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Response surface regression of some polyurethane filled with modified cellulose

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The work consists of preparing some polyurethane filled with modified cellulose, and the evaluation of the response surface regression, using an experimental design. Optimization of the synthesis was studied based upon a design matrix with 13 experiences and a forward stepwise regression procedure was engaged to realize a statistically significant regression equation. This work intends to establish a series of products with increased mechanical and wettability properties. The influence of the amount of hydroxypropyl cellulose (HPC) and respectively hydroxylethyl cellulose (HEC), used as renewable resources, versus mechanical and wettability properties of the ensued polyurethanes was studied. Therefore, we conducted an optimization study using an experimental data matrix which gives the following general regression equation:

$$Y_i = b_o + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i<j} b_{ij} X_i X_j \quad (1); \quad \text{where:}$$

X_i, X_j – the independent variable: HPC and HEC amount; Y_i, - the dependent variable: the value of the measured property (mechanical tests, Young's modulus and wettability); b_o, b_{ii}, b_{ij} - regression coefficients.
Tensile strength and wettability values were performed on an Instron apparatus and respectively Sigma 700 tensiometer. The interaction between the experimental evaluation of algorithm behaviour and the theoretical analysis of algorithm performances plays an important role in our research. Comparing the own experimental and theoretical data on the basis of these equations, a good agreement resulted. This creates the possibilities to select the samples with pre-established and useful properties.

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1. Introduction

Many polymeric materials are emerging based on renewable resources that offer great possibilities for improving ecological and environmental performance. These new materials are an important aspect of broader developments in sustainable engineering. The replacement of classical polymers with new polymers from annually renewable sources to reduce petroleum dependence and the negative impact on the environment is currently receiving increasing attention [1-5].

Polyurethane is a class of very useful and versatile material and widely used as individual polymer possessing network structure [6-9]. Few biodegradable elastomers have been synthesized, and new materials are required to meet the need for a more and more diverse range of physical properties. It is valuable to note that block-polyurethanes based on cellulose derivatives were found to be biodegradable and possess hemocompatibility [10]. Biodegradable elastomers are expected to be suitable for any application requiring the use of a flexible, elastic material, such as soft tissue engineering.

Some authors [11-16] have demonstrated the possibility of using a series of designed experiments for determined the optimum condition by combining the method of two-level compete factorial design and a constrained technique. The interaction effects may be determined by means of the experimental protocol based on statistical description. Selection of program permits realization, with a minimum number of measurements and calculations required by experimental data processing, of a model prediction process, which are acceptably precise. In time, an ample theory devoted to the development of optimum programs for factorial experiments has been proposed.

The number of experiments based on a methodical factorial description increases exponentially with the number of variables. The concept of rotatability introduced by Box and Hunter is an important design criterion for response surface design [17].

The expression for variance-covariance matrix of the estimated axial slopes at a point in the factor space is obtained for a symmetric balanced two dimensional second-order design (eq.1). Rotatable designs have the good property that the variance of the estimated response is constant at points equidistant from the centre of the design, conventionally taken to be the origin of the factor space, after transformations if necessary. Rotatable designs generate information about the response surface equally in all directions and are therefore useful when no or little prior knowledge is available about the nature of the response surface. If interest is in difference between responses at points close together in the factor space, the estimation of local slopes of the response surface becomes important. Estimation of slopes is particularly relevant in situations where the experimenter wishes to determine optimal settings of the factors in order to produce the maximum (minimum) value of the response [18].

In this work, we present the optimization of the synthesis process of new cellulose derivative polyurethanes based on 4,4'-diphenylmethane diisocyanate - MDI, poly(ethylene adipate)diol – PEA and 1,4-butanediol –BD, having HPC and HEC incorporated in the formulations. A design matrix with 13 experiments and a forward stepwise regression procedure were employed, to achieve a statistically significant regression equation. The interaction between the experimental evaluation of algorithm behaviour and the theoretical analysis of algorithm performances plays an important role in our research. Comparing the own experimental with the theoretical data on the basis of these equations, a good agreement resulted. This creates the possibilities to select the samples with pre-established and useful properties. The regression models were then plotted as 2D and 3D graphically representation of physico-mechanical and wettability properties versus reaction composition.

2. Experimental

2.1. Materials

The basic materials used in this research were poly(ethylene-adipate)diol (PEA, local market) Mn 2000, mp 50-55 ^{o}C, hydroxyl number 56 mgKOH/g; 4,4'-diphenylmethane diisocyanate (MDI-Hungary), Mw 250,14, mp 42-44 ^{o}C, bp 152-156 ^{o}C / 0,2-0,3mmHg, was distilled, prior to utilization, under reduced pressure; 1,4-butanediol (Fluka), Mw 90.12, d 1.017; hydroxypropyl cellulose (HPC-Aldrich), Mn 10000, Mw 80000, viscosity 150-700 cP at 10wt % in water, 25 ^{o}C; hydroxyethyl cellulose (HEC-Fluka), viscosity 145 mPa.s at 1wt % in water, 20 ^{o}C; N,N- dimethylformamide (DMF-Aldrich), Mw 73.10, d 0.944, as solvent. The removal of traces of water from DMF is difficult. The solvent is refluxed over calcium hydride and distilled under vacuum using a high reflux ratio and a good fractionating column. The middle fraction is collected.

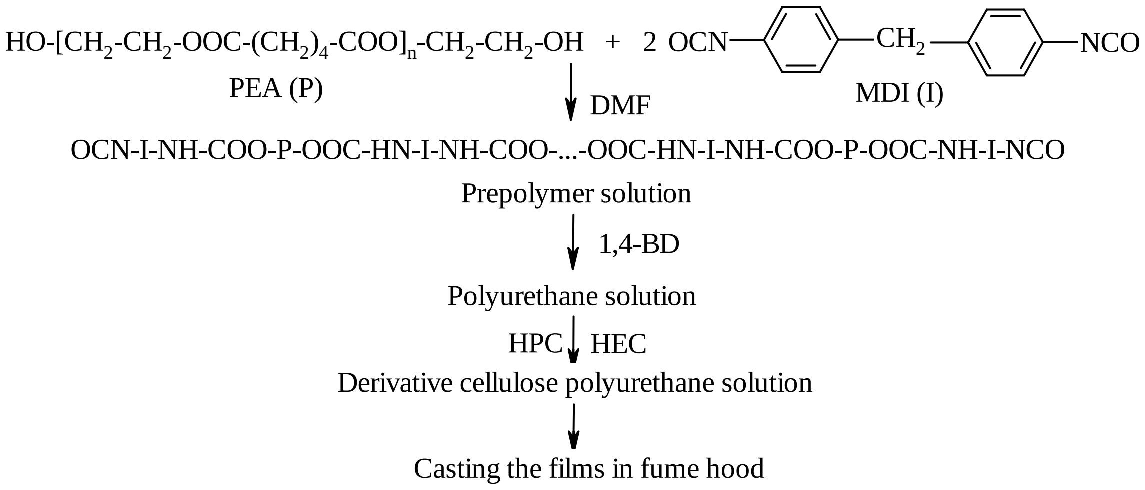
2.2. Measurements

Stress-strain measurements were performed on dumbbell-shaped samples cut from thin films on a TIRA test 2161 apparatus, Maschinenbau GmbH Ravenstein Germany. Measurements were run at an extension rate of 50 mm/min, at room temperature 25 ^{o}C. All samples were measured three times and the averages were obtained.

Dynamic contact angles were performed by the Wilhelmy plate procedure, using a Sigma 700 precision tensiometer produced by KSV Instruments. The sample plate dimensions were 50x8x2 mm and rate of immersion-emersion was 5 mm/min in water. Immersion depth was 5 mm in standard conditions. All measurements were the average of 3 contact angle measurements of samples.

2.3. Procedure

The cellulose derivative polyurethanes from this study were prepared by solution polymerization, using 4,4'-diphenylmethane diisocyanate (MDI), poly(ethylene-adipate) diol (PEA) and 1,4-butanediol as chain-extending agent, in absence of catalysts. The synthetic route for the polyurethane samples preparation is described in Scheme 1.



Scheme 1. Synthetic route for preparation of the polyurethane samples.

The polyurethane elastomers were prepared by solution polymerization. The molar ratio of polymer was PEA: MDI: BD of 1: 2: 1 (1.544 %o mole urethane –HN-COO-).

Poly(ethylene-adipate)diol (PEA) - 0.03 mole, dried under vacuum at 100 °C for 2 hrs, was reacted with 0.06 mole of 4,4'-diphenylmethane diisocyanate (MDI) at 80 °C for 1 hour to yield a prepolymer, which was dissolved in DMF, resulting an urethane prepolymer solution (40% wt.), which in next step was extended with 0.03 mole of 1,4-butanediol (BD). The polyurethane solution it's stirred for 2 hrs at 60 °C temperature. The viscosity of polyurethane solution increase and then the process will be stopped by adding of 5 mL of alcohol-DMF, 1:1 wt. This final solution was divided in 13 portions, which were mixed with HPC and/or HEC prior dissolved in DMF, in according to an experimental program central, composite, rotational, k=2. Cellulose derivative polyurethane solution is cast in a form to realise a film with dimension 100x100x0.5 mm and then thermally treated to evaporate DMF, at 40 °C for 24 hrs into fume hood. In this way were prepared all the samples for this study.

3. Results and discussion

Response surface regression (RSR) was employed to optimize the mechanical and wettability properties of polyurethane materials under different amounts of HPC and HEC from polymers composition. Optimization was performed to assess maximum values for tensile strength and Young's modulus and minimum value of contact angle (hydrophilic behaviour – necessary condition for tissue engineering application).

RSR is a set of techniques that include: setting up a series of experiments that will produce an enough and reliable measurements of the response of interest, determining a mathematical model that best fits the data collected from the experimental measurements by conducting appropriate tests of hypotheses concerning the model's parameters, and determining the optimal settings of the experimental factors that produce the maximum (or minimum) value of the response.

Thus, RSR is a useful statistical technique for the investigation of complex processes particularly in the field of chemical and engineering processes, industrial research, biological investigations, etc with an emphasis on optimizing a process or a system [18]. The main advantage of RSR is the reduced number of experimental runs needed to provide sufficient information for statistically acceptable results, faster and less expensive as compared to the classical one variable at-a-time or full factorial experimentation.

The input parameters to the system (independent variables) are called factors whose values or settings can be controlled by an experimenter. The response variable (dependent) is the measured quantity whose value is assumed to be affected by changing the levels of the factors. It was assumed that a continuous mathematical function f_k (k = 1, 2, 3…) exists for each response variable Y_k (stress strain measurements, Young modulus, and wettability values) in terms of two factors: HPC levels (P) and HEC levels (E), then,

$$Y_k = f_k\,(P,E) \tag{2}$$

To approximate the function f_k, second order polynomial equation of the following form was assumed:

$$Y = b_o + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \tag{3}$$

where Y is the predicted response; b_0, b_1, b_2, b_{11}, b_{22} and b_{12} are the coefficients and X_1 and X_2 are the coded independent factors viz. HPC and HEC levels, respectively which are linearly related by the following equation with the original values.

There are presumed that the multivariable interaction effects were relatively insignificant as compared to the main and two variable interaction effects. This is usually reasonable assumption if the response surface regression is smooth and continuous.

Classical experimental designs were concerned with comparative experiments, that is, experiments in which the primary objective is to compare the effects of various components of polyurethane and, especially, to estimate their contribution on physico-mechanical properties.

The amounts, in grams, of HPC and HEC, which represent the independent variables, and their level of interest, are presented in Table 1.

In this study we utilized a program central, composite, rotational, k=2 which have followed statistical protocol:

Table 1. X_1 (HPC) and X_2 (HEC) amounts utilized in experimental protocol (coded and uncoded value)

Independent variable	Level				
	$-\sqrt{2}$	-1	0	1	$\sqrt{2}$
X_1 (grams HPC)	0.4	0.2	0	0.1	0.3
X_2 (grams HEC)	0.3	0.1	0	0.2	0.4

In Table 2 are presented the experimental and predicted values of tensile strength (Y_1), Young's modulus (Y_2) and dynamic contact angle (Y_3).

Table 2 .Coded units of independent variable(X_1, X_2), real and predicted values of Y_1, Y_2 and Y_3

Code	HPC X_1	HEC X_2	Tensile Strength MPa Y_1^r	Tensile Strength MPa Y_1^p	Young's Modulus MPa Y_2^r	Young's Modulus MPa Y_2^p	Contact Angle deg Y_3^r	Contact Angle deg Y_3^p
Sample 1	-1.0	-1.0	27.78	27.88	3.48	3.84	83.22	83.89
Sample 2	1.0	-1.0	28.36	28.28	3.80	3.87	83.53	83.10
Sample 3	-1.0	1.0	26.47	27.05	3.75	3.74	84.80	83.56
Sample 4	1.0	1.0	26.29	26.21	3.25	3.65	83.66	82.32
Sample 5	$-\sqrt{2}$	0.0	28.78	29.67	4.07	3.95	83.00	84.76
Sample 6	$\sqrt{2}$	0.0	29.78	29.06	3.91	3.87	82.90	83.32
Sample 7	0.0	$-\sqrt{2}$	29.63	29.46	4.02	3.98	82.40	82.79
Sample 8	0.0	$\sqrt{2}$	29.98	29.15	3.83	3.81	81.73	82.01
Sample 9	0.0	0.0	21.75	22.17	2.56	2.58	90.90	91.42
Sample 10	0.0	0.0	20.55	22.17	2.65	2.58	91.60	91.42
Sample 11	0.0	0.0	22.75	22.17	2.55	2.58	91.40	91.42
Sample 12	0.0	0.0	22.00	22.17	2.60	2.58	92.54	91.42
Sample 13	0.0	0.0	23.80	22.17	2.55	2.58	90.88	91.42

^{r} – Real values; ^{p} – Predicted values.

In Tables 3 and 4 are presented the regression coefficients and response equations of Y_1, Y_2 and Y_3 (the statistically software, which were utilized for determining of these parameters, was Systat 5.0, Quasi-Newton method).

Table 3. Estimated regression coefficients for Y_1, Y_2 and Y_3, using data in uncoded units

Term	Y_1 Coefficients	Y_2 Coefficients	Y_3 Coefficients
b_o	22.170	2.580	91.464
b_1	0.711	-0.080	-0.023
b_2	-0.079	-0.092	0.067
b_{11}	1.367	0.319	-1.827
b_{22}	1.785	0.302	-2.236
b_{12}	0.154	-0.040	-0.181

Table 4. Response equations and R Squared for Y_1, Y_2 and Y_3, using data in uncoded units

$Y_1=22.17+0.711X_1-0.079X_2+1.367X_1^2+1.785X_2^2+$ $+0.154X_1X_2$ R Squared =94.04%
$Y_2=2.58-0.08X_1-0.092X_2+0.319X_1^2+0.302X_2^2-$ $-0.04X_1X_2$ R Squared =96.11%
$Y_3=91.464-0.023X_1+0.067X_2-1.827X_1^2-2.236X_2^2-$ $-0.181X_1X_2$ R Squared =97.97%

Where:

Y_1 - equation for response to experimental values of tensile strength (MPa);

Y_2 - equation for response to experimental values of Young's Modulus (MPa);

Y_3 - equation for response to experimental values of advanced dynamic contact angle (Deg);

R Squared - statistical measure of how well a regression line approximates real data points; an R-squared of 100% indicates a perfect fit.

The regression coefficients are used in determining the direction of the most inclined slope. It is known that the self interaction effect of a variable become significant in the vicinity of the optimum; as a consequence an adequate regression equation has to include $X_{i,j}$ quadrate terms in this area. From the coefficients of the equation the higher influence towards the optimum of the HPC: HEC ratio may be obtained.

Objective function's gradients for maximization and respectively minimization are obtained by derivation of Y_1, Y_2 and respectively Y_3.

Computer generated response surfaces, canonical analysis and contour plot interpretation revealed good correlations of experimental and predicted values.

From Figs. 1-6 we can evidence that the optimum (maximum or minimum) values for tensile strength, Young's modulus and respectively contact angle versus HPC:HEC ratio are distributed in four zones (for $X_1=0$ and $X_2=+/-\sqrt{2}$, and $X_1=+/-\sqrt{2}$ and $X_2=0$).

Response surface regression demonstrated that the introduction of HPC and/or HEC means to introduce as a filler and/or crosslinking to the system, determine an increase of the values of tensile and modulus, more when more modified cellulose is introduced. Modified cellulose is hydrophilic, and therefore, its introduction increases the hydrophilicity of the polyurethane. It is therefore not surprising that these are the results obtained (more tensile and lower contact angle at maximum load of modified cellulose (samples 5, 6, 7 and 8).

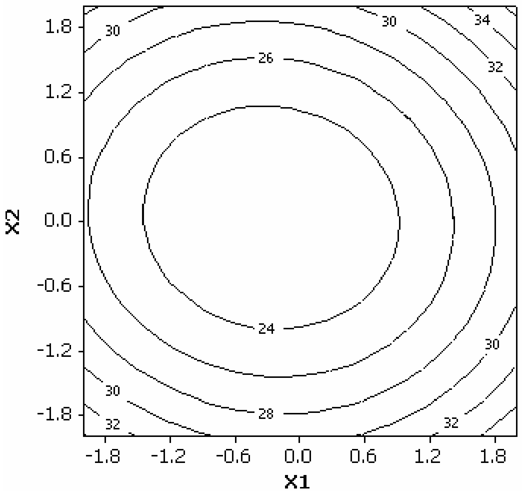


Fig. 1. Contour plot of Y_1 vs. X_1, X_2
(Tensile strength versus HPC: HEC ratio).

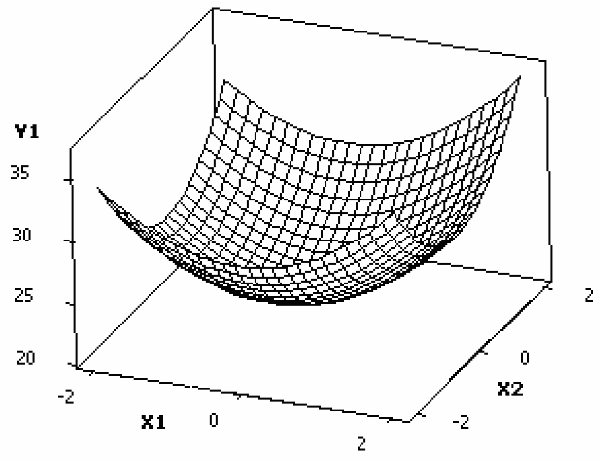


Fig. 2. Surface plot of Y_1 vs. X_1, X_2
(Tensile strength versus HPC: HEC ratio)

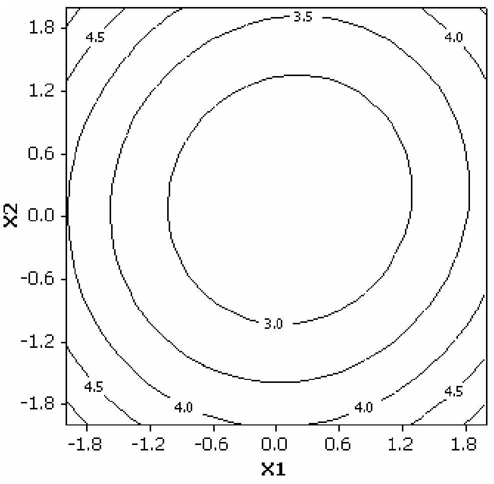


Fig. 3. Contour plot of Y_2 vs. X_1, X_2
(Young's modulus versus HPC: HEC ratio)

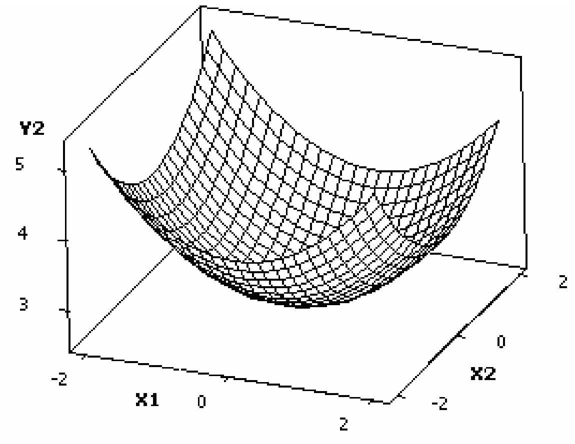


Fig. 4. Surface plot of Y_2 vs. X_1, X_2
(Young's modulus versus HPC: HEC ratio)

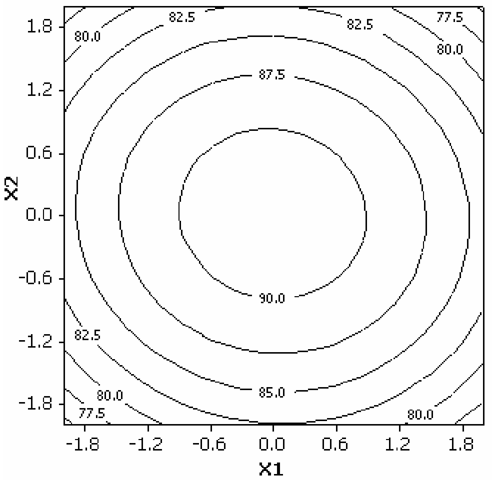


Fig. 5. Contour plot of Y_3 vs. X_1, X_2
(Contact angle versus HPC: HEC ratio).

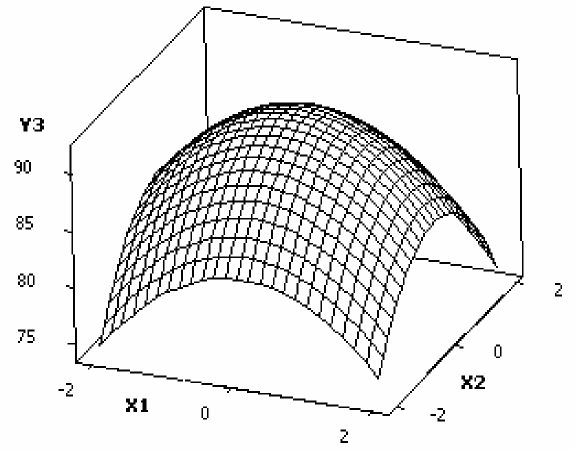


Fig. 6. Surface plot of Y_3 vs. X_1, X_2
(Contact angle versus HPC: HEC ratio).

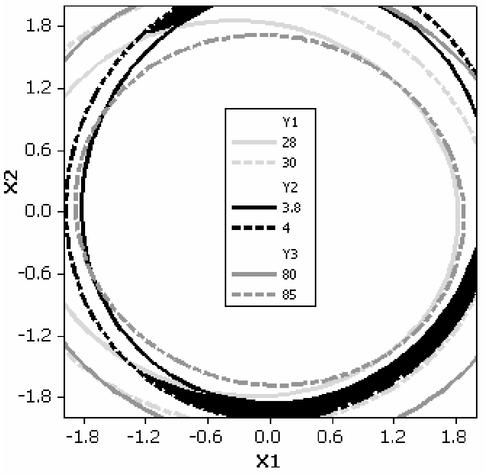


Fig. 7. Contour plot of Y_1, Y_2 and Y_3 vs. X_1, X_2

Following a particular target can be selected a maximum and minimum limit, so that one or more samples to realize this objective. Thus, in Figure 7 is presented a situation in which the desired tensile, Young's modulus and contact angles to fall within certain limits. From the figure, we observe that these conditions are realized, at the same time, in the dark zones (the optimum solution was outside the experimental region confined between +/-$\sqrt{2}$).

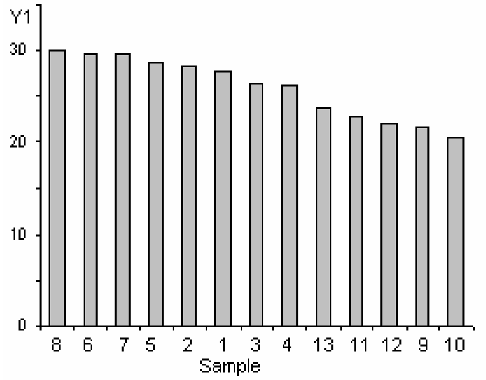


Fig. 8. Pareto chart of Y1 (Tensile strength versus HPC: HEC ratio).

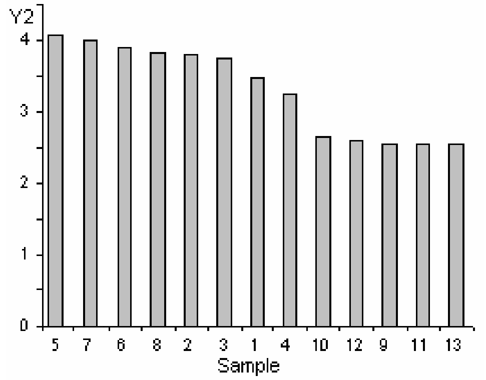


Fig. 9. Pareto chart of Y2 (Young's modulus versus HPC: HEC ratio).

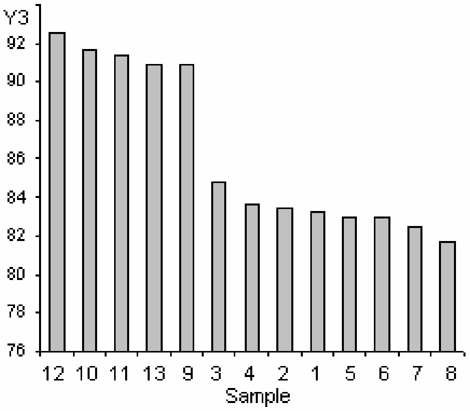


Fig. 10. Pareto chart of Y3 (Contact angle versus HPC: HEC ratio).

In Figs. 8-10 are presented the Pareto charts of Y_1, Y_2 and Y_3, which confirm, another time, the prevue comments attribute of figures 1-7. So, the best results are observed to samples: 8>6>7and >5 for Y_1; 5>7>6>8 for Y_2; and 8>7>6 and >5 for Y_3.

4. Conclusions

Polyurethanes filled with modified cellulose have been prepared by varying the amount of HPC and/or HEC in order to achieve different physico-mechanical and wettability properties. From experimental data were determined the coefficients of empirical equation of two orders with two parameters. Using a limited number of experiments was successfully modelled a compositional polyurethane based on renewable materials (HPC and HEC). Comparing the own experimental and predicted results based on the statistical equation we remarked a good correlation between the both results, experimental and predicted. The diagnostic of the empirical model involve multiple graphical representations (3D surface, contour, Pareto charts, etc). Therefore, this statistical analysis permits a selection of optimum synthesis based on a protocol matrix. So, when high quality of final product is necessary we have possibility to select a synthesis, from protocol matrix, which is suitable for this intention. From graphical representations, a limited number of samples correspond with proposed criteria (maximum of tensile strength and Young's modulus and good hydrophilicity). These samples are, in following order: 8, 6, 7 and 5 for tensile strength - 5, 7, 6 and 8 for Young's modulus and 8, 7, 6 and 5 for hydrophilicity. However, for HPC and HEC amount influence, the optimum solution was outside the experimental region confined between +/-$\sqrt{2}$ (synthesis 5-8), and maximum predicted solution, in this case, were synthesis 8 and 7. These syntheses are suitable for these criteria, and good correlations of experimental and predicted values are remarked.

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