Search for composition of nanoparticles containing poly (vinyl alcohol)/poly (vinyl acetate) blend composites having the highest value of the modulus of elasticity by the response surface methodology.

A Kovalovs¹, N Jelinska², M Kalnins², A Chate¹
¹Riga Technical University, Faculty of Civil Engineering, Institute of Materials and Structures, Kipsalas Street, 6B/6A, Riga, LV-1048, Latvia
²Riga Technical University, Faculty of Material Science and Applied Chemistry, Institute of Polymer Materials, P. Valdena Street 3, Riga, LV-1048, Latvia
E-mail: andrejs.kovalovs@rtu.lv

Abstract. The aim of this study was to investigate the dependence of elastic modulus on component’s proportion of nanoparticles containing PVA/PVAc blend composites by means of response surface methodology. Full factorial design method was used to perform a series of experiment. The statistical analysis of experimental results showed that adding of nanoparticles to the PVA/PVAc compositions has substantial effect on the tensile properties. The higher values of the tensile elastic modulus show systems with almost equal content of polymers in the blend. Regardless of PVA/PVAc content relationships, the higher modulus values present systems that contain both nanoparticles. Composition, which provide greatest value of elastic modulus was determined and experimentally verified.

1. Introduction
Poly(vinyl alcohol) (PVA) is the it is the world's most produced synthetic water-soluble polymer. It is produced commercially by the hydrolysis of poly vinyl acetate (PVAc). To improve mechanical and other properties PVA is blended with different synthetic polymers. Composites prepared by blending of comparatively rigid poly vinyl alcohol (PVA) with rather compliant poly vinyl acetate (PVAc) show attractive strength-deformation characteristics which change significantly with PVA/PVAc proportions [1]. For example, the elastic modulus of blends changes up to seven times, from 0.3 GPa to 2.2 GPa. It seemed interesting to strengthen PVA/PVAc compositions by addition of some particles with reinforcing effect: placoid particles of montmorillonite (MMT) [2] and particles of microcrystalline cellulose (MC) [3]. Efficiency of presence of small amounts (less than 5%) of such nanoparticles on strength-deformation characteristics of number of thermoplastic polymers is proven frequently [4-6].

Application of response surface methodology (RSM) allows finding out the relationship between components proportions and tensile characteristics of composite significantly reducing the number of experiments [7]. The RSM is widely used to optimize process parameters, especially in determining optimum conditions for chemical investigations. The helpfulness of RSM in the development and optimization of a variety of composites has been highlighted by several authors [8].

The aim of this study was to investigate the dependence of elastic modulus on component’s proportion of PVA/PVAc blend composites containing nanoparticles of montmorillonite clay (MMT), microcrystalline cellulose (MC) by means of RSM and to find the composite composition with greatest value of elastic modulus.
2. Materials and method

2.1. Optimisation procedure

The general flowchart of the optimisation procedure that should be followed in the present research is shown in Figure 1. The optimisation process consists of six stages. In the first stage (Experimental Design), a plan of experiments is produced according to the number of design variables and number of experiments. In the second stage (Test), the specimens are created in order to model the response of a structure and testing is performed in the reference points of the experimental design. In the third stage (Approximation), the numerical data obtained by the testing of specimens in the sample points is used in order to build the approximating functions using the response surface method. These simple mathematical models obtained from the data of experiments are used as the objective functions in the optimal design problem. The non-linear optimisation problem is executed by the random search method using the obtained response surfaces in the next stage (Optimisation). The optimal result of non-linear optimisation is checked using the testing in the fifth stage (Result validation). The optimal design variables are used for preparation of the specimen in order to compare difference between the optimisation result and the experimental solution. If the difference between the optimal result and the experimental solution is higher than 5% it is needed to improve the correlations of the approximating functions or change the design space for some parameters. The procedures are executed before obtaining the final optimal solution.

![Flowchart of the optimisation procedure.](image)

2.2. Materials

PVA (from Merck Schuchardt) (molecular weight of 133,000 Da, content of acetate groups 0.98%), as well as a PVAc water emulsion (Mowilith DHS S1, from Celanese Emulsions GmgH) with solid content 50% were used as initial materials. Diethylene glycol (Sigma-Aldrich) was used as plasticizer for both polymer components.

Montmorillonite clay (from Dellite, Laviosa Chimica Mineraria) with dimensions of particle size after dispersion in water 1x500 nm and microcrystalline cellulose as 9% water gel were used. A 10% water solution of PVA was mixed with a 10% PVAc water emulsion in different proportions providing the specified volume fractions $\varphi$ of the components in the blend. MMT was added to polymers in a form of 4% water dispersion. Dispersion was prepared by mixing for 8 hours (magnetic stirrer) followed by ultrasonic technique for 10 minutes.

The films were obtained by casting: the mixtures were poured into Petri dishes 140 mm in diameter (the initial thickness of the layer was 2 mm) and dried at a temperature of 17°C up to a constant content of water about 3%. The thickness of the films obtained was 150 ± 10 μm.

2.3. Mechanical test

The strength values were obtained according to EN ISO 527 standard of Determination of tensile properties and were measured by Zwick/Roell universal machine at constant crosshead speed 20 mm/min at room temperature.

The data obtained were processed by using the testXpert V11.0 program. The stress–strain relationship $\sigma(\varepsilon)$ was determined up to the failure of specimens. Each set of experimental design was replicated
five times and the average values of initial elasticity modulus \( E = \lim (d\sigma/d\varepsilon)_{\varepsilon \to 0} \) were determined. The average error of tensile elastic modulus values did not exceed ± 10 %.

2.4. Experimental design

The experiments were designed according to Full Factorial design (FFD). FFD of experiment is the most popular designs owing to their simplicity and relatively low cost. It is very useful for preliminary studies or in initial optimization steps. A FFD contains all the combination of the different levels of all the design variables.

The plan of experiments is formulated for 3 design variables, namely, nanoparticles of montmorillonite clay (\( X_1 \)), nanoparticles of microcrystalline cellulose (\( X_2 \)), volume fraction of PVA in PVA/PVAc blend (\( X_3 \)) and 27 experiment points. The experimental plan with coded and uncoded levels of design factors and experimental results are given in Table 1.

| Experiment No. | Coded variables | Actual variables | Response (Elastic modulus, MPa) |
|----------------|-----------------|------------------|--------------------------------|
|                | \( X_1 \) | \( X_2 \) | \( X_3 \) | \( x_1 \) | \( x_2 \) | \( x_3 \) | Y     |
| 1              | 1             | 1                | 1              | 5            | 5            | 90     | 434   |
| 2              | 1             | 1                | 0              | 5            | 5            | 50     | 453   |
| 3              | 1             | 1                | -1             | 5            | 5            | 10     | 407   |
| 4              | 1             | 0                | 1              | 5            | 2.5          | 90     | 401   |
| 5              | 1             | 0                | 0              | 5            | 2.5          | 50     | 418   |
| 6              | 1             | 0                | -1             | 5            | 2.5          | 10     | 366   |
| 7              | 1             | -1               | 1              | 5            | 0            | 90     | 362   |
| 8              | 1             | -1               | 0              | 5            | 0            | 50     | 370   |
| 9              | 1             | -1               | -1             | 5            | 0            | 10     | 320   |
| 10             | 0             | 1                | 1              | 2.5          | 5            | 90     | 406   |
| 11             | 0             | 1                | 0              | 2.5          | 5            | 50     | 421   |
| 12             | 0             | 1                | -1             | 2.5          | 5            | 10     | 369   |
| 13             | 0             | 0                | 1              | 2.5          | 2.5          | 90     | 412   |
| 14             | 0             | 0                | 0              | 2.5          | 2.5          | 50     | 441   |
| 15             | 0             | 0                | -1             | 2.5          | 2.5          | 10     | 376   |
| 16             | 0             | -1               | 1              | 2.5          | 0            | 90     | 356   |
| 17             | 0             | -1               | 0              | 2.5          | 0            | 50     | 368   |
| 18             | 0             | -1               | -1             | 2.5          | 0            | 10     | 316   |
| 19             | -1            | 1                | 1              | 0            | 5            | 90     | 348   |
| 20             | -1            | 1                | 0              | 0            | 5            | 50     | 366   |
| 21             | -1            | 1                | -1             | 0            | 5            | 10     | 310   |
| 22             | -1            | 0                | 1              | 0            | 2.5          | 90     | 337   |
| 23             | -1            | 0                | 0              | 0            | 2.5          | 50     | 363   |
| 24             | -1            | 0                | -1             | 0            | 2.5          | 10     | 307   |
| 25             | -1            | -1               | 1              | 0            | 0            | 90     | 313   |
| 26             | -1            | -1               | 0              | 0            | 0            | 50     | 344   |
| 27             | -1            | -1               | -1             | 0            | 0            | 10     | 288   |

Subsequently in the points of plan of experiment the results of testing were obtained. In the next stage the numerical data obtained by the testing in the points of plan of experiments was used in order to build the approximating functions.

Eglais [9] proposed the algorithm of selection of the terms for non–polynomial regression function. In his work, the “correlation” approach for the optimal choice of the number of terms was also
proposed. This approximation method proposed by Eglais is employed for the solution of the optimisation problem considered here. In the present approach the form of the regression equation is unknown in advance. There are two requirements for the regression equation: accuracy and reliability. Accuracy is characterised as a minimum of standard deviation of the table data from the values given by the regression equation. It is possible to obtain a complete agreement between the table data and values given by the regression equation, by increase of the number of terms in the regression equation. However, it is necessary to note that prediction in the intervals between the table points may not be accurate.

For an improvement of prediction, it is necessary to decrease the distance between the points of the experiments by increasing the number of experiments or by decreasing the domain of factors. Reliability of the regression equation can be characterised by the affirmation that standard deviations for the table points and for any other points are approximately the same. Obviously, the reliability is greater for a smaller number of terms of the regression equation.

The regression equation can be written in the following form:

\[ y = \sum_{i=1}^{p} A_i f_i(x_j) \]  

(1)

where \( A_i \) are the coefficients of the equation of regression, \( f_i(x) \) are the functions from the bank of simple functions \( \varphi_1, \varphi_2, \ldots, \varphi_k \) which are assumed as

\[ \varphi_k(x_j) = \prod_{i=1}^{n} x_j^{a_{ij}} \]  

(2)

where \( n \) is the number of the object parameters and \( a_{ij} \) is a positive or negative integer including zero. Synthesis of the equation from the bank of simple functions is carried out in two stages: selection of perspective functions from the bank and then step-by-step elimination of the selected functions.

In the first stage, all variants are tested with the least square method and the function, which leads to the minimum of the sum of deviations, is chosen for each variant. In the second stage, the elimination is carried out using the standard deviation:

\[ \sigma_0 = \sqrt{\frac{S}{k - p + 1}} \]  

(3)

\[ \sigma = \sqrt{\frac{1}{k-1} \sum_{i=1}^{k} \left( y_i - \frac{1}{k} \sum_{j=1}^{k} y_j \right)^2} \]

or correlation coefficient:

\[ c = \left( 1 - \frac{\sigma}{\sigma_0} \right) \times 100\% \]  

(4)

where \( k \) is the number of experimental points, \( p \) is the number of the selected perspective functions and \( S \) is the minimum sum of deviations. It is more convenient to characterise the accuracy of the regression equation by the correlation coefficient.

3. Results and discussion

Relationship between the design variables \( x \) and the corresponding behavior functions \( Y \) is given as (correlation \( c = 93.4\% \)):

\[ Y = 2627 + 27.74x_1 + 20.94x_2 + 2.499x_3 + 2.093x_1x_2 - 4.124x_1^2 - 3.11x_2^2 - 0.02x_3^2 \]  

(5)
After selection of equation of regression the parametric studies were carried out additionally to scrutinize the influence of design parameters on behaviour function. This was done by displaying 3D graphs of approximating functions. The view of the response surfaces is shown in Figure 2. This figure shows the estimated response function for the different amount of nanoparticles with different combinations of volume fraction of PVA.

![Figure 2](image_url)

**Figure 2.** Dependence of elastic modulus $E$ on of nanoparticles content (volume fraction of PVA: a - 10%, b - 50% and c - 90%).

It can be seen that the value of elastic modulus increases proportionally to an increase of nanoparticles. When the amount of nanoparticles begins to grow, the elastic modulus increase significantly up to a certain point and then increases slightly. In according to individual main effects of design variables, the most effective factor on elastic modulus is nanoparticles of montmorillonite clay. Figure 2b shows that maximum value of elastic modulus is achieved when amount of PVA and PVAc is equal.

4. Optimisation

The search of the optimal composition of PVA/PVAc blend films on the basis of the mathematical model was the final stage of this research. Non-linear optimisation problem was solved by the random search method using the response surface obtained in the corresponding program EdaOpt [10]. The optimisation result obtained for PVA/PVAc blend film is outlined in Table 2. The maximum elastic modulus reaches 454 MPa, when content of montmorillonite clay is 4.5%, microcrystalline cellulose is 5.0% and volume fraction of PVA in the blend PVA/PVAc is 60%. The optimal result obtained with the response surface method was compared with the experimental result in the point of optimal solution. It is seen that differences between the optimal and experimental results using nanoparticles to the PVA/PVAc compositions obtained by the optimisation are very small. Mostly residuals do not exceed 2.5%, which show good correlation of the approximating functions.
Table 2. Optimal solution for a maximal elastic modulus.

| Title                      | Design variables | Objective function |
|---------------------------|------------------|--------------------|
| Optimisation              | 4.5 5.0 60       | 454                |
| Experimental verification | 4.5 5.0 60       | 443                |

5. Conclusion
The effect of the nanoparticles of montmorillonite clay, nanoparticles of microcrystalline cellulose and PVA/PVAc ratio on the elastic modulus of PVA/PVAc blends was investigated using response surface method. Data obtained and 3D graphs show that adding nanoparticles to the PVA/PVAc compositions has a substantial effect on the tensile properties. Irrespective of type of nanoparticles, the higher values of tensile elastic modulus show systems with equal content of polymers in the blend. Regardless of PVA/PVAc content relationships, the higher modulus values present systems that contain both kinds’ nanoparticles. Composition, which provide greatest value of elastic modulus was determined and experimentally verified.

Acknowledgments
The present work was supported by the European Social Fund within the project 2013/0017/1DP/1.1.1.2.0/13/APIA/VIAA/06

References
[1] Jelinska N, Kalhins M 2011 Strenght and deformation characteristics of polymer blend films obtained from water systems Mechanics of Composite Material 47(5) 236-250
[2] Pavlidou S, Papaspyrides CD 2008 A review on polymer–layered silicate nanocomposites Progress in Polymer Science 33(12), 1119–1198
[3] Laka M, Chernyavskaya S 2007 Obtaining and properties of microcrystalline cellulose from hardwood pulp RTU Material Sciences and Applied Chemistry 14 7-14
[4] Sinha Ray S, Okamoto M 2003 Polymer/layered silicate nanocomposites: a review from preparation to processing Progress in Polymer Science 28(11) 1539–1641
[5] Ma J, Xu J, Ren J, Yu Z, Mai Y 2003 A new approach to polymer/montmorillonite nanocomposites Polymer 44(16) 4619–4624
[6] Tjong SC 2006 Structural and mechanical properties of polymer nanocomposites Materials Science and Engineerin 53(3-4) 73–197
[7] Montgomery DC 2012 Design and Analysis of Experiments (NY: Wiley)
[8] McCarron PA, Woolfson AD, Keating SM 2000 Response surface methodology as a predictive tool for determining the effects of preparation conditions on the physicochemical properties of poly(isobutylcyanoacrylate) nanoparticles 193 37–47
[9] Eglais V 1981 Approximation of data by multi–dimensional equation of regression Problems of dynamics and strength 39 120–125
[10] Auzins J, Janushevska J, Janushevskis J, Skukis E 2014 Software EdaOpt for experimental design, analysis and multiobjective robust optimization Proc. OPT-i Int. Conf. Engineering and Applied Science Optimization (Kos Island, Greece, 4–6 June 2014) (Athens: National Technical University) pp 101-123