Graphical user interface for investigation and optimization of electron beam induced grafting of starch

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Abstract. The challenge of this paper consisted in optimization application in the case of starch grafting with a vinyl monomer under accelerated electron field. Thus, the robust engineering approach and multi-criteria optimization were considered. Methods based on graphical optimization as well as on overall optimization were implemented. Moreover, a graphical user interface previously developed was uplifted and its usage mode is detailed in the present work. To uplift the graphical interface both previously reported experimental data and new one were used. This graphical user interface is useful for investigation, optimization and education in the field of material processing by using ionizing radiation. Furthermore, other new functions can be implemented in the future.

1. Introduction
Optimization is a key tool frequently applied for the most technological, engineering, scientific and economic activities in order to obtain the best available output for a system or process [1].

Electron beam (EB) grafting is able to modify the polymer substrates by implementing radiation-induced graft copolymerization in order to yield water-soluble copolymers for flocculation processes [2-4]. The synthesis of new polymeric materials through a grafting reaction under ionizing radiation involves several parameters that should be balanced in order to obtain the desired properties of the synthesized grafted polymer. The involved parameters refer to both the radiation processing parameters (irradiation dose, dose rate) and the characteristics of the monomer mixture (i.e. concentrations of monomers, ratio of monomers).

In order to facilitate the irradiation grafting process and to economically use the resources, different methods of optimization may be applied. For instance, 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 [5, 6]. The observations in this case are called heteroscedastic (variance varies with the factor levels). The regression models for the mean and the variance of the properties of the final product can be estimated taking into account the repeated observations as well as the influence of the qualitative factors. Parameter optimization in terms of
obtaining repeatability of the product parameters and quality improvement by minimization of variations in the quality properties can be performed. Moreover, multi-criteria optimization which involves various requirements for the final product is indicated to be achieved.

In the present paper both the robust engineering approach and multi-criteria optimization were considered for the electron beam induced grafting of starch. Additionally, a graphical user interface (GUI) previously developed [7] was uplifted and its functional elements are presented herein. This graphical interface helps the operator to choose the appropriate work regimes in order to synthesize the polymeric products with desired quality properties. More exactly, the paper is a part of a series of works [8-11] carried out within a bilateral cooperation Romanian-Bulgarian initiated few years ago. In order to complete the GUI uplifting, both previous experimental data [7-10] and new ones were used in this work.

2. Experimental conditions
The experiments for EB grafting starch with a vinyl monomer (acrylamide) were performed into two stages: (1) Preparation of solutions based on starch and monomer, resulting in various acrylamide/starch (AMD/St weight ratios) homogenous aqueous solutions; (2) Electron beam irradiation of prepared solutions. Also, the experiments using silver nanoparticles (nAg) as a qualitative factor were carried out. The irradiations were performed at ambient temperature and pressure by using linear electron accelerators of mean energy of 6.23 and 5.5 MeV with different irradiation doses and dose rates.

The synthesized graft copolymers were characterized by monomer conversion coefficient [%], residual monomer concentration [%], apparent viscosity [mPa·s] and/or intrinsic viscosity [dL/g], and Huggins’ constant.

The variation regions $[z_{min}-z_{max}]$ of the process parameters for each experiment set are presented in table 1.

| Experimental set | Starch type | EB energy [MeV] | Qualitative factor | Dose [kGy] | Dose rate [kGy/min] | AMD/St weight ratio |
|------------------|-------------|----------------|-------------------|------------|---------------------|-------------------|
| A (large range)  | corn        | 6.23           | -                 | 0.65       | 5.50                | 0.41              |
|                  |             |                |                   | 1.50       |                     | 0.20              |
|                  |             |                |                   | 11.00      |                     |                   |
| B (small range)  | corn        | 5.5            | -                 | 0.64       | 1.44                | 0.45              |
|                  |             |                |                   | 1.40       |                     | 5.00              |
|                  |             |                |                   | 10.02      |                     |                   |
| C                | corn        | 6.23           | nAg               | 0.67       | 1.37                | 0.55              |
|                  |             |                |                   | 0.81       |                     | 4.98              |
|                  |             |                |                   | 9.97       |                     |                   |
| D                | potato      | 6.23           | -                 | 0.30       | 2.70                | 0.70              |
|                  |             |                |                   | 2.10       |                     | 6.00              |
|                  |             |                |                   | 17.00      |                     |                   |

In the experiments related to the corn starch grafting by EB irradiation of 6.23 MeV – small range (set B), the St concentration was 1.8%, whereas the AMD concentration range was from 9.8 to 19.6% [8]. The concentration of St for experiments of set C varied from 2.00% to 6.15% and the concentration of AMD varied from 10.00% to 33.67% [9]. For samples of set D, the St concentration was constant of 3.33%, the concentration of AMD varied from 16.6% to 33.2%, and certain nAg amount to the aqueous solutions before irradiations was added [10]. For set E, the concentration of potato starch was also constant (1.7%) while the concentration range of AMD was between 9.9% and 29.4% [7].
3. Methodologies

In the present paper two methodologies are implemented for the modeling and optimization of the considered quality parameters, based on the obtained experimental data. They are briefly discussed below:

3.1. Robust engineering design approach

The grafted copolymer quality characteristics (monomer conversion coefficient, the residual monomer concentration, the apparent viscosity, the intrinsic viscosity and the Huggins’ constant) were estimated using three measurements and the following equations:

\[ \bar{y}_u = \frac{1}{n} \sum_{i=1}^{n} y_{ui} \quad s_u^2 = \frac{1}{n-1} \sum_{i=1}^{n} (y_{ui} - \bar{y}_u)^2 \quad u = 1, 2 \ldots N \]  

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

The estimated mean value \( \bar{y}_u \) and variance \( s_u^2 \) can be considered as two responses at the design points, and Ordinary least squares method (OLSM) can be used to fit the regression models of the mean value and the variance for the quality characteristic [12]:

\[ \tilde{y}(\bar{x}) = \sum_{i=1}^{k} \hat{\theta}_{yi} f_{yi}(\bar{x}) \]
\[ \ln\left(\tilde{s}^2(\bar{x})\right) = \sum_{i=1}^{k} \hat{\theta}_{ui} f_{ui}(\bar{x}), \]

where \( \hat{\theta}_{yi} \) and \( \hat{\theta}_{ui} \) are estimates of the regression coefficients, and \( f_{yi} \) and \( f_{ui} \) are known functions of the process parameters \( x_i \).

In the case of qualitative factor \((w)\) of the experiment, the models look like:

\[ \tilde{y}(\bar{x}, w) = \sum_{i=1}^{k} \hat{\theta}_{yi} f_{yi}(\bar{x}, w) \]
\[ \ln\left(\tilde{s}^2(\bar{x}, w)\right) = \sum_{i=1}^{k} \hat{\theta}_{ui} f_{ui}(\bar{x}, w) \]

The variance of normally distributed observations has a \( \chi^2 \) - 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.

3.2. Multi-criteria 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 (by minimization of the variance of these quality parameters) was performed. Methods based on graphical optimization and on overall optimization were implemented for solving this task. The set of requirements was the following:

- residual monomer concentration: < 5% \( \rightarrow \) assurance of low toxicity;
- monomer conversion coefficient: > 90% \( \rightarrow \) economic efficiency;
- apparent viscosity: > 3 mPa·s \( \rightarrow \) copolymer efficiency in flocculation process;
- intrinsic viscosity: > 6 dL/g \( \rightarrow \) copolymer efficiency in flocculation process;
- Huggins’ constant: 0.3 \( \div \) 1 \( \rightarrow \) good solubility in water.
3.2.1. **Graphical optimization.** In order to build the contour plots of the investigated quality characteristics, depending on the process parameters, the graphical optimization applied the models estimated by robust engineering approach. Therefore, the regions of the process parameters were identified so that the requirements for the quality characteristics are simultaneously fulfilled. The optimal regions were 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.

3.2.2. **Overall optimization.** A multi-response optimization problem requires an overall optimization, i.e. simultaneous satisfaction with respect to the mean and standard deviation of all quality characteristics by using a combined desirability function between optimization and robustness. The overall desirability function can be defined as follows [12]:

\[
D_{\text{overall}}(\bar{x}) = D_{\text{opt}}(\bar{x})^{\omega_{\text{opt}}} \times D_{\text{rob}}(\bar{x})^{\omega_{\text{rob}}}
\]  

(6)

where the optimization desirability function \(D_{\text{opt}}\), defined as the weighted geometric average of the individual optimization desirability functions, is:

\[
D_{\text{opt}}(\bar{x}) = d_{o1}(\bar{x})^{\omega_{1\mu}} \times d_{o2}(\bar{x})^{\omega_{2\mu}} \times ... \times d_{om}(\bar{x})^{\omega_{m\mu}}
\]  

(7)

and the robustness desirability function \(D_{\text{rob}}\), defined as the weighted geometric average of the individual robustness desirability functions, is:

\[
D_{\text{rob}}(\bar{x}) = d_{r1}(\bar{x})^{\omega_{1\sigma}} \times d_{r2}(\bar{x})^{\omega_{2\sigma}} \times ... \times d_{rm}(\bar{x})^{\omega_{m\sigma}}
\]  

(8)

where \(\omega\) is weights and \(d_{ij}\) and \(d_{ij}\) are individual optimization desirability functions of the mean values of each response and individual robustness desirability functions, respectively.

In order to formulate weights for a given magnitude of predictive capability, the relative value of the predictive capability index (squared multiple correlation coefficient, \(R^2\)) is determined by:

\[
\omega_j^{ij} = \frac{R_j^2}{\sum_{j} R_j^2}
\]  

(9)

4. **Graphical User Interface (GUI)**

In this section, the usage mode of the developed graphical user interface is gradually described.

When the software is started, the following window is loaded (figure 1) and gives the possibility to the operator to choose the operation language, either Bulgarian or English.

![Figure 1](image1.png)  
**Figure 1.** Start window of GUI.

After the language is chosen, the user is given the possibility to use the functional parts by choosing from the menu bar, shown in figure 2, where the marked numbers mean:

1. Home – directs the user to the Start window (figure 1);

2. Calculator – calculates the mean and variance of the product quality characteristics. For data processing, the operator can select one of the experimental data set from all five experiments (figure 3);
3. Investigation – gives the opportunity to the user to visualize and evaluate the copolymer characteristics at different working regimes. For this operation, the operator can select any experimental data set from all five experiments (figure 4);
4. Optimization – Graphical and Overall optimizations are used in order to find the regions of the process parameters where the requirements for the quality characteristics are fulfilled simultaneously. GUI display for the optimization is presented in figure 5.
5. Experiment info – loads a .pdf file that contains short descriptions of experiments and methodologies used;
6. Български – gives the possibility to switch on Bulgarian language.

As an example, figure 3 displays the calculator view of experimental data set D. The arrows numbered from 1 to 3 point at the input parameter ranges (table 1) and the regions where the user can choose working conditions to be investigated. With 4 is indicated the case, when the qualitative factor (nAg) is present (silver nanoparticles are added to the solutions). This factor is missing in all the other four experimental sets (A, B, C and E).

The quality characteristics of the product are marked with numbers from 5 to 8 and their standard deviations (SD) from 9 to 11.

The Calculator has three functional buttons:
- Calculate – after the user types the values of a virtual point for the input parameters, the Quality characteristics and SD for this concrete virtual point are calculated by pressing this button;
- Clear Results – all results are cleared by pressing the button, but the input process parameters stay untouched;
- Clear all – all the results and the input parameters are cleared.

The Investigation window is presented in figure 4. Here, again the input parameters are shown by using arrows marked 1-3. These input parameters are in the shape of radio buttons, and the operator has to select just one of them. The checkbox marked as 4 is for nAg, which is missing in the other experimental data sets.

The Investigation has three functional buttons:
- Calculate – after the user introduces the value of a virtual point for the chosen input parameter, the Quality characteristics (5) and SD (6) are calculated, and their contour graphs are plotted by pressing this button;
- Clear Figures – the contour plots are cleared by pressing the button, but the input process parameter remains untouched;
- Clear all – all plots and the input parameter are cleared.
In the contour plots displayed in both Investigation section and Optimization section, every quality parameter has the same specific color for all experimental data sets, as it follows:

- monomer conversion coefficient → blue;
- residual monomer concentration → red;
- apparent viscosity → cyclamen;
- intrinsic viscosity → black;
- Huggins’ constant → light green.

Figure 5 shows the Optimization window. The numbers 1-3 point the radio buttons of the input parameters while the check box for nAg is pointed by number 4.

The Optimization window has four buttons:

- Calculate – after the user types the value of a virtual point for the chosen input parameter, the Quality characteristics (5) and SD (6) are calculated, and their contour graphs are plotted by pressing this button;
- Overall – the pop-up of a third contour graph (figure 6) mirroring the Overall optimization for the chosen input parameter displays by pressing this button. In the range of the chosen input parameter where the overall function has a maximum value, the best possible quality characteristics and less standard deviation can be obtained for a synthesized copolymer. Thus, this optimization helps the user to choose the appropriate irradiation parameters as well as the chemical composition;
- Clear Figures – the contour plots are cleared and Overall plot is closed by pressing the button, but the input process parameter remains untouched;
- Clear all – all plots and the input parameter are cleared.

5. Conclusions
The developed and presented graphical user interface facilitated the investigation of the starch grafting by EB irradiation and the optimization of process parameters. The Calculate functional block of this software has been implemented to predict the characteristics of grafted copolymers related to different process parameter regimes, which are not covered by real experimental data. Further, the Optimization function of this graphical interface allowed a rapid access to the best values of grafted starch features that meet the required quality criteria. The adding of a functional block for sequential generation of new experimental points will be considered in our future work.
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