Multicriterial optimization strategies for electron beam grafting of corn starch

Lilyana Koleva[1*], Zlatina Petrova[1], Elena Koleva[1,2**], Mirela Braşoveanu[3], Monica R. Nemţanu[3], Georgi Kolev[1]
University of Chemical Technology and Metallurgy, Bulgaria[1]
Institute of Electronics, Bulgarian Academy of Sciences, Bulgaria[2]
National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, Romania[3]
sura@uctm.edu[*], eligeorg@uctm.edu[**]

Abstract: *Grafting is the most effective way of modifying and regulating the properties of natural polysaccharides for the production of highly efficient graft copolymers, which have applications as flocculating agents for the treatment of different wastewaters. An experimental investigation connected with the modification of starch by grafting acrylamide with the application of electron beam irradiation is performed. In this paper the implementation of different multi-criteria optimization strategies, solving the problem with the choice between several compromise Pareto-optimal solutions are presented and compared for the process of electron beam grafting of corn starch. The compromise Pareto-optimal solutions are obtained by implementation of genetic algorithm and a set of requirements for the desired reference direction (minimum or maximum) and the constraints of the investigated quality characteristics and their variances under production conditions, which ensure the fulfilment of several goals – economic efficiency, assurance of low toxicity and high copolymer efficiency in flocculation process.*

***Keywords**: GRAFT COPOLYMERIZATION, ELECTRON BEAM IRRADIATION, WATER-SOLUBLE COPOLYMERS, STARCH, ACRYLAMIDE, FLOCCULATION PROPERTIES, MULTI-CRITERIA OPTIMIZATION, DECISION MAKING*

1. Introduction

Electron beam (EB) grafting is a process that is able to modify the polymer substrates by implementing radiation-induced graft copolymerization in order to yield water-soluble copolymers for flocculation processes [1-3]. It is widely 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. [4].

Robust or 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 [5, 6]. The observations in this case are called heteroscedastic (variance varies with the factor levels). This is the situation, when the analyzed data are obtained under production conditions. In order to estimate the variances of the quality characteristics there are several approaches. In the current investigation the models for the mean values and the variances of the quality characteristics of the product, are estimated by performing repeated observations. Multicriterial parameter optimization in terms of obtaining repeatability of the product parameters and quality improvement at the same time is performed by minimization of variations of the quality characteristics and fulfilling the technological requirements for these characteristics in production conditions simultaneously.

In this paper the implementation of different multi-criteria optimization strategies, solving the problem with the choice between several compromise Pareto-optimal solutions are presented and compared for the process of electron beam grafting of corn starch. The compromise Pareto-optimal solutions are obtained by implementation of genetic algorithm and a set of requirements for the desired reference goals (minimum or maximum) and the constraints of the investigated quality characteristics and their variances under production conditions, which ensure the fulfilment of several goals – economic efficiency, assurance of low toxicity and high copolymer efficiency in flocculation process.

2. Experimental conditions

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 solutions containing starch and monomer; (2) irradiation of solutions by electron beam.

Step 1: Starch aqueous solutions were prepared by dissolving corn starch in distilled water. Acrylamide was added to starch aqueous solution with further stirring, resulting in various acrylamide/starch (AMD/St weight ratios) homogenous aqueous solutions.

Step 2: Therefore, homogenous aqueous solutions prepared in previous step were exposed to electron beam irradiation. The irradiations were carried out at ambient temperature and pressure by using linear electron accelerators of mean energy of 6.23 MeV with different irradiation doses and dose rates.

The synthesized graft copolymers were characterized by residual monomer concentration, Mr, %; monomer conversion coefficient, Conv., % and intrinsic viscosity, η, dL/g. The variation regions 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 AMD/St weight ratio (z_3) – 2 ÷ 11.

The dependencies of the mean values and the variances of the product quality characteristics: residual monomer concentration - y_1 (%), monomer conversion coefficient - y_2 (%) and apparent viscosity - y_3 (mPa·s) on the variation of the process parameters: electron beam irradiation dose, electron beam irradiation dose rate and AMD/St weight ratio are estimated.

The estimated mean value $\tilde{\bar{y}}_{ui}$ and $\tilde{s}^2_{ui}$ variance can be considered as two responses at the design points, and ordinary least squares method can be used to fit the models of the mean value and the variance for the quality characteristic [6, 7]:

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

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

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 obtained models for the mean values $\tilde{\bar{y}}_j$ and the variance $\tilde{s}^2_j$ for each of the considered *j = 1, 2, ..., m* quality characteristics are presented and discussed in [4].

3. Multicriterial optimization

In the case of EB induced grafting of corn starch multi-criteria optimization unifying requirements for economic efficiency, assurance of low toxicity and high copolymer efficiency in flocculation process, as well as the repeatability of the obtained results is performed.

The set of defined technological requirements is the following:

- residual monomer concentration: $\tilde{\bar{y}}_1 < 5\%$ → assurance of low toxicity;
- monomer conversion coefficient: $\tilde{\bar{y}}_2 > 90\%$ → economic efficiency;

- apparent viscosity: $\tilde{\bar{y}}_3$ > 3 mPa·s → copolymer efficiency in flocculation processes.

For the satisfaction of all pre-defined requirements simultaneously the optimization task is set as follows:

$$\begin{cases} \tilde{\bar{y}}_1 \rightarrow \text{minimum},\ \tilde{\bar{y}}_1 < 5\%; \\ \tilde{\bar{y}}_2 \rightarrow \text{maximum},\ \tilde{\bar{y}}_2 > 90\%; \\ \tilde{\bar{y}}_3 \rightarrow \text{maximum},\ \tilde{\bar{y}}_3 > 3 \text{ mPa·s}; \\ \tilde{\sigma}_1^2 \rightarrow \text{maximum}; \\ \tilde{\sigma}_2^2 \rightarrow \text{maximum}; \\ \tilde{\sigma}_3^2 \rightarrow \text{maximum}. \end{cases}$$

The implemented for solving the multicriterial optimization task models for the mean values $\tilde{\bar{y}}_j$ and the variance $\tilde{s}_j^2$ for each of the considered $j = 1, 2, ..., m$ quality characteristics are presented in [4].

Pareto-optimal compromise solutions are obtained (50 solutions) by applying genetic algorithm and the statistical software QstatLab [8]. Each solution makes some compromise toward some or all quality criteria to a certain extend at the same time. If we compare randomly chosen two Pareto-optimal solutions some of the quality characteristics will have better values, but at least one will be worse. In order to choose one solution from all we need additional analysis. This choice can be done by considering additional criteria (not included in the optimization task), by evaluation based on expert opinion or by definition of an overall function like loss function, desirability function, etc.

In the present work, methods based on reference point strategies optimization are implemented for solving this task. They are compered by estimation of the overall relative error for all best solutions that are obtained.

Optimistic strategy

The *optimistic strategy* is based on the method of the function of losses. This optimization approach is called "optimistic" because the best possible values q_j^{Opt} (j = 1, 2, 3, …, m) are assigned to the reference (uncompromised) values of the quality characteristic $q_i(x)$. The reference values depend on the required minimum or maximum value for each of the quality characteristics. They are determined from the obtained Pareto-optimal solutions or in this case the differences between the best values and the optimistic reference values are minimized. The generalized function of losses $F^{Opt}(x)$ that has to be minimized is [9]:

$$F^{Opt}(x) = \frac{1}{m}\sum_{j=1}^{m}\left(\frac{q_j^{Opt} - q_j(x)}{\Delta_j}\right)^2, \tag{4}$$

$$\Delta_j = q_{max,j} - q_{min,j}, \tag{5}$$

where $q_j(x)$ is the value for the j-th quality characteristic obtained at a given Pareto-optimal solution, $q_{max,j}$ and $q_{min,j}$ are the maximal and minimal values of each characteristic from all obtained 50 Pareto-optimal solutions and are presented in Table 1, together with calculated value for Δ_j. Each reference value q_j^{Opt} is obtained usually for different set of optimal process parameters z_i and cannot be obtained simultaneously.

Table 1: *Goals, reference values and the maximal and minimal characteristic values $q_j(x)$.*

Param.	$\tilde{\bar{y}}_1$ %	$\tilde{\sigma}_1^2$	$\tilde{\bar{y}}_2$ %	$\tilde{\sigma}_2^2$	$\tilde{\bar{y}}_3$ mPa·s	$\tilde{\sigma}_3^2$
Goal	min↓	min↓	max↑	min↓	max↑	min↓
q_j^{Opt}	0.003	0.008	98.689	0.163	5.564	0.163
q_j^{Pes}	4.996	0.136	90.874	3.602	3.359	0.617
$q_{j,max}$	4.996	0.136	98.689	3.602	5.534	0.617
$q_{j,min}$	0.003	0.008	90.874	0.163	3.359	0.163
Δ_j	4.996	0.128	7.815	3.439	2.175	0.454

The best ten optimal solutions obtained by implementation of the Optimistic method are presented in Table 2. They have smallest values of the function of losses $F^{Opt}(x)$ from the arranged in ascending order results from all obtained 50 Pareto-optimal solutions (their numbers are kept in the table). It can be seen that the best result, obtained for $F^{Opt}(x)$ = 0.128 is obtained for Pareto-optimal solution № 10, as well as the optimal values of the process parameters (z_i) at which it can be obtained in production conditions.

Table 2: *Optimal solution by Optimistic strategy.*

№	F^{Opt}	z_1	z_2	z_3	$\tilde{y}_1$	$\tilde{\sigma}_1^2$	$\tilde{y}_2$	$\tilde{\sigma}_1^2$	$\tilde{y}_3$	$\tilde{\sigma}_1^2$
10	**0.128**	**4.7**	**0.6**	**3.9**	**1.4**	**0.06**	**98.2**	**0.95**	**4.09**	**0.19**
9	0.129	4.8	0.6	3.8	1.0	0.07	96.6	0.82	4.39	0.19
43	0.130	4.7	0.6	4.0	1.3	0.06	98.3	0.95	4.01	0.18
28	0.144	5.1	1.1	2.0	3.9	0.02	97.1	0.19	4.99	0.34
22	0.149	5.1	1.1	2.3	3.6	0.03	95.4	0.23	4.78	0.27
39	0.153	4.9	0.6	3.9	1.9	0.07	95.6	0.90	4.22	0.18
2	0.154	5.0	1.0	2.7	3.3	0.02	94.7	0.28	4.61	0.22
30	0.156	5.0	1.1	3.4	3.4	0.02	94.9	0.24	4.61	0.25
6	0.172	4.8	0.6	4.2	1.6	0.06	95.4	1.00	3.95	0.16
18	0.176	5.2	1.1	2.0	4.2	0.03	95.4	0.19	5.15	0.32

Pessimistic strategy

The pessimistic strategy is based on the function of usefulness method. In this strategy the worst possible (among the obtained Pareto-optimal solutions) or the "pessimistic" values q_j^{Pes} (j = 1, 2, 3, …, m) are assigned as reference values of the quality characteristic $q_i(x)$, again depending on the required minimum or maximum value for each quality characteristic from Pareto-optimal solutions. The function $F^{Pes}(x)$ that has to be maximized is [9]:

$$F^{Pes}(x) = \frac{1}{m}\sum_{j=1}^{m}\left(\frac{q_j(x) - q_j^{Pes}}{\Delta_j}\right)^2 \tag{6}$$

The best ten optimal solutions obtained by implementation of the Pessimistic strategy are presented in Table 3. They have largest values of the function of usefulness $F^{Pes}(x)$ from the arranged in descending order results from all obtained 50 Pareto-optimal solutions (their numbers are kept in the table).

Table 3: *Optimal solution by Pessimistic strategy.*

№	F^{Pes}	z_1	z_2	z_3	$\tilde{y}_1$	$\tilde{\sigma}_1^2$	$\tilde{y}_2$	$\tilde{\sigma}_1^2$	$\tilde{y}_3$	$\tilde{\sigma}_1^2$
43	**0.571**	**4.7**	**0.6**	**4.0**	**1.3**	**0.06**	**98.3**	**0.95**	**4.01**	**0.18**
28	0.560	5.1	1.1	2.0	3.9	0.02	97.1	0.19	4.99	0.34
10	0.559	4.7	0.6	3.9	1.4	0.06	98.2	0.95	4.09	0.18
18	0.526	5.2	1.1	2.0	4.2	0.03	95.4	0.19	5.15	0.32
22	0.522	5.1	1.1	2.3	3.6	0.03	95.4	0.23	4.78	0.27
42	0.522	4.9	0.5	3.2	2.6	0.12	98.0	0.68	5.29	0.28
23	0.518	5.3	1.0	2.4	4.7	0.05	91.2	0.21	5.47	0.24
2	0.515	5.0	1.0	2.7	3.3	0.02	94.7	0.28	4.61	0.22
1	0.514	5.4	1.1	2.0	4.9	0.03	91.4	0.16	5.53	0.32
49	0. 514	5.2	1.0	2.4	4.5	0.04	92.5	0.21	5.36	0.25

Bracketing approach for multi-criteria optimization

The bracketing multi-criteria optimization strategy combines the optimistic and pessimistic approaches. Here the optimal compromise solution is searched by simultaneously minimizing the under-achievement to the best values (reference values) q_j^{Opt} and maximizing the over-achievement over the required (worst) values q_j^{Pes} [9].

The optimization function that has to be maximized in this case is:

$$F^{Br}(x) = \frac{1}{m}\sum_{j=1}^{m}\left(\frac{q_j(x) - q_j^{Pes}}{\Delta_j}\right)^2 - \frac{1}{m}\sum_{j=1}^{m}\left(\frac{q_j^{Opt} - q_j(x)}{\Delta_j}\right)^2 \tag{7}$$

The best ten optimal solutions obtained by implementation of the Bracketing strategy are presented in Table 4. They have largest values of the function of usefulness $F^{Br}(x)$ from the arranged in descending order results from all obtained 50 Pareto-optimal solutions (their numbers are kept in the table).

It can be seen, that the best result in this case coincides with the best result obtained when the Pessimistic strategy is applied (Pareto-optimal solution №43).

Table 4: *Optimal solution by Bracketing approach.*

№	F^{Br}	z_1	z_2	z_3	$\tilde{y}_1$	σ_1^2	$\tilde{y}_2$	σ_2^2	$\tilde{y}_3$	σ_3^2
43	**2.777**	**4.7**	**0.6**	**4.0**	**1.3**	**0.06**	**98.3**	**0.95**	**4.01**	**0.18**
10	2.750	4.7	0.6	3.9	1.4	0.06	98.2	0.95	4.09	0.18
42	2.647	4.9	0.5	3.2	2.6	0.12	98.0	0.68	5.29	0.28
9	2.361	4.8	0.6	3.8	2.0	0.07	96.6	0.82	4.39	0.19
28	2.359	5.1	1.1	2.0	3.9	0.02	97.1	0.19	4.99	0.34
37	2.291	5.0	0.7	3.2	3.1	0.10	95.9	0.54	5.31	0.25
22	2.099	5.1	1.1	2.3	3.6	0.03	95.4	0.23	4.78	0.27
26	2.069	5.1	0.6	3.2	3.2	0.11	95.4	0.57	5.42	0.26
2	2.049	5.0	1.0	2.7	3.3	0.02	94.7	0.28	4.61	0.22
14	2.026	4.7	0.5	4.6	0.6	0.08	98.0	1.74	3.73	0.19

In order to compare the implemented optimization strategies: *Optimistic and Pessimistic/Bracketing approaches,* the absolute errors are calculated for the best chosen compromise solutions by:

$$\delta_{aj} = |q_{j,opt}(x) - q_j{}^*(x)|$$

where $q_j{}^*(x)$ is the best value from all Pareto-optimal solutions for the *j-th* quality characteristic, coinciding with the reference point of the optimistic approach. The relative error in this case can be calculated by:

$$\delta_{rj} = \frac{\delta_{aj}}{\Delta_j} * 100\%$$

The calculated results are presented in Table 5.

Table 5: *Comparison of implemented optimization strategies.*

№	$\tilde{y}_1$	σ_1^2	$\tilde{y}_2$	σ_2^2	$\tilde{y}_3$	σ_3^2
q_j^*	0.003	0.008	98.689	0.163	5.564	0.163
Δ_j	4.996	0.128	7.815	3.439	2.175	0.454
$\boldsymbol{q_{j,opt}}$, *Opt*	1.4	**0.06**	98.2	**0.95**	**4.09**	0.19
$\boldsymbol{\delta_{aj}}$	1.397	0.052	0.489	0.787	1.474	0.027
$\boldsymbol{\delta_{rj}}$**,%**	27.96	40.63	6.26	22.88	67.77	5.95
$\boldsymbol{q_{j,opt}}$, *Pes/Br*	**1.3**	**0.06**	**98.3**	**0.95**	4.01	**0.18**
$\boldsymbol{\delta_{aj}}$	1.297	0.052	0.389	0.787	1.554	0.017
$\boldsymbol{\delta_{rj}}$**,%**	25.96	40.63	4.98	22.88	71.45	3.74

From Table 5 can be seen that the implemented strategies give very close results. The only quality parameter, which is a little better for the solution, given by the Optimistic approach, is the result for the apparent viscosity $\tilde{y}_3$, responsible for copolymer efficiency in flocculation processes. All the other criteria values are better or equal for the case of implementation of the pessimistic or bracketing strategies.

4. Conclusions

In this paper, three multicriteria optimization approaches were applies and compared, aiming to simultaneously fulfil the technological requirements for economic efficiency, assurance of low toxicity and high copolymer efficiency in flocculation process, as well as the repeatability of the obtained results.

The implementation of multi-criteria optimization strategies, by definition of one overall optimization criterion, solves the problem with the choice between several compromise Pareto-optimal solutions. Optimistic, pessimistic and bracketing multi-criteria optimization strategies are implemented and compared for the process of electron beam grafting of corn starch.

The comparison of obtained best working regimes of the applied multi-criteria optimization strategies give very close results. The biggest compromise is done with the apparent viscosity $\tilde{y}_3$, responsible for copolymer efficiency in flocculation processes, which is around 70% from the region of the optimal values of obtained Pareto-optimal solutions Δ_3.

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References

1. G. Craciun, E. Manaila, M. Niculescu, D. Ighigeanu, Polym. Bull. 1299 (2017)
2. M. R. Nemţanu, M. Braşoveanu, Polymer science: research advances, practical applications and educational aspects, ed. A Méndez-Vilas and A. Solano-Martín (Badajoz: Formatex Research Center) 270-277 (2016)
3. M. Braşoveanu, L. St. Koleva, M. R. Nemţanu, E. G. Koleva, T. P. Paneva. J. of Phys.: Conf. Ser., 1089 (2018)
4. L. Koleva, E. Koleva, M. Nemtanu, M. Braşoveanu, Inter. Sci. J. of Sci. Tech. Union of Mech. Eng. "Industry 4.0", **4**, 2, 48-51 (2019)
5. E. Koleva, I. Vuchkov, Vacuum, **77**, 423-428 (2005)
6. I. N. Vuchkov, L. N. Boyadjieva, *Quality improvement with design of experiments* (The Netherlands, Kluwer Academic Publishers, 2001)
7. S. Najafi, A. Salmasnia, R. B. Kazemzadeh, AJBAS, **5**/9, 1566-1577 (2011)
8. QstatLab home page: http://www.qstatlab.co.uk/eng/index.html
9. S. Stoyanov, Bioautomation, **13**(2), 1-18 (2009)