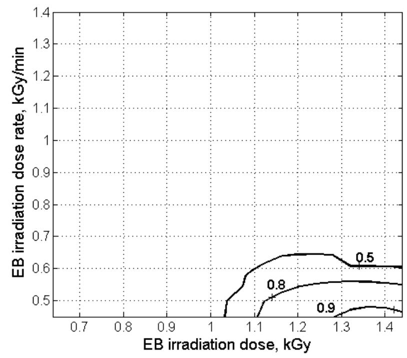

Fig. 1 *Overall desirability function as a function of the process parameters EB irradiation dose (z_1) and the EB irradiation dose rate (z_2) at (AMD/St) weight ratio $z_3 = 7.7108$ – case 3.*

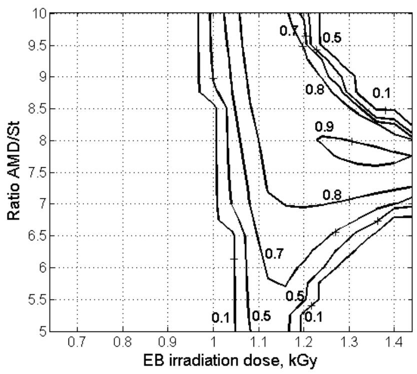

Fig. 2 *Overall desirability functions as a function of the process parameters EB irradiation dose (z_1) and (AMD/St) weight ratio (z_3) at EB irradiation dose rate $z_2 = 0.45$ kGy/min – case 3.*

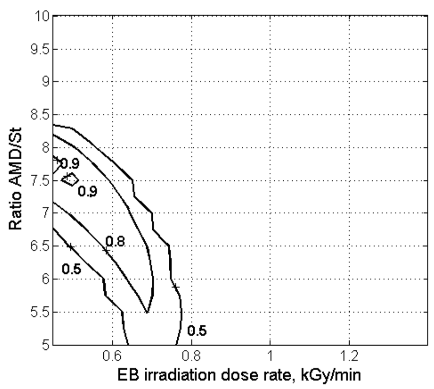

Fig. 3 *Overall desirability functions, as a function of the process parameters EB irradiation dose rate (z_2) and (AMD/St) weight ratio (z_3) at EB irradiation dose $z_1 = 1.38$ kGy – case 3.*

In Table 3 the individual (d_i) and overall desirability functions $D_{overall}$ are presented for the four considered cases, together with the obtained optimal process parameter values. The corresponding values of the estimated means and variances of the performance characteristics are shown in Table 4. It can be seen that there are no considerable differences in the obtained optimal process parameters and the means and variances of the quality characteristics, despite the differences in the calculated optimal overall desirability function values.

Fig. 1 – Fig. 3 display the contour plots of the overall desirability function as a function of different combinations of the process parameters: EB irradiation dose (z_1), the EB irradiation dose rate (z_2) and (AMD/St) weight ratio (z_3) for case 3.

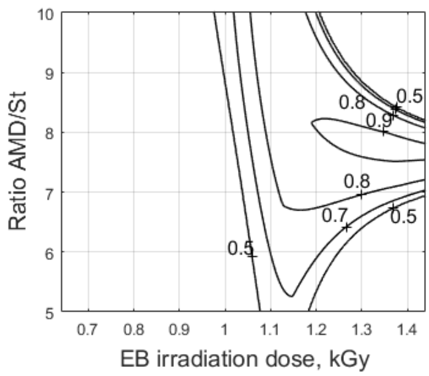

Fig. 4 *Overall desirability functions as a function of the process parameters EB irradiation dose (z_1) and (AMD/St) weight ratio (z_3) at EB irradiation dose rate $z_2 = 0.45$ kGy/min – case 1.*

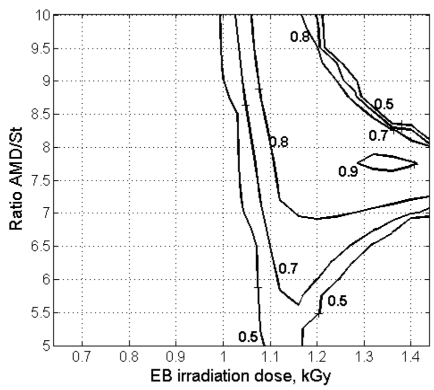

Fig. 5 *Overall desirability functions as a function of the process parameters EB irradiation dose (z_1) and (AMD/St) weight ratio (z_3) at EB irradiation dose rate $z_2 = 0.45$ kGy/min – case 2.*

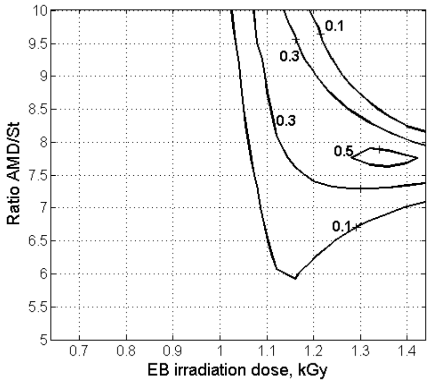

***Fig. 6** Overall desirability functions as a function of the process parameters EB irradiation dose (z_1) and (AMD/St) weight ratio (z_3) at EB irradiation dose rate z_2 = 0.45 kGy/min – case 4.*

Fig. 4 – Fig. 6 represent the contour plots of the overall desirability function as a function of the process parameters EB irradiation dose (z_1) and (AMD/St) weight ratio (z_3) at a constant value of the EB irradiation dose rate z_2 = 0.45 kGy/min for case 1, case 2 and case 4.

5. Conclusions

A multiple response optimization approach, based on overall desirability function, which considers the robustness as well as optimization of the process parameters at production conditions, is considered. Robustness and optimization desirability functions are calculated by evaluation of individual desirability functions of the means and variances of the product quality characteristics. The applied approach gives possibility to use weights for adjustment of the desirability functions according to the quality of model prediction and in favor of robustness or multiple response optimization.

Electron beam induced graft copolymerization used to synthesize water-soluble copolymers having flocculation abilities is investigated. The parameter optimization is performed in direction of fulfilling requirements for economic efficiency, assurance of low toxicity, high copolymer efficiency in flocculation process, good solubility in water, bias, robustness, quality of prediction and the relative importance of the quality characteristics.

Acknowledgements

This research was conducted under bilateral joint project between the Institute of Electronics at Bulgarian Academy of Sciences and the National Institute for Lasers, Plasma and Radiation Physics at the Romanian Academy. This work was also partially supported by a grant of the Romanian National Authority for Scientific Research, CNDI–UEFISCDI, project number 64/2012.

References

[1]. Vuchkov I. N, Boyadjieva L. N. Quality improvement with design of experiments, The Netherlands, Kluwer Academic Publishers, 2001.

[2]. Koleva E., I. Vuchkov, Model-based approach for quality improvement of EBW applications in mass production, Vacuum 77, 2005, pp. 423-428.

[3]. Box G., S. Jones. Designing Products that are robust to the Environment. Quality and Productivity Report 56 Univ. of Wisconsin, CPQI, 1990.

[4]. Vining G. G., R. H. Myers. Combining Taguchi and Response Surface Philosophies; A Dual-Response Approach. Journal of Quality Technology, 22, 1990, pp. 38-45.

[5]. Myers R. H., D. C. Montgomery, G. G. Vining, C. M. Borror, S. M. Kowalski. Response Surface Methodology: A Retrospective and Literature Survey. Journal of Quality Technology, 36,1, 2004, pp. 53-77.

[6]. Chiao C., M. Hamada. Analyzing Experiments with Correlated Multiple Responses. Journal of Quality Technology, 33, 2001, pp.451-465.

[7]. Najafi S., A. Salmasnia, R. B. Kazemzadeh. Optimization of Robust Design for Multiple Response Problem. Australian Journal of Basic and Applied Sciences, 5(9), 2011, pp. 1566-1577

[8]. Koleva E., L. Koleva, V. Tzotchev, M. Nemtanu, M. Brașoveanu, K. Vutova. Robust engineering approach for optimization of electron beam grafting of corn starch. Science, Engineering & Education, v.1(1), 2016, pp. 89-96.

[9]. Stephen C. Lapin, Modification of Polymer Substrates using Electron Beam Induced Graft Copolymerization, UV+EB Technology • Issue 1, 2015, pp. 44-49.

[10]. Nasef M.M., Radiation-grafted copolymers for separation and purification purposes: Status, challenges and future directions, Progress in Polymer Science, 37, 2012, pp. 1597– 1656.

[11]. Derringer, G., R. Suich, Simultaneous optimization of several response variables. Journal of Quality Technology, 12, 1980, pp. 214-219.