

Mathematical Design of the Experiments for Improving the Properties of Road Bitumen

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A method for obtaining, with low experimental effort, desired properties for road bitumen, was conceived. This method is applicable in those situations when the quality of the road bitumen is understandard, there are no physical interaction between the used components for modification and their concentration varies in very narrow limits.

Keywords: physical modification, road bitumen, polymer, experiments design.

The bitumen performances, especially for road application, can be improved by physical modification [1-14]. The main theoretical problem of the physical modification, is the necessity to find, for a blend with n components and m properties, those formulations that simultaneously ensure, at a minimum experimental effort and price, the required properties for the resulted polymer modified road bitumen.

Usually this problem is empirically solved, „step by step”, and needs, as a rule, a great experimental effort.

The aim of this paper is to present a method that was designed for obtaining, with minimum experimental effort, a preferred composition, that ensure the required properties for the resulted road bitumen. This method can be used in those situations when the quality of the road bitumen is understandard, there are no physical interaction between the components used for physical modification and their concentration varies in very narrow limits.

Experimentals part

Design of the experiments

The first problem that must be solved for the experiments design regards the quantitative blend characterization according to the available reglementations in the field.

The factorial programs can not be used to study the blend answer because the condition according to which the components sum must be equal to 1 must be fulfilled [15, 19]. That is why, an original approach for studing the blend answer was found and will be presented as follows.

For a blend with n components, the main assumptions are:

-each blend component ratio (C_i) must be higher than zero and smaller than 1:

$$0 \leq C_i \leq 1 \quad (1)$$

-the components concentration sum must be equal to 1:

$$\sum_{i=1}^n C_i = 1 \quad (2)$$

-the dependence of a certain property on the blend composition, $Y = f(C_1, C_2, \dots, C_n)$, can be approximate, with a good accuracy, with a polynomial equation by 1, 2, 3 or 4 degree. For instance for a three components blend, depending on the model type, such polynomial equations, can have the following expression:

-the linear model:

$$Y = \beta_1 \cdot C_1 + \beta_2 \cdot C_2 + \beta_3 \cdot C_3 \quad (3)$$

-the square model:

$$Y = \beta_1 \cdot C_1 + \beta_2 \cdot C_2 + \beta_3 \cdot C_3 + \beta_{12} \cdot C_1 \cdot C_2 + \beta_{13} \cdot C_1 \cdot C_3 + \beta_{23} \cdot C_2 \cdot C_3 \quad (4)$$

-the cubic model:

$$Y = \beta_1 \cdot C_1 + \beta_2 \cdot C_2 + \beta_3 \cdot C_3 + \beta_{12} \cdot C_1 \cdot C_2 + \beta_{13} \cdot C_1 \cdot C_3 + \beta_{23} \cdot C_2 \cdot C_3 + \gamma_{12} C_1 \cdot C_2 \cdot (C_1 - C_2) + \gamma_{13} C_1 \cdot C_3 \cdot (C_1 - C_3) + \gamma_{23} C_2 \cdot C_3 \cdot (C_2 - C_3) + \gamma_{123} C_1 \cdot C_2 \cdot C_3 \quad (5)$$

By definition,

$$C_1 + C_2 + C_3 = 1. \quad (6)$$

Considering the cubic mode, that estimates in the most suitable manner, the blending problems, the following equivalences can be assumed:

-the terms $\beta_1 C_1, \beta_2 C_2, \beta_3 C_3$ represent the system answer determined by the individual components, without considering the interactions between them. As consequence, the equation $Y = \sum_{i=1}^n \beta_i C_i$ (7) that represents the linear model, describes the linear effect of the components on the system answer. This can be an acceptable equivalence for many blending situations;

- the terms $\beta_{12} C_1 C_2, \beta_{13} C_1 C_3, \beta_{23} C_2 C_3, \gamma_{12} C_1 C_2 (C_1 - C_2), \gamma_{13} C_1 C_3 (C_1 - C_3), \gamma_{23} C_2 C_3 (C_2 - C_3), \beta_{123} C_1 C_2 C_3$ describes the non-linear effect of the blending, and represents the binary or ternary interactions between components;

-in non-linear blending, a possitive β_{ij} coefficient is an expression of a synergism effect of the blend components and a negative one represents the antagonism between them.

The equation coefficients show the specific contribution of each component to the answer of the system. The determination of the equation coefficients imply nevertheless an important experimental effort. In case of the cubic model this is a difficult task because of the experimental errors that determined the results dispersion.

All the mentioned difficulties are eliminated in case of the linear model. In the equations no. (8-11) the main bitumen properties: penetration (P), ring and ball softening point (I), ductility (D), and elastic recovery (R) will be

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considered. C_1, C_2, C_3, C_4 represent the concentration of the blend components (bitumen, oil and rubber) and $\alpha_i, \beta_i, \gamma_i, \delta_i$ the regression coefficients ($1 \leq i \leq 4$) of the system that describes the physical modified of the road bitumen with the selected additives.

$$P = \alpha_1 C_1 + \alpha_2 C_2 + \alpha_3 C_3 \quad (8)$$

$$I = \beta_1 C_1 + \beta_2 C_2 + \beta_3 C_3 \quad (9)$$

$$D = \gamma_1 C_1 + \gamma_2 C_2 + \gamma_3 C_3 \quad (10)$$

$$R = \delta_1 C_1 + \delta_2 C_2 + \delta_3 C_3 \quad (11)$$

where: $0 \leq C_1 \leq 1, 0 \leq C_2 \leq 1, 0 \leq C_3 \leq 1$.

In the practical bitumen formulation, the prevailing reason that makes possible the utilization of a linear model is the variation of the components concentration in very narrow limits (fig. 1). In this context, because of the lack of the interaction between the bitumen components, for a very small concentration change, the dependence between the blend properties and its composition can be well approximated by a linear one.

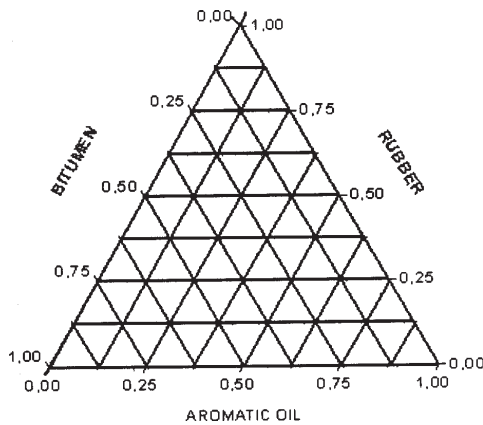


Fig. 1

The present approaches have a distinct working procedure regarding the experiments design and experimental results explanation, which involves the following four steps:

- the identification of the blend components and of the limits of the concentration variation;
- the determination of the regression coefficients;
- the description of the system compatibility or incompatibility;
- the optimization of the system solution.

The identification of the components and of the limits of their concentration variation is made as follows based on literature dates [20,21] and / or previous experience [22] and / or of the preliminary experiments.

The regression coefficients can be find based on particular experiments. For describing these experiments the following symbols will be used:

- $A_1, A_2, A_3 \dots A_n$ for the system components, in order of their introduction into the blend. A_1 is the main component of the blend;
- $C_1, C_2, C_3 \dots C_n$ for the component concentration;
- $P_a, P_b, P_c \dots P_i$ for the studied blend properties.

In the first experimental serie, the properties of the blends that contain two components, A_1 and A_2 , at different C_2 concentration must be measured. After checking the linearity of the dependence between the blend properties and the concentration C_2 , the regression concentration α_1 and β_1 for P_a property are determined. It follows then the determination of the regression coefficients α_2 and β_2 for the P_b property.

In the second experimental series, different quantities from the component A_3 at a concentration from its variation field (C_3), into an $A_1 + A_2$ blend with known and constant composition ($C_2/C_1 = \text{cst}$) are introduced. Then the $P_a, P_b, P_c \dots P_i$ properties of the resulted $A_1 + A_2 + A_3$ blend are measured. If the dependence of the blend properties as a function of C_3 concentration is linear, the regression coefficients for each property are determined. So, the α_1, β_1 and γ_1 regression coefficient for P_a property, then α_2, β_2 and γ_2 for P_b property, and so on, are determined. This type of experiments is repeated for every component of the blend. Each time, the new component A_i (at different concentrations C_i) is introduced in a blend with known and constant composition formed from every previous components ($C_1/C_2/C_3/\dots/C_{i-1} = \text{cst}$).

The values of the regression coefficients obtained in the last experimental series are compared with those obtained in the previous ones. Thus obtained experimental data can be statistically analysed.

As we have already mentioned, this working method is based on the idea that, in the studied concentration field, the linear model can be used. The physical meaning of this hypothesis is that, in this concentration field, the interactions between the blend components can be neglected.

The possibility of the determination of regression coefficients for penetration, one of the main road bitumen properties, is presented in tables 1-3 and figures 2-3.

The regression coefficients are determined by the slope of the penetration regression line (fig.3) and their values are presented in table 3.

The regression coefficients for the other road bitumen properties like softening point and ductility, in the same manner, are determined (softening point - figures 4, 5 and tables 4, 5, 6; ductility - figures 6, 7 and tables. 7, 8, 9). The regression coefficients for softening point are presented in table 6 and those for ductility in table 9.

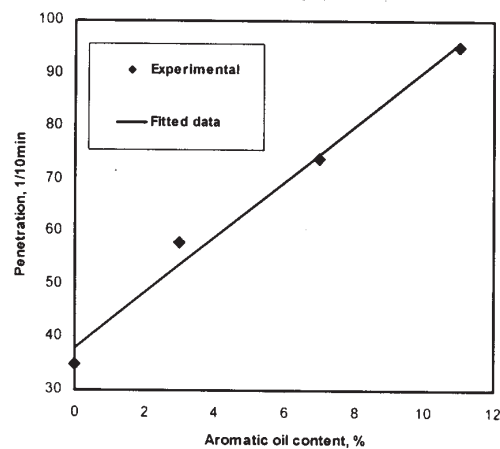


Fig. 2

Table 1

Aromatic oil content, %	0	3	7	11
Penetration, 1/10 min	35	58	74	95

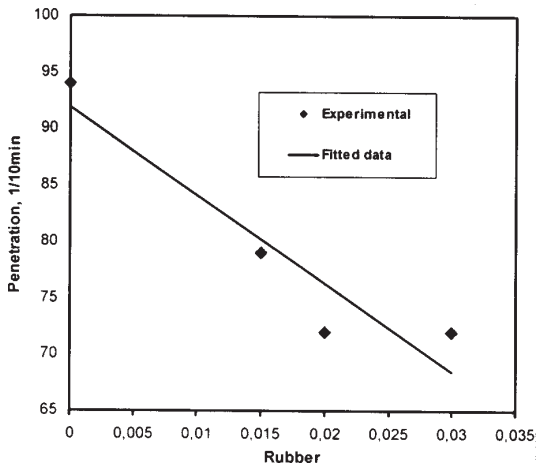


Fig. 3

Rubber content, %	0	1,5	2	3
Penetration, 1/10 min	94	79	72	52

α_1 (bitumen)	α_2 (aromatic oil)	α_3 (rubber)
43,1	525,8	-1324

Aromatic oil content, %	0	3	7	11
Softening Point, $^{\circ}\text{C}$	57	54,7	48	45

Rubber content, %	0	1,5	2	3
Softening Point, $^{\circ}\text{C}$	45	50	56	61

β_1 (bitumen)	β_2 (aromatic oil)	β_3 (rubber)
57,3	-113,7	505,3

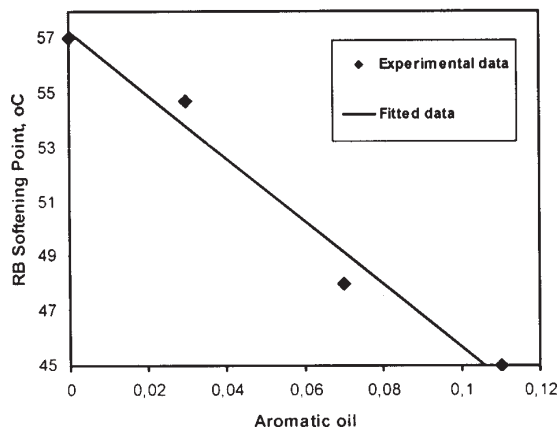


Fig. 4

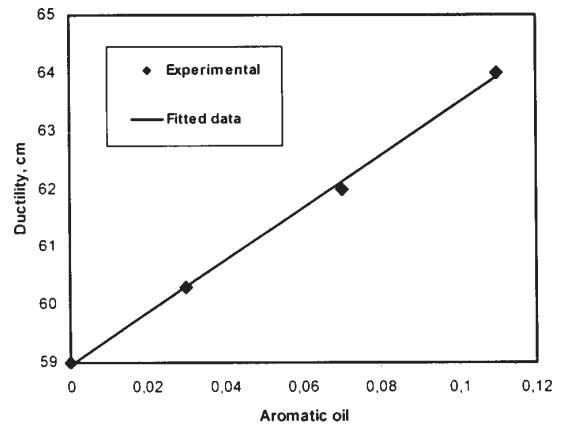


Fig. 6

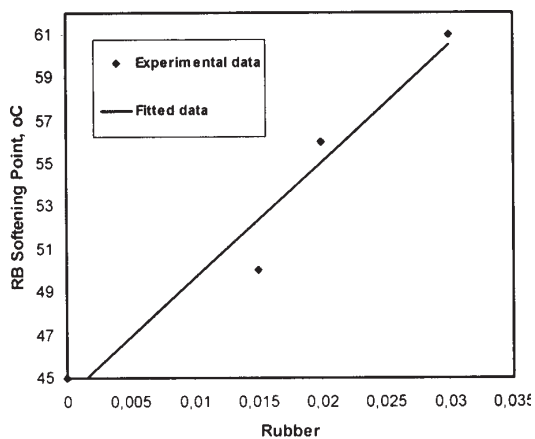


Fig. 5

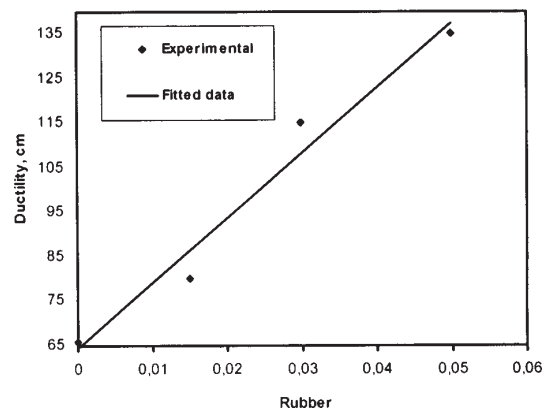


Fig. 7

Table 7

Aromatic oil content, %	0	3	7	11
Ductility, cm	59	60,3	62	64

Table 8

Rubber content, %	0	1,5	3	5
Ductility, cm	66	80	115	135

Table 9

γ_1 (bitumen)	γ_2 (aromatic oil)	γ_3 (rubber)
57,3	-113,7	505,3

Estimation of the system compatibility

In the considered systems, the unknown numbers (m), are different of those of equations (n). If $n > m$, the system can be incompatible. This means that the system containings those m equations has not a common solution. As a function of the way in which the system equations were chosen, different values for m unknowns are obtained.

Practically the system can be incompatible because of the following three main reasons:

- the blends properties can not be reached simultaneously by all the m components of the blend;
- the dependence of the blend properties by the components concentration is an unlined one, even for small concentration variation;
- the improper values of regression coefficients because of the measurements errors.

Considering the equations (8-11) and the conditions (6) according to which $C_1 + C_2 + C_3 = 1$ the dependences no (12-15) can be obtained .

$$\left\{ \begin{array}{l} (\alpha_1 - \alpha_2)C_1 + (\alpha_2 - \alpha_3)C_2 = P - \alpha_3 \\ (\beta_1 - \beta_2)C_1 + (\beta_2 - \beta_3)C_2 = I - \beta_3 \\ (\gamma_1 - \gamma_2)C_1 + (\gamma_2 - \gamma_3)C_2 = D - \gamma_3 \\ (\delta_1 - \delta_2)C_1 + (\delta_2 - \delta_3)C_2 = R - \delta_3 \end{array} \right. \quad (12)$$

$$\left\{ \begin{array}{l} (\beta_1 - \beta_2)C_1 + (\beta_2 - \beta_3)C_2 = I - \beta_3 \\ (\gamma_1 - \gamma_2)C_1 + (\gamma_2 - \gamma_3)C_2 = D - \gamma_3 \\ (\delta_1 - \delta_2)C_1 + (\delta_2 - \delta_3)C_2 = R - \delta_3 \end{array} \right. \quad (13)$$

$$\left\{ \begin{array}{l} (\gamma_1 - \gamma_2)C_1 + (\gamma_2 - \gamma_3)C_2 = D - \gamma_3 \\ (\delta_1 - \delta_2)C_1 + (\delta_2 - \delta_3)C_2 = R - \delta_3 \end{array} \right. \quad (14)$$

$$\left\{ \begin{array}{l} (\delta_1 - \delta_2)C_1 + (\delta_2 - \delta_3)C_2 = R - \delta_3 \end{array} \right. \quad (15)$$

The system that contains the 4 equations (12-15) has 2 unknown variables, C_1 and C_2 . This system is compatible if the conditions imposed by Rouche' theorem [23] is carried out. Because of the experimental errors, this theorem is impossible to be used.

In practice, the system compatibility is verified considering the equations system defined by the components number and the analysed properties. For its solving, at the beginning, two equations will be considered. After finding the solution, another two equations will be solved. The procedure is repeated till all the equations were considered. The system is compatible if the equations solutions are not dependent, in an acceptable experimental errors limits, by the chosen manner of the two equations pairs that are consequently solved for determining the system compatibility.

In case of physical bitumen modification, the simple form for the equations (12) and (13) will be first considered. Taking into account the experimental values of regression coefficients, the $\alpha_1 - \alpha_3$, $\alpha_2 - \alpha_3$, $\beta_1 - \beta_3$, $\beta_2 - \beta_3$ differences will be replaced with their numerical values.

In this manner the equations (16)-(17) will be obtained.

$$1367 \cdot C_1 + 1850 \cdot C_2 = 1384 \quad (16)$$

$$443.23 \cdot C_1 + 618 \cdot C_2 = 455.267 \quad (17)$$

The system has the following solutions: $C_1 = 0,85$; $C_2 = 0,12$ and $C_3 = 0,03$.

In the second and the third steps, the equations (13)-(14) and (14)-(15) respectively will be considered.

The results that were obtained for C_1 , C_2 and C_3 by solving the equation (12)-(13) / (13)-(14) / (14)-(15) are:

-for equations (12)-(13) the solutions are: $C_1 = 0.85$; $C_2 = 0.12$; $C_3 = 0.03$;

- for equations (13)-(14) the solutions are: $C_1 = 0.848$; $C_2 = 0.121$; $C_3 = 0.031$;

- for equations (14)-(15) the solutions are: $C_1 = 0.845$; $C_2 = 0.123$; $C_3 = 0.032$.

These results show that the studied system is compatible.

Application of the designed method

The experimental method was applied for finding the best physical modification solution for Romanian oxidation road bitumen and also for a distilled one. The results will be presented in a future paper.

Conclusions

A new experimental method that makes easier the effort to find the optimum formulation for polymers road bitumen physically modified was elaborated.

The main theoretical approach of the new experimental method is that for very small change of the components concentration, the synergetic or antagonic effects from the blend components can be neglect.

The new method is based on a well defined manner for running the experiment. The regression coefficient of the linear model for blends is determined with smaller experimental effort.

Practical application of the new experimental method for road bitumen leads to remarkable results. These results will be presented in a future paper.

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