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PREDICTION OF IRREVERSIBLE SUSCEPTIBILITY AND ELASTIC RECURRENCE OF ASPHALTS MODIFIED WITH WASTE PLASTOMERS IN MSCR STUDY

PROGNOZOWANIE NIEODWRACALNEJ PODATNOŚCI I NAWROTU SPRĘŻYSTEGO ASFALTÓW MODYFIKOWANYCH PLASTOMERAMI ODPADOWYMI W BADANIU MSCR

STRESZCZENIE. W artykule dokonano oceny możliwości prognozy charakterystyk mikrostruktury nieodwracalnej części modułu podatności i procentowego nawrotu w badaniu MSCR za pomocą podstawowych właściwości asfaltu. W badaniach poddano kontrolowaniu 7 zmiennych. W ramach badania zastosowano dwa typy asfaltów 20/30 i 70/100 oraz dwa rodzaje plastomeru odpadowego. Cały proces badawczy został podporządkowany planowi Placketta-Burmana. Rezultaty wzbogacono o analizę mikrostruktury dyspersji plastomeru odpadowego w asfalcie. W rezultacie stwierdzono, że wpływ mikrostruktury na nieodwracalną część modułu podatności i procentowego nawrotu nie był znaczący. Natomiast proces mieszania istotnie wpływał na stan rozproszenia cząstek plastomeru w asfalcie. Dzięki technice MARS udało się powiązać podstawowe cechy asfaltu, takie jak penetracja, temperatura mięknienia, temperatura łamliwości oraz lepkość dynamiczna z nieodwracalną częścią modułu podatności i procentowym nawrotem ze skutecznością wyrażoną przez współczynnik determinacji R2=99%. Wskazano również, że rodzaj plastomeru odgrywa znaczącą rolę w kształtowaniu wartości procentowego nawrotu asfaltu.

SŁOWA KLUCZOWE: modyfikacja asfaltu, plastomer odpadowy, MARS, morfologia polimeru, recykling.

ABSTRACT. This paper evaluates the possibility of predicting the microstructure characteristics of the irreversible part of the susceptibility modulus and the percentage recurrence in the MSCR test by means of basic asphalt properties. Seven variables were controlled in the research. Two types of asphalt 20/30 and 70/100 and two types of waste plastomer were used for the research. The entire research process was governed by the Plackett-Burman plan. The results were enriched by microstructure analysis of the waste plastomer dispersion in asphalt. As a result, it was found that the effect of microstructure on the irreversible part of the susceptibility modulus and percentage recurrence was not significant. In contrast, the mixing process significantly influenced the dispersion state of the plastomer particles in the asphalt. With the MARS technique, it has been possible to relate basic asphalt characteristics such as penetration, softening temperature, fracture temperature and dynamic viscosity to the irreversible part of the susceptibility modulus and percentage recurrence with efficiency expressed by a determination coefficient of R2=99%. It was also pointed out that the type of plastomer plays a significant role in shaping the percentage of asphalt conversion.

KEYWORDS: asphalt modification, waste plastomer, MARS, polymer morphology, recycling.

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1. INTRODUCTION

Bitumen binders are by-products obtained during the distillation of crude oil. They are thermoplastic materials and play a crucial role in determining the durability [1] and rheological properties [2] of mineral-bitumen mixtures. Currently, bitumen is predominantly used in the production of mineral-bitumen mixtures through the "hot mix" technology, which is energy-intensive and environmentally unfriendly. An alternative gaining traction worldwide in recent years is the production of mixtures using "warm mix" or "half-warm mix" technology. Research indicates that lowering process temperatures and utilizing water foaming contribute to reducing the negative aging process of the binder, significantly affecting the durability of bitumen surfaces [3].

Due to the nature of their work, bitumen pavements are subject to destructive processes. The vast majority of damage occurring on bitumen surfaces results from the impact of both high and low temperatures, cyclic loading on the pavement structure, and the aging of the bitumen. Therefore, the binder should exhibit high parameters; otherwise, its inadequate quality may lead to additional financial expenses associated with repair costs. The most well-known and widely used method to enhance the rheological and functional properties of bitumen, aiming to obtain high-quality binders, is the introduction of polymers into the bitumen matrix [2, 4]. The most commonly known method of bitumen modification is the use of elastomers, for example: SBS [5]. Its introduction into the bitumen structure significantly expands the viscoelastic range of the base bitumen, providing excellent usability at low temperatures [6, 7]. On the other hand, the use of polymers from the plastomer group significantly increases its resistance to permanent deformation [8]. In the case of bitumen modification with a plastomer, the polymer should be chosen so that its softening temperature is below the mixing temperature, typically in the range of 160–170°C [9, 10]. If a hard plastomer is used, its presence results in an increase in the softening temperature, lower stability, and resistance to rutting in MMA, as well as lower resistance to low temperatures in the mineral-bitumen mixture. However, the final properties of polymer-modified bitumen depend on the type and properties of the polymer, bitumen, their mutual proportions, and, significantly, the mixing process [11]. The reactivity and chemical structure of the polymer affect its compatibility with bitumen, influencing the quality of the mixture [12]. During bitumen modification by a plastomer, situations may arise where component segregation occurs due to the high molecular weight of the polymer, its polarity, or insufficient maltene fraction in the bitumen [13]. The mixing process itself may be disturbed by a high mixing temperature maintained for an extended period, causing additional aging of the bitumen resulting from the degradation of the maltene fraction and even polymer oxidation [14]. Consequently, there is a rapid decrease in the stability during the mixture's storage. One solution to the problem of low storage stability is to reduce the proportion of non-polar polymer chains by using, for example, butyl acrylate or a reactive polymer [15, 16]. On the other hand, bitumen modification with a plastomer introduces additional polar groups due to the higher modification temperature than a regular elastomer, resulting from aging, causing increased compatibility of the components [17]. Therefore, the technological modification process is an extremely important factor to consider during the homogenization of bitumen and plastomer.

Currently, special attention is given to the possibility of using various types of polymers, considering their origin and chemical composition. It is worth noting that the introduction of recycled polymer materials was a significant part of the EATA 2023 conference. Successful attempts at modifying bitumens with PEHD, PELD, and PET have been discussed in the presented publications [18]. There are numerous methods for plastomer recycling, including storage, sorting, and shredding, as well as chemical methods like pyrolysis and gasification. However, the most popular method is the mechanical one mentioned one, providing material in the form of pellets with varying granularity [19]. There are many plastomers available in the market, among which two are particularly popular and widely available. The first is polypropylene (PP), and the second is polyethylene terephthalate (PET).

Polypropylene (PP) currently constitutes 21% of the global polymer production and 19% of production in Europe [20]. It is used in the manufacturing of automotive parts, food packaging, and pipes. Several studies indicate a decrease in the storage stability of bitumen modified with PP [21]. However, contrary findings are mentioned in the article [22], some authors suggest adding a certain amount of polyphosphoric acid to enhance storage stability [15]. Nevertheless, there are promising studies suggesting that the use of PP may have a favourable impact on bitumen modification [2].

PET is the polymer used in most water bottles and food packaging. Its wider use is limited by its price. has a broader range of applications, limiting its cost. It is characterized by a high softening temperature, making its homogenization more challenging compared to other plastomers [2]. Nevertheless, many authors confirm its beneficial effect on bitumen properties [23]. Additionally, studies indicate its positive influence on the resistance to permanent deformation in mineral-bitumen mixtures, especially in the dry mixing process [24]. The use of PET as a plastomer is considered a good choice for bitumen modification.

According to the authors' best knowledge, there are very few published comprehensive studies related to the use of plastomers, taking into account their modification process, utilization, and comparative data, which would allow for their application in road construction. The utilization of plastomers currently poses a challenge in the European Union concerning environmental protection, attracting the attention of many researchers in terms of their implementation in road construction [25]. In this context, the present paper provides information on the process of modifying bitumen with waste plastomers and its impact on the irreversible part of the susceptibility module and percentage recovery according to the MSCR methodology. In practice, conducting MSCR studies requires specialized research equipment. However, basic bitumen features can be quickly determined in almost any road laboratory. The proposed model will facilitate an effective assessment of whether a given bitumen modified with selected plastomers (PP and PET) influences the increase in resistance to rutting when introduced into MMA. Furthermore, the explicit form of the proposed model will allow for determining the level of required basic bitumen properties that will enable obtaining bitumen with the desired value of the irreversible part of the susceptibility module and percentage recovery.

2. MATERIAL AND METHODS

2.1. WASTE PLASTOMERS

The modification of the properties of road bitumen was carried out by adding two waste plastomers, where the first was PET (polyethylene terephthalate), and the second was PP (polypropylene). The utilized synthetic materials belong to the group of thermoplastic materials with a crystalline structure, with PET characterized by a high softening temperature compared to PP. According to the supplier's declarations, the PP polymer was characterized by a flow temperature Tp = 165°C and glass transition temperature of Tz=-10°C, while PET had a Tp= 256°C and Tz=-75°C respectively.

2.2. BITUMEN

The adopted methodology of the experimental plan required the use of two different types of bitumen. Their selection was driven by the need to replicate different rheological states of bitumen. Therefore, for the study, "gel" type bitumen with a penetration range of 20/30 and "sol-gel" with a penetration of 70/100 were chosen. In the analysis, a commercially available bitumen modified with SBS copolymer type PmB 45/80-55 was also used as a reference base. All bitumens underwent

Table 1. Test results for road bitumen

Feature	Road bitumen		Reference bitumen	Norm
	20/30	70/100	PmB 45/80-55	
Penetration at 25°C, 0.1 mm	27.4±2.1	91.5±3.1	66.6±2.8	PN-EN 1426 [26]
Softening temperature $T_{R\&B}$, °C	61.3±1.2	44.7±0.7	63.7±2.5	PN-EN 1427 [27]
Fracture temperature, °C	-10.4±2.2	-15.4±2.0	-17.7±1.8	PN-EN 12593 [28]
Dynamic viscosity at 135°C, Pas	1.43±0.01	0.32±0.01	3.32±0.01	ASTM D 4402 [29]

basic rheological tests. The research results, along with a 95% confidence interval, are presented in Table 1.

2.3. PLACKETT-BURMAN EXPERIMENT DESIGN

A crucial aspect of any experiment is the selection of an appropriate sampling system, as it determines how measurement errors will be controlled. It is essential to consider the balance between the number of factor combinations and their quantity. Due to the need to account for a large number of factors, the Plackett-Burman design was the optimal choice for pilot studies. The Plackett-Burman design (P–B) represents a special case of saturated orthogonal factorial designs. P–B is characterized by the number of experiments (N) being different from the number of independent variables k increased by 1 [30]. P–B is an elimination plan designed to preliminarily reduce independent variables that do not significantly contribute to predicting the dependent variable. Therefore, its aim is to reduce the dimensionality of the problem at hand. The P–B model is based on a multiple regression equation without interactions, as presented below (1):

$$y = b_0 + b_1 \cdot x_1 + \ldots + b_n \cdot x_n + \varepsilon \,, \quad (1)$$

where:
b_0 – regression coefficient (for j>0),
x_1 – independent variable (input factor),
y – dependent variable,
ε – estimation error.

Estimating the impact of all effects (independent variables) using the least squares method is orthogonal concerning the number N with uniform precision. The variance required to determine the significance of the model coefficients can be estimated based on additional experiments. In this case, the entire experiment must be replicated at least once. Experiment replication was necessary because random errors are unavoidable with such a large number of input variables. This plan assumes the absence of interaction effects between variables. In their presence, the estimation error of the model (1) would take large values, and the coefficient of determination R^2 would decrease rapidly.

Input variables in the P–B elimination design take values at two levels. For quantitative variables, these were the minimum and maximum values, while qualitative variables included two states on at least an ordinal scale (e.g., 0 and 1). The number of experiments in the P–B plan for two levels is a multiple of 4, so the number N is at least 8. Therefore, the smallest feasible plan must consider 7 independent variables. This is the number of variables used to control the course of the experiment. The variables and their corresponding levels are presented in Table 2.

The initial definition of value ranges assigned to individual variables was based on a review of literature [32, 33]. For quantitative variables, the range was established to replicate both high-speed and low-speed mixing processes. The content of plastomer was limited to 5% to avoid the possibility of excessive dynamic viscosity (>3Pas) at a temperature of 135°C [34] at low and intermediate temperatures, and the flow behaviour, at high temperatures, of polymer modified bitumen (PMB). Additionally, the experiment considered the influence of plastomer fragmentation. Therefore, for pilot studies, a material with grain size in the state supplied by the manufacturer (>5.6mm) was adopted, and an individually granulated fraction <5.6mm was also included. The final experimental plan, accepted for further analysis, comprised 8 combinations of factors with a replicated sample at least twice. The adopted experimental plan is presented below (Table 3).

Table 2. Structure of Variables in the Plackett-Burman Experimental Design [31]

No.	Variable	Type of variable	Unit	Code	Low level	High level
1	Mixing speed	quantitative	rpm^{-1}	A	120	9500
2	Mixing temperature	quantitative	°C	B	160	180
3	Mixing time	quantitative	min.	C	30	180
4	Plastomer content	quantitative	%	D	2	5
5	Bitumen	qualitative	-	E	20/30	70/100
6	Plastomer	qualitative	-	F	PP	PET
7	Granulation	qualitative	-	G	<5.6 mm	>5.6 mm

Table 3. Adopted combinations of factors within the P-B design

Combination	Combinations of independent variables						
	A	B	C	D	E	F	G
	rpm^{-1}	°C	min	%	-	-	-
1s	120	160	30	5	70/100	PP	<5.6
2s	9500	160	30	2	20/30	PP	>5.6
3s	120	180	30	2	70/100	PET	>5.6
4s	9500	180	30	5	20/30	PET	<5.6
5s	120	160	180	5	20/30	PET	>5.6
∂x	9500	160	180	2	70/100	PET	<5.6
7s	120	180	180	2	20/30	PP	<5.6
8s	9500	180	180	5	70/100	PP	>5.6

In the experiment plan, three qualitative variables were appropriately encoded to appear in at least an ordinal scale. Otherwise, determining their significance in a linear model would be impossible. Accordingly, the 'plastomer' variable for the PP-type polymer assumed the value of 1, while the PET type was assigned the value of 0. Concerning the "Bitumen" variable, the adhesive 70/100 was assigned the value of 1, while 20/30 had the value of 0. The last variable, "Granulation," received the value of 1 for the state "<5.6," and the value of 0 for the second state.

2.4. MARS METHOD

Multivariate Adaptive Regression Splines (MARSplines) is a nonparametric statistical regression method used in data mining tasks. It allows for the quick estimation of modelling complex, nonlinear relationships with a large number of independent variables [35]. The advantage of this modelling is obtaining an explicit model that can be directly implemented, unlike other data mining solutions where the result is a file with a set of weights. The MARS method utilizes the division of the variability space of independent variables (predictors, explanatory variables) into intervals in which they have different effects on the values of the dependent variable. Points where a change in the type of influence occurs are called knots. Therefore, the obtained MARS model is a sum of products of basic functions. Thus, the MARS model is additive, consisting of the sum of basic functions h for the predictor y in the form of equations (2) and (3):

$$h_{+}(t;x)=\begin{cases}0 \text{ dla } x<t \\ x-t \text{ dla } t\geq t\end{cases}=\max(0;x-t) \qquad (2)$$

or

$$h_{-}(t;x)=\begin{cases}t-x \text{ dla } x<t \\ 0 \text{ dla } x\geq t\end{cases}=\max(0;t-x) \;. \qquad (3)$$

The obtained model using the MARS technique is essentially a spline function that, through an appropriate number of knots, allows for the accurate representation of strongly nonlinear issues or those for which the selection of monotonic functions would be impossible, much like spline functions, it has the same limitations. These include a high sensitivity to outliers causing excessive fitting to measurement errors. It is also essential to pay attention to collinearity between features during model construction. One undeniable advantage of using the MARS model is the ability to utilize variables that do not follow a normal distribution and the rapid elimination of insignificant variables. In the MARS model, irrelevant variables are eliminated by a specified threshold value to achieve minimal GCV error (generalized cross-validation error) and maximum coefficient of determination R^2 [36]. The GCV error in the model implementation process is calculated based on the classic MSE error (mean square error) and takes into account the complexity (coefficient C). Its form is shown below (4):

$$GCV = MSE\frac{1}{\left(1-\frac{C}{N}\right)^{2}}\;, \qquad (4)$$

where:

MSE – the average squared estimation error,

C – a measure of the model's complexity proportional to its components,

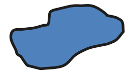
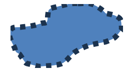
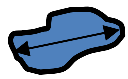
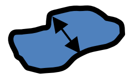
N – the number of cases.

2.5. RESEARCH METHODS FOR MODIFIED BITUMEN

The process of studying the impact of bitumen modification by selected plastomers began with conducting basic tests. The tests were carried out according to the sampling plan outlined in Table 3. The list of tests along with the assigned set of standards and the code designation is presented below:

- Softening temperature (TR&B) according to EN1427 [27],
- Penetration (Pen, 0.1mm) according to EN 1426 [26],
- Fracture temperature (TFraass) according to EN 12593 [28],
- Dynamic viscosity (eta@135degC) at 135°C according to ASTM D4402 [29],

Table 4. Characteristics for describing the shape of polymer particles

Surface area (Surface area, (10e-6) m^2)	
Circumference (Circumference, (10e-6) m)	
Coefficient of oblongness [40] described by equation (6)	$\text{Coefficient of oblongness} = 4 \cdot \pi \cdot \frac{\text{Surface Area}}{\text{Circumference}^2}$ (5)
Long diagonal of the ellipse describing the plastomer particle (long diagonal)	
Short diagonal of the ellipse describing the plastomer particle (short diagonal)	

- Irreversible compliance modulus (Jnr) and percentage recovery (R) for shear stress of 100Pa (Jnr 0.1) and 3200Pa (Jnr 3.2) at temperatures of 50°C, 60°C, 70°C, and 80°C, according to the MSCR study [37],
- The difference in the irreversible compliance modulus (Jnr diff) and percentage recovery (R diff),
- Evaluation of the dispersion structure of the polymer in the bitumen [38].

Photographs obtained during the evaluation of polymer dispersion in polymer-modified bitumens were supported by image analysis using the ImageJ program [39]. This was necessary to perform a detailed quantitative analysis of polymer particle dispersion in the bitumen. For all particles observed in the bitumen samples under a fluorescence microscope, the following characteristics were determined (Table 4).

3. TESTS AND ANALYSES RESULTS

3.1. THE INFLUENCE OF THE MIXING PROCESS ON THE DISPERSION STRUCTURE OF THE PLASTOMER IN THE BITUMEN

One of the important cognitive aspects was to determine how the mixing process affects the formation of the dispersion structure of polymer particles in the bitumen. The assessment of the impact was based on the P–B plan (Table 3) using a classical regression approach, considering the model (1). The results of the significance assessment of the factors at a significance level of 0.05 are presented in Table 5.

The results presented in Table 5 suggest that all process factors had a significant impact in at least one pair of combinations

Table 5. Evaluation of the significance of model parameters

Parameter	Dependent variable		
	Circumference, μm	Surface area, μm^2	Coefficient of oblongness
Intercept	<0.0001	<0.0001	<0.0001
Mixing speed, rpm	<0.0001	<0.0001	<0.0001
Bitumen temperature, deg. C	<0.0001	<0.0001	<0.0001
Mixing time, min	<0.0001	<0.0001	0.0007
Plastomer content, %	<0.0001	<0.0001	<0.0001
Plastomer	<0.0001	<0.0001	<0.0001
Bitumen	0.0063	<0.0001	<0.0001
Granulation	<0.0001	<0.0001	0.00004
R^2	0.27	0.25	0.1

(1s÷8s) concerning the designated characteristics of the microstructure of waste polymer in bitumen. However, based on this analysis, it is not possible to determine in detail how the structure of polymer dispersion in bitumen changes. A precise comparison of microstructure differences of polymer dispersion in bitumen is presented in Figure 1 and Fig. 2, utilizing basic statistical characteristics (median, 1st and 3rd quartiles) along with grouping based on the mixing process combinations.

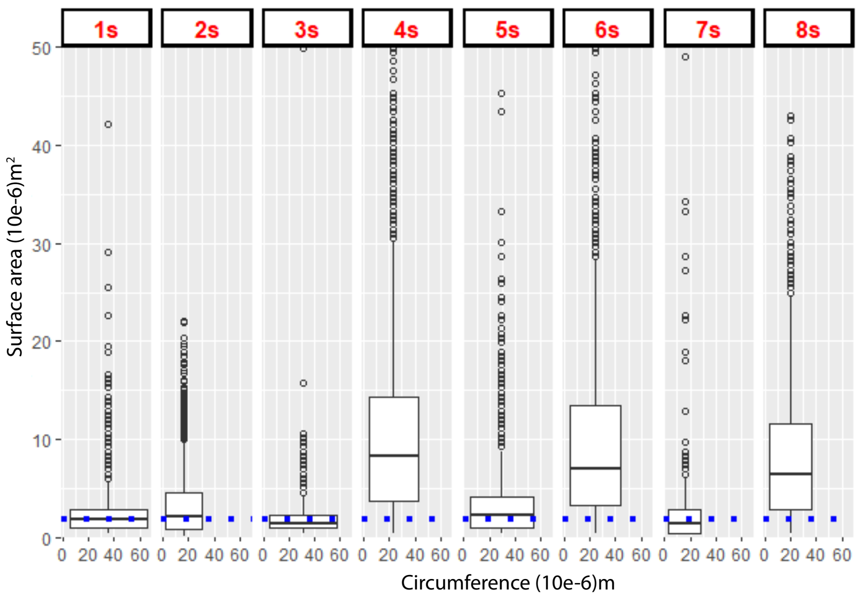


Fig. 1. Relationship between the surface area and circumference of polymer particles

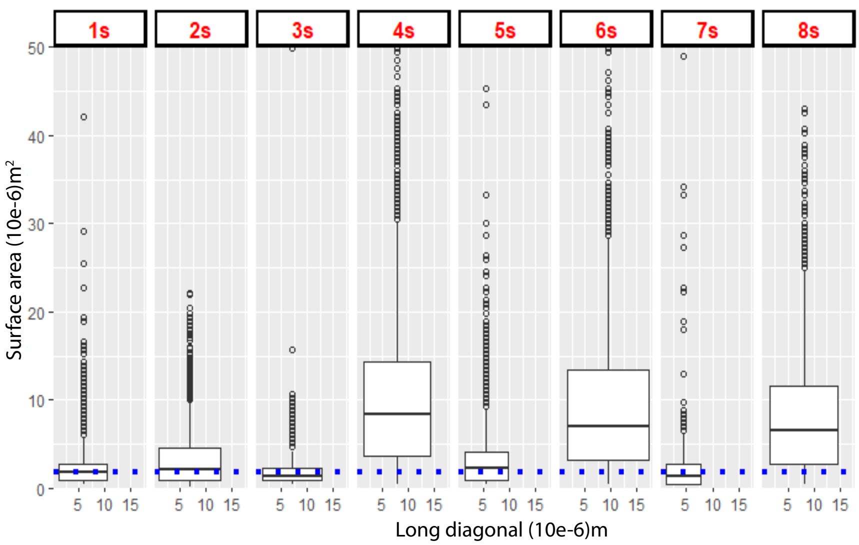


Fig. 2. Relationship between the surface area and the long diagonal of the ellipse describing the plastomer particle

The results presented in Fig. 2 indicate that, in most cases, the particle surface area is at a comparable level to the overall median (1.85 µm²) calculated for the entire set of studies. Only combinations 4s, 6s, and 8s (according to Table 3) had particles with an average specific surface area greater than the overall median of the set and were characterized by the largest dimension of the longer diagonal of the particle. Comparing these combinations with the results of the perimeter (Fig. 1), it can be observed that cases 4s, 6s, and 8s contain plastomer particles with a large surface area and a cubic shape. The common denominator for these bitumen combinations was that they were mixed at a speed of 9500 rpm, the polymer used had a coarse-grained character (>5.6mm), and PET plastomer was applied. Therefore, it can be concluded that such a high mixing speed and high temperature cause the deposition of the polymer on the blender walls and its further coagulation.

The smallest dimension of the particle with the smallest perimeter was observed in combinations 2s and 7s. These combinations have two common features: PP was used, and its amount was 2%. In the case of these combinations, the range of the perimeter values is clearly smaller than in the other cases. It should be noted that PP is a plastomer with a lower softening temperature, so its breakdown is easier than PET. On the other hand, the use of 70/100 bitumen and the use of low rotational speed (120 rpm) in combinations 1s and 3s caused the formation of a large number of irregular particles, which were characterized by a high perimeter value relative to the surface area. In conclusion, to obtain the smallest dimension of a plastomer particle in bitumen, controlling the mixing speed and the granulation of the plastomer will be crucial in shaping the morphology of bitumen modified with a plastomer.

It should also be emphasized that the assessment of the significance of the influence of mixing process factors on features characterizing the microstructure of bitumen modified with a plastomer was carried out with a low coefficient of determination value $R^2 < 0.27$ (Table 5). This means that a series of factors other than those related to the mixing process are responsible for the structure of the plastomer in bitumen. Contact phenomena between bitumen and plastomer as well as changes in the chemical composition of the bitumen/plastomer phase are essential.

3.2. CORRELATIONAL RELATIONSHIPS BETWEEN FEATURES OF BITUMEN MODIFIED WITH A PLASTOMER

As mentioned earlier, the mixing process was not the only factor influencing the structure of plastomer dispersion in bitumen. The conclusion was formulated that there are other factors that shape the microstructure of bitumen. Therefore, it can be hypothesized that the variability of values of the irreversible part of the modulus of susceptibility (Jnr) as well as the percentage recovery (R) will be dependent not only on the mixing process. The natural next step in the analysis was to build a correlation matrix covering the designations: properties of bitumen modified with a plastomer, its microstructure, and mixing process factors. The correlation matrix is presented graphically in Fig. 3.

The legend below Fig. 3 indicates the strength and direction of the correlation. The oblong shape of the ellipse suggests a low correlation between variables, while a shape close to a straight line suggests a high correlation. This chart allows for a quick assessment of the level of correlation between variables enriched with numerical values. Empty fields indicate an insignificant value of the correlation coefficient; therefore, these values have been omitted. An interesting observation is the very low value of the correlation coefficient between the irreversible part of the modulus of susceptibility and the percentage recovery with characteristics of the plastomer dispersion structure in bitumen samples. This confirms the previous hypothesis about the weak connection between the microstructure of bitumen combinations and their rheological properties. However, both characteristics of the MSCR test show moderate correlation with basic bitumen properties such as Fraass temperature, softening temperature, and penetration. The correlation of Jnr 3.2 with dynamic viscosity at 135°C is also noteworthy. The property Jnr 3.2 also exhibits a strong negative correlation between plastomer content, its granulation, and the type of plastomer. Taking into account the encoding of qualitative variables, an increase in Jnr 3.2 can be achieved by using finely granulated PET plastomer in an amount below 5%. On the other hand, the value of the R feature increased when using coarse-grained granulation of plastomer (>5.6mm) in an amount of >3% of PP type. Therefore, the type of plastomer, its chemical properties, and its softening temperature are crucial in predicting rheological features in the MSCR test. It is worth emphasizing that the factors

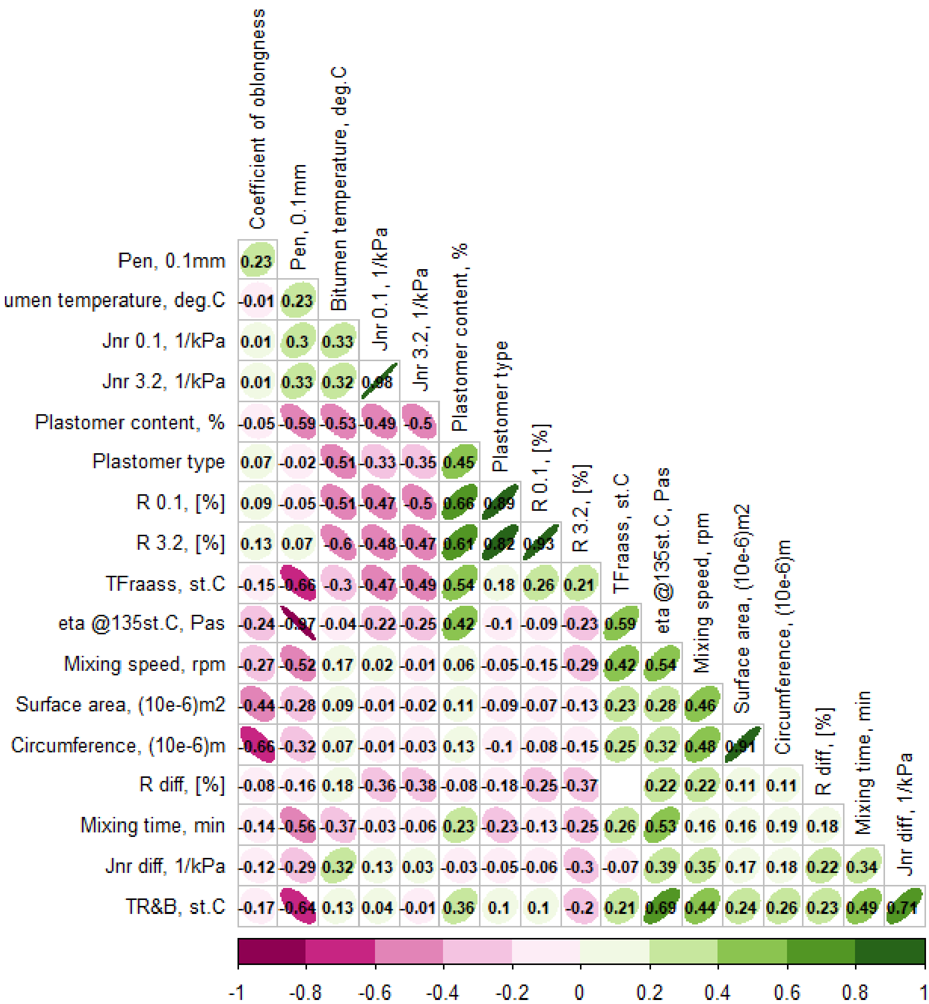


Fig. 3. Correlation matrix

of the mixing process are strongly correlated with the basic properties of bitumen modified with a plastomer. Therefore, there is a real possibility of predicting the variability of the Jnr 3.2 and R features using basic bitumen properties that link numerous physical and chemical phenomena that occur during the mixing of bitumen with a plastomer.

3.3. INFLUENCE OF THE MIXING PROCESS ON THE IRREVERSIBLE PART OF THE CREEP COMPLIANCE AND PERCENTAGE RECOVERY ACCORDING TO THE MSCR

For all combinations of mixing process factors carried out according to the Plackett-Burman plan, a study of creep compliance and recovery was performed according to the MSCR methodology at a shear stress of 3200Pa. This shear stress range reproduces the nonlinear range of bitumen deformation and correlates very well with the resistance of the bitumen mixture to permanent deformation [41] adding to the complexity of asphalt binder behaviour that requires more time, effort, and material resources during laboratory work. The purpose of this research was to use Artificial Neural Networks (ANNs). The tests were conducted at four temperatures: 50°C, 60°C, 70°C, and 80°C. The results of the average values obtained, together with an additional projection of the results for the reference bitumen: 20/30, 70/100 and PMB 45/80-55 are shown in Fig. 4.

Analysing the research results, it is evident that the application of plastomer in any mixing process significantly altered the rheological properties of bitumen compared to reference bitumens. At temperatures below 70°C (Fig. 4), almost all combinations achieved an irreversible part of the creep compliance required for very heavy traffic (Jnr3.2 < 1.0 kPa-1) [42]. Undoubtedly, bitumen 70/100 obtained the lowest irreversible part of the creep compliance, indicating that it is not a suitable choice for standard traffic at temperatures above 60°C according to the MSCR methodology recommendation. However, for two combinations, 1s and 7s, where granulation <5.6mm of PP-type polymer was applied, a high decrease in the irreversible part of the creep

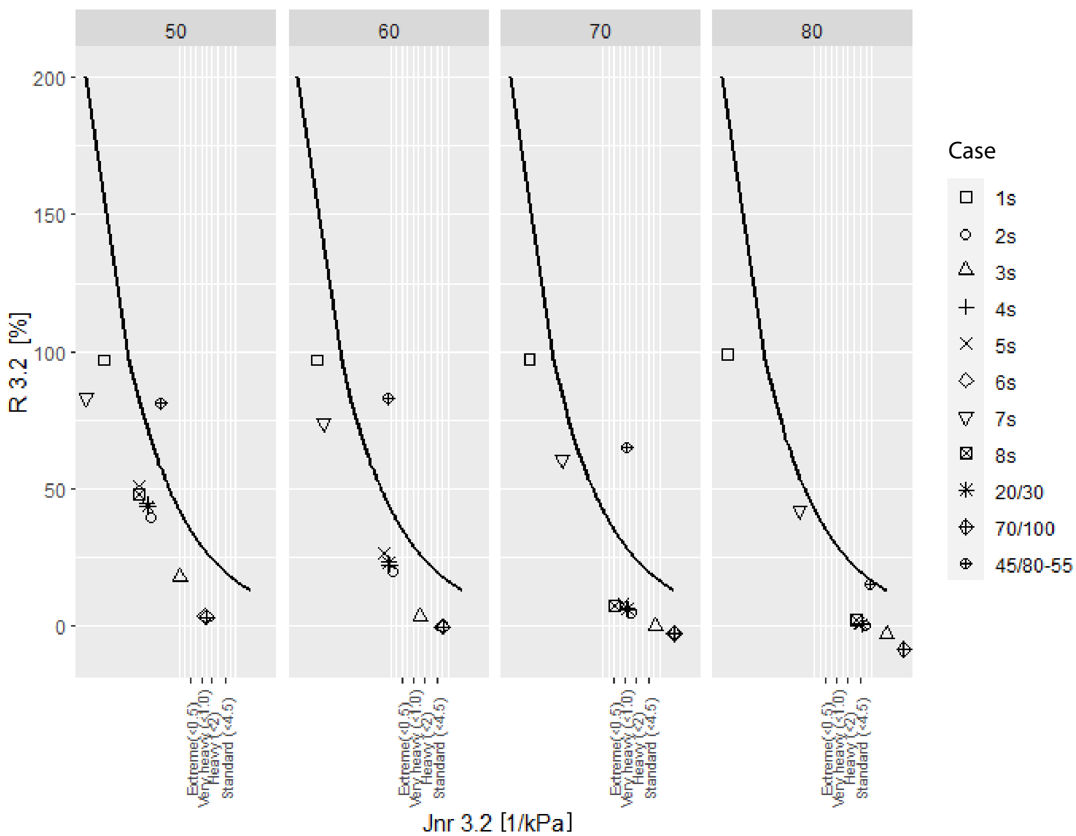


Fig. 4. MSCR test results for plastomer-modified bitumen

Table 6. Evaluation of the model parameters for the feature Jnr 3.2 and R

Feature	Jnr 3.2			R		
	Parameter	Standard error	Pr(>|t|)	Parameter	Standard error	Pr(>|t|)
Intercept	11.065	0.492	<0.001	88.196	1.014	<0.001
Mixing speed, rpm	0.000	0.000	<0.001	-0.004	0.000	<0.001
Bitumen temperature, deg. C	-0.024	0.003	<0.001	-0.353	0.006	<0.001
Mixing time, min	0.001	0.000	<0.001	-0.050	0.001	<0.001
Plastomer content, %	-1.299	0.021	<0.001	5.895	0.043	<0.001
Plastomer	-4.386	0.062	<0.001	38.175	0.128	<0.001
Bitumen	3.601	0.062	<0.001	0.121	0.128	0.345
Granulation	0.255	0.062	<0.001	-29.904	0.128	<0.001
R^2	0.29 (p-value: < 0.001)			0.66 (p-value: < 0.001)		

compliance (Jnr 3.2) and an increase in the percentage recovery (R) were observed. Nevertheless, all cases of bitumen modified with a plastomer were located below the arbitrary line characteristic of polymer-modified bitumens with elastomer properties. Only at a temperature of 80°C did the properties of PmB 45/80-55 bitumen reach a rheological state comparable to combinations: 2s, 5s, 8s. The observed relationship between Jnr and R in bitumens modified with a plastomer may suggest a reduced range of linear viscoelasticity. This may manifest as a rapid loss of stiffness in plastomer-modified bitumen after exceeding the threshold stress. Therefore, to obtain information on how and to what extent the mixing process determines the value of the irreversible part of the creep compliance and the percentage recovery of bitumen modified with a plastomer, the identification of linear model parameters was performed based on the assumed topology of the Plackett-Burman plan. The results of fitting model parameters are presented in Table 6.

Results of the linear model fitting indicate low correlation between Jnr 3.2 results and the parameters of the bitumen and waste plastomer mixing process. Despite the low correlation, all mixing process parameters significantly influenced the prediction of the Jnr 3.2 feature. In the case of the R feature, the correlation level was moderate, reaching 66%. For this feature, the type of bitumen did not have significant importance. It should be noted that from the perspective of resistance to permanent deformation, the Jnr 3.2 feature is of the utmost importance. The low degree of correlation and the accompanying high estimation error suggest that finding another effective statistical tool for predicting this feature is necessary.

3.4. PREDICTING THE IRREVERSIBLE PART OF THE CREEP COMPLIANCE AND PERCENTAGE RECOVERY USING THE MARS METHOD

The MARS method is an extension of generalized additive models. Its evident advantage is the transparency of the equation, which can be quickly implemented for other optimization tasks. To predict the Jnr 3.2 and R features, the assigned levels of process factors were not used. Their variability includes two levels, which would not allow the full potential of the MARS algorithm to be utilized. This function uses linear basis functions, so the result would be almost identical to the results obtained using a classic linear model from equation (1). In the previous chapter, it was stated that the process factors alone do not fully explain the variability of the Jnr 3.2 feature (R^2 = 0.29). During the construction of the correlation matrix, significant correlations were also revealed between basic properties (penetration, softening temperature, and fracture temperature) and MSCR parameters as well as mixing process factors. The results of the variability of basic bitumen properties undoubtedly link both the effects of the mixing process and probably the effects related to chemical changes in the bitumen. Therefore, their use instead of bitumen and plastomer mixing process factors is the right choice. Additionally, considering the results of the dispersion structure of the plastomer (long diagonal, short diagonal, surface area, circumference, sphericity coefficient) in the bitumen allows for an accurate representation of the variability of the Jnr 3.2 and R features. It should be added that the analysis also included results for bitumens 20/30, 70/100, and PmB 45/80-55. The results of predicting Jnr

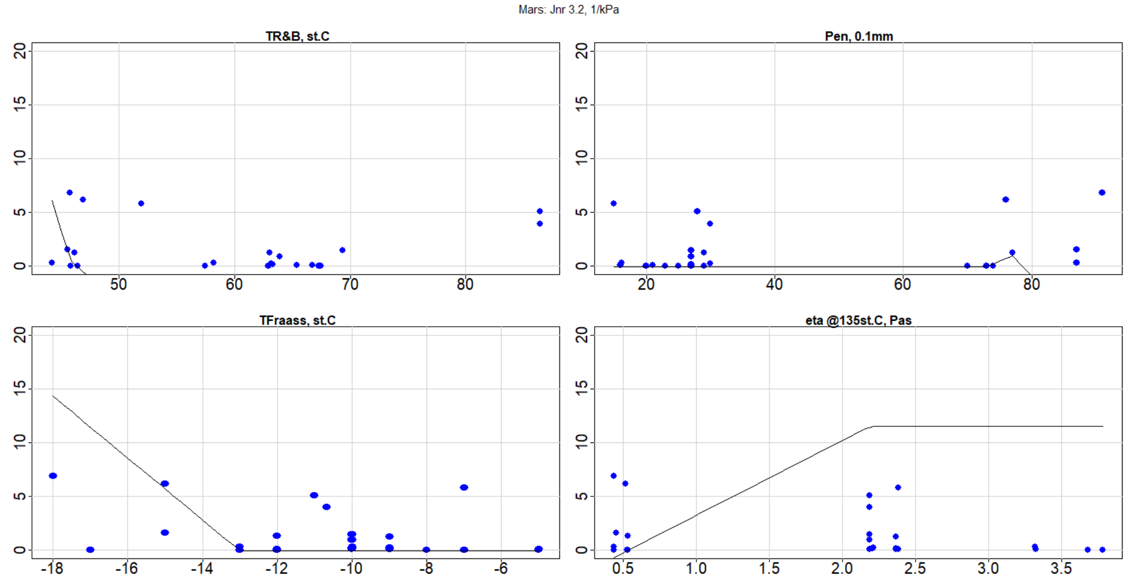


Fig. 5. Predicting the values of Jnr 3.2 using the MARS model in relation to significant bitumen properties

3.2 relative to significant bitumen features using the MARS technique are presented in Fig. 5.

Figure 5 represents changes in the values of the Jnr 3.2 feature in relation to the midpoints of dependent variables. Essentially, this is a cross-section made on the hyperplane of Jnr 3.2 results at a precisely defined location. The process of selecting the appropriate model form, i.e., the number of basis functions and interaction effects, requires very time-consuming computations. Therefore, all analyses along with graphical representation were performed in the R program [43]. The *caret* library was used for this purpose, among others. The process of identifying model parameters presented in Fig. 5 revealed that the scale of variability in the microstructure of modified bitumen did not significantly affect the Jnr 3.2 feature. Only features related to the basic properties of bitumens indicated a significant impact. Also, the measurement temperature was not considered in the final form of the regression model. The obtained form of the model allowing the prediction of the Jnr 3.2 feature is presented in Table 7 with an accuracy of 4 significant figures to achieve satisfactory representativeness and the forecasting capability of the empirical model.

Observing the results in Table 7, it is noteworthy that the model of the Jnr 3.2 feature exhibits a high degree of fit (R^2=0.99). It is worth mentioning that the model also took into account the influence of road bitumens such as: 20/30, 70/100, and those modified with plasticizers like PmB

Table 7. MARS model parameters for the feature Jnr 3.2

i	$y = b + \sum_{i=1}^{M} a_i H_i(x)$	a_i
0	Intercept (a_0)	-53.82
1	H_i(\`TR&B, deg.C\`-65.4)	-3.236
2	H_i(65.4-\`TR&B, deg.C\`)	3.368
3	H_i(-13-\`TFraass, deg.C\`)	2.884
4	H_i(2,19-\`eta @135deg.C, Pas\`)	-6.98
5	H_i(\`Pen, 0.1mm\`-77)	-0.886
6	H_i(\`TR&B, deg.C\`-86.5)	-167.6
7	H_i(\`TR&B, deg.C\`-58.2)	1.064
8	H_i(\`TR&B, deg.C\`-45.8)	2.387
9	H_i(\`Pen, 0.1mm\`-73)	0.262
R^2=0.99		
GCV = 0.06 kPa^{-1}.		

45/80-55. Furthermore, the variability of the Jnr 3.2 feature required the use of more than 2 basis functions assigned to penetration and softening temperature. This suggests a nonlinear relationship between these bitumen properties and Jnr 3.2, which would be impossible to achieve with classical regression consisting of a monotonic function. The MARS model using the backward elimination method does not directly allow for assessing the significance of parameters. The analysis used a feature Importance measure that gauges the influence of included significant features in the set on the Generalized Cross Validation (GCV) prediction error generated by the model. In other words, this means that the impact of a given feature on the model's extrapolation ability is linked to the "Importance" parameter. This parameter does not measure the impact of the individual functions created for a given feature. It should be emphasized that the R^2 fitting value depends on the number of included features in the model and their nonlinear relationships, not the "Importance" coefficient. The results of the "Importance" characteristics assigned to significant features in the Jnr 3.2 model are presented in Fig. 6.

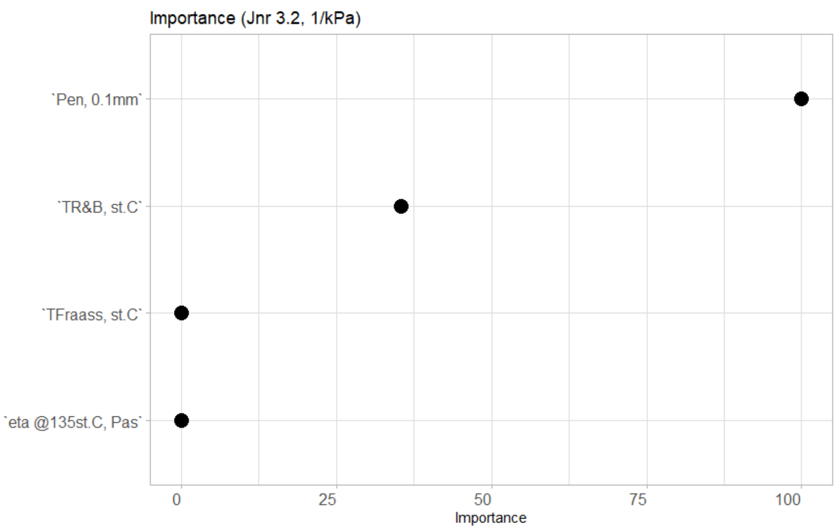


Fig. 6. Importance values relative to significant properties affecting Jnr 3.2 in the MARS model

The results presented in Fig. 6 indicate that the penetration and softening temperature of the bitumen had the greatest impact on shaping the estimation error of the model predicting the value of the Jnr 3.2 feature, while dynamic viscosity and the temperature of brittleness measured at 135°C had the least impact.

Another characteristic determined using the MARS technique was the percentage recovery R. Once again, the MARS technique was employed to find the optimal number of basic functions with the appropriate number of interaction factors. The results, in the form of cross-sectional diagrams illustrating the influence of significant bitumen features and interactions between them on the R feature, are presented in Fig. 7.

Similar to the analysis of the Jnr 3.2 feature, in the case of the R feature, the impact of microstructure on its variability was marginal. However, the influence of the penetration property was described by more than one basis function. Unlike the Jnr 3.2 model, the R feature also included interaction components, mainly between the softening temperature, penetration, dynamic viscosity, brittleness temperature, and measurement temperature. It was found that a decrease in penetration and dynamic viscosity favoured achieving a high value of the R feature. Observing the correlation matrix in Fig. 3, the correlation coefficient

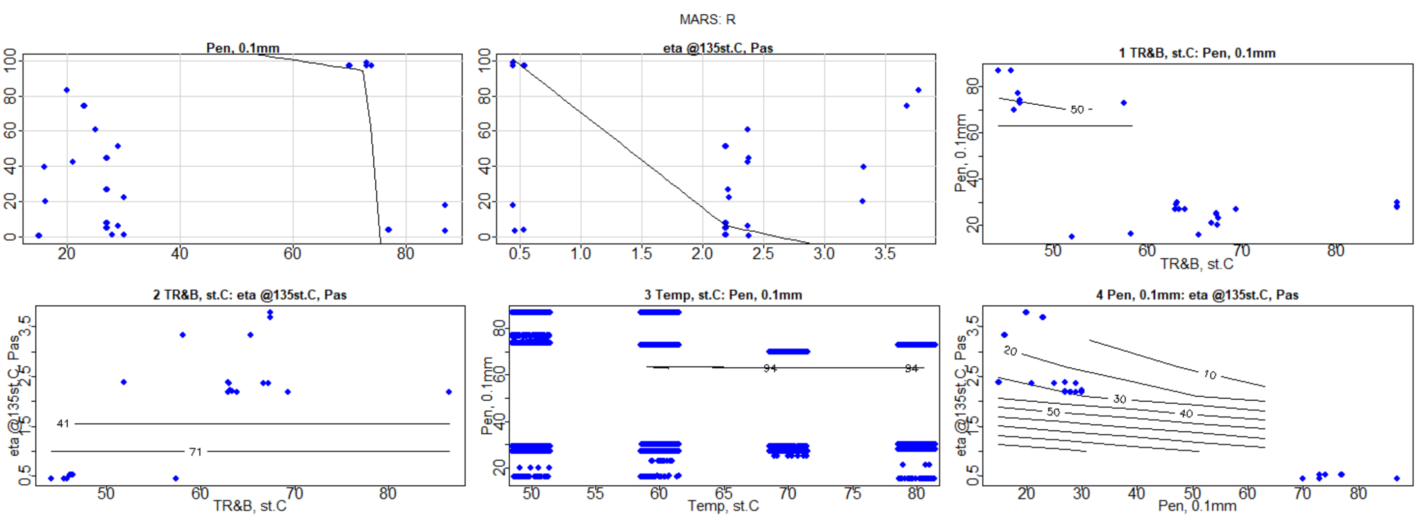


Fig. 7. Predicting the value of R using the MARS model with respect to the significant properties of bitumen and their mutual interactions

between R and penetration was r=0.07. However, when using the MARS technique, penetration turned out to be a crucial feature. This is because the correlation matrix evaluates only linear relationships and is a tool that can be used for initiating research processes. The results of identifying the parameters of the regression model for the R feature are presented in Table 8.

Table 8. MARS model parameters for the feature R

i	$y = b + \sum_{i=1}^{M} a_i H_i(\boldsymbol{x})$	a_i
0	Intercept (a_0)	4.758
1	H_i(`Pen, 0.1mm`-73)	112.2
2	H_i(70-`Temp, deg.C`)* H_i(73-`Pen, 0.1mm`)	0.049
3	H_i(`Pen, 0.1mm`-73)* H_i(`eta @135deg.C, Pas`-0.53)	-3828
4	H_i(`Pen, 0.1mm`-73)* H_i(0.53-`eta @135deg.C, Pas`)	-153.4
5	H_i(73-`Pen, 0.1mm`)* H_i(`eta @135deg.C, Pas`-3.33)	-9.823
6	`TR&B, deg.C`* H_i(`Pen, 0.1mm`-73)	-2.367
7	H_i(`eta @135deg.C, Pas`-2.19)	-14.68
8	H_i(2,19-`eta @135deg.C, Pas`)	54.02
9	H_i (`TR&B, deg.C`-65.4)* H_i(`eta @135deg.C, Pas`-2.19)	83.51
R^2=0.99		
GCV = 8.6%		

It should be noted that the model fit to the experimental data was 99%. Therefore, the range of unexplained variance by the model was 1%. The forecasting quality turned out to be significantly better than when using only binary factors of the mixing process according to the Plackett-Burman design. The Importance coefficient was also determined for the R feature. The results are presented in Fig. 8.

In the case of the R feature, the most significant factor influencing the quality of the prediction for the R feature turned out to be dynamic viscosity, while the least significant was the measurement temperature. However, unlike the Jnr 3.2 feature, the measurement temperature affected the value of the percentage recovery. It should also be noted that the results of penetration and the softening temperature of the bitumen strongly influenced the outcome of the R feature. In contrast to the regression model for the Jnr 3.2 feature, the relationship between the Fraass temperature and R was not of significant importance.

It is important to emphasize that there are certain limitations regarding the obtained regression models. Their form and inference were made within the range specified in Table 3. Therefore, the ability to extrapolate results using other elastomers may lead to conflicting outcomes. Nevertheless, it serves as a good starting point for further analyses that enable effective prediction of the Jnr 3.2 and R features.

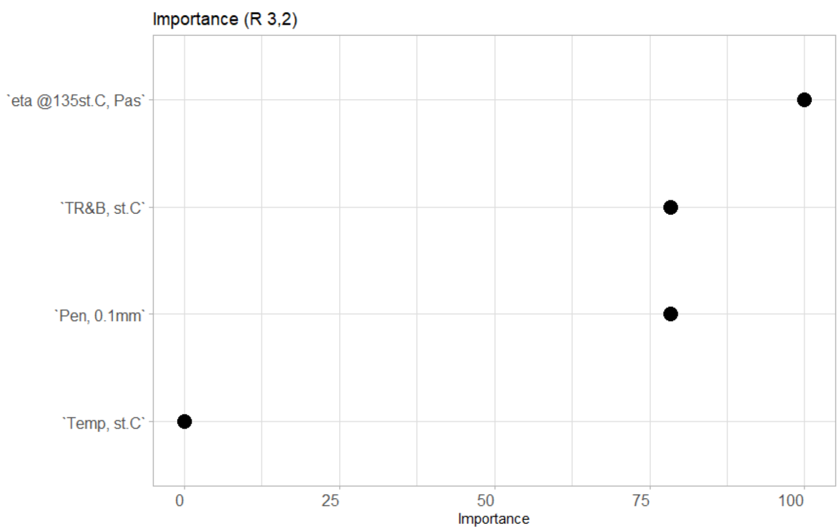


Fig. 8. Importance values relative to significant properties affecting R in the MARS model

4. CONCLUSIONS

Based on the research and analysis performed, the following conclusions were formulated:

- The MARS technique is an excellent tool for elucidating complex nonlinear relationships between variables.
- The microstructure of bitumen depends primarily on the degree of dispersion of the elastomer, its softening temperature, and the speed of the process.
- Changes in morphology did not significantly affect the variability of the irreversible compliance modulus and the percentage recovery. However, mixing parameters significantly influenced changes in the structure of bitumen modified with plastomers.

- Using the MARS technique, a regression model was obtained that demonstrated high efficiency in predicting the irreversible compliance modulus and percentage recovery using basic bitumen properties at a level of 99%.
- A key factor in predicting the irreversible compliance modulus of bitumen modified with elastomers was penetration and softening temperature. In the case of the percentage recovery, the most important features were dynamic viscosity and penetration.
- The use of elastomers resulted in bitumen with a lower value of the irreversible compliance modulus than reference bitumen modified with elastomers, allowing such bitumen to be used for very heavy traffic. The decrease in the irreversible compliance modulus was correlated with an increase in the percentage recovery. However, the relationship between Jnr and R suggests that bitumen modified with elastomers undergoes a reduction in the range of linear viscoelasticity, indicating thixotropic behaviour.
- The application of fine-grained PP plastomer (<5.6mm) led to a sharp decrease in the value of the irreversible compliance modulus and the percentage recovery.
- A rapid increase in the Jnr feature could be achieved by using PET plastomer with fine grain (<5%) with the use of soft bitumen (70/100). Conversely, an increase in the R feature was directly correlated with cases where coarse-grained elastomer (>5.6mm) was applied in quantities >3%, such as PP.

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