BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LXII No. 1/2010	87 - 95	Seria Tehnică

Application of Variance Analysis in the Study for Obtaining Advanced Polymeric Materials

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Abstract

The work is the development of laboratory studies for obtaining multifunctional composite materials, made from EPDM synthetic rubber and high density polyethylene (1:1 mass ratio) in the presence of various vulcanization accelerators. The experimental results were interpreted using specialised software dedicated to ANOVA method for analysis of variance; a bifactorial regression model for programming the experiments was developed. As expected, it was proved the strong interaction between sulphur (vulcanizing agent) and the accelerator with an amplitude depending on the nature of accelerator. However, since the technological systems studied are quite complex, the ANOVA statistical analysis did not explicitly evidenced optimal manufacturing system, the studied material being obtained in a very wide range, to meet various practical requirements in the economic, social or financial fields.

Key words: *statistics, analysis of variance, EPDM rubber, polyethylene, composite, vulcanization*

Introduction

Contemporary economic development is affected by the limited nature of some resources of raw materials and energy, by high demand for new materials with outstanding performances with special uses in various fields (from the traditional ones to the highest level) as well as by the need for environmental protection, in order to limit the amount of wastes. An example is the development of polymeric materials industry, where the obtaining of new polymers by synthesis attracts higher costs in research and investments. In recent years in USA, Japan, France, Italy, etc., some advanced composite polymers have been achieved, these materials having an elasto-plastic structure due to the rubber (elastomer) microstructured in a thermoplastic matrix.

Worldwide, micro- or nanostructured materials and their manufacturing technologies represent today one of the priorities in the fields of scientific and technological development. The existing raw materials can combine to obtain materials with improved properties, able to fulfil the quality requirements imposed by the producers, processors and end users to these new polymers.

Companies of reputation, recognized worldwide in the field of polymeric materials – Monsanto Polymer Products (USA), Mitsubishi Monsanto Chemical (Japan), Advanced Elastomer

Systems (USA), Du Pont (USA) *et al.* – were focussed on achieving a lot of modified polymers [1-8], with elastomer-polyolefinic structure and higher physico-mechanical properties compared with those of basic constituents considered individually. These properties give a great utilization value in technological areas where the following performances are required: stability in atmospheric conditions, radiations, ozone, micro-organisms or solvents, impermeability to water or other fluids, electrical insulation, lack of toxicity, opportunities for use in a wide range of temperature etc.

The elasto-plastic materials behave differently according to the elastomer and thermoplast materials nature, degree of chemical micro-structuring of elastomer in the plastic matrix, size of particles, elastomer/ plastomer ratio. The microstructuring process is simultaneously carried out by both chemical reactions (using appropriate chemical agents, depending on type and degree of unsaturated macromolecular chains) and mechanical processing (establishing suitable operating parameters during mixing the elastomer with thermoplastomer). The composite microstructuring is mainly evidenced through large flowing indices (showing a good machinability), thermal stability and elasticity, high resistance to breaking or tearing, thermal non-aging for a long time (in the 60-150^{0}C temperature range), stability by immersing into petroleum products, acidic or basic media etc.

In Romania, some composite products based on various rubbers as EPDM-type (ethylene propylene dien monomer) as well silicon or fluorinated polymers are already manufactured and available commercially. However, we consider that a more investigation of materials on the basis of special rubbers and polyolefines is justified because the complexity of such composite structures leads to new properties, although the capabilities of processing are similar to usual plastic materials. These novel materials represent an alternative to existing products on the market, but with a superior quality by combining the properties of vulcanized rubber with those of plastic polymer. Additionally, the multifunctional composites obtained from synthetic rubber and plastics can be considered as entirely recyclable materials because, owing to their thermoplastic and thermal stability, they may be re-introduced into the technology for obtaining various products without influencing significantly their properties.

These products will be useful not only for chemical companies in areas of production and processing plastic materials, that will diversify their materials sorts, but also for companies in other economic sectors such as electronic industry, auto transportation, footwear, telecommunications etc., that will use preferentially these new materials for manufacturing specific products.

Regarding the new proposed technology for obtaining the materials of this type the following assessments can be made:

- the process is engaged in a continuous operating stream;
- the vulcanization, which is specific for an elastomer component, would be performed simultaneously with the mixing of rubber, plastomer and filling materials (processing step);
- the process has decreased emissions of noxious and does not produce wastes;
- can be integrated for industrial applications in various economic areas.
- the innovation is stimulated since the composite polymer materials will replace other materials such as wood, glass, metallic materials etc.;
- it makes a possible restructuring of traditional industrial activity in the field of polymer materials production.

It was studied the industrial obtaining of elastomer-thermoplast polymer materials on the basis of EPDM and polyethylene mixture was studied. The investigation of various additives for activation, reticulation and processing was also carried out by us. There are evidenced {1-7}distinguished properties the EPDM rubbers vulcanized with sulphur or peroxides in the temperature range from -55^{0}C to +255^{0}C, *i.e.*, stability in atmospheric conditions, resistance to ultraviolet radiation, ozone, micro-organisms, acids and bases, chlorides, petrol, turpentine, other corrosive fluids at high temperature, impermeability to water or aerosols, electrical insulation to 1000V voltage and non-toxicity. The high-density polyethylene is also a durable material to chemicals, as acids, bases, organic solvents etc. We have shown that by combining these two types of compatible materials better performances are expected and the composite will be processed as a usual plastic material.

In the present paper we have applied an analysis of variance (a dispersion analysis) for investigating the correctness of programming experiments in the laboratory and for a possible recalculating of optimized technological parameters.

Description of the Variance Analysis Method (ANOVA Analysis)

A dispersion analysis sometimes called the ***analysis of variance***, ANOVA [8-14] is one of the processes most relevant on statistical processing of experimental data and consists in a series of statistical methods for analysis of obtained data to note how these depend on several factors of influence and to discriminate those with significant influence. The procedure (proposed by R. A. Fisher) consists in the decomposition of total variance (the scattering measured by dispersion) at least into two components: an influence of one factor (or more) and a residual influence (of unspecified factors).

The assembly of the two dispersions gives information on separate significance for each factor. The simplest model of ANOVA-type is unifactorial one:

$$\Omega : \begin{cases} y_{ij} = \mu + \alpha_i + \beta_i + e_{ij}, i = \overline{1, I}, j = \overline{1, J} \\ \sum_{1}^{I} \alpha_i = \sum_{1}^{J} \beta_i = 0 \\ e_{ij} \in N(0; \sigma^2) \text{ and are also independent errors} \end{cases} \quad (1)$$

In the expression (1), μ is a general average, α_i is the effect of the i^{th} level for the factor acting on y characteristics, and e_{ij} are the corresponding errors.

In this formalism, the statistical hypothesis for null value may be expressed as:

$$H_0: \alpha_1 = \alpha_2 = \ldots = \alpha_J = 0 \quad (2)$$

with an alternative that H_1: exists at least one "i" level for which $\alpha_i \neq 0$.

The e_{ij} errors are random variables normally distributed, of zero average and the same scattering, σ^2 (this is the assumption of homo-scedesticity), and also are independent among them. The ANOVA methods are robust towards general inobservance of model restrictions and the conclusions are affected in particular if the independence criterion is not met.

In the carried out experiments it was considered that, along with the accelerators as essential factors of influence to the performances of reaction product, the accelerator/sulphur ratio has also an effect; this is a reason for which the interaction should be taken explicitly into account by the development of ANOVA model.

The *bifactorial model with interactions* takes into account the situation frequently encountered in practice in which factors acting on a characteristic under the study influence each other. If we are dealing with two factors, their interaction should be also investigated. It is possible that the effects of interaction between the two factors on variable investigated to be null, but one cannot know this fact before performing the experiments.

The mathematical expression of this new situation is formally written as:

$$\Omega:\begin{cases} y_{ij} = \mu + \alpha_i + \beta_i + (\alpha\beta)_{ij} + e_{ij}, i = \overline{1,I}, j = \overline{1,J} \\ \sum_{i=1}^{I}\alpha_i = 0, \sum_{j=1}^{J}\beta_i = 0, \sum_{i=1}^{I}(\alpha\beta)_{ij} = 0, \sum_{j=1}^{J}(\alpha\beta)_{ij} = 0 \\ e_{ij} \in N(0;\sigma^2) \text{ and are also independent errors} \end{cases} \tag{3}$$

The expression (3) show a *bifactorial model with interactions* without repetition, when a single measurement appears inside the cell. If the experiment would be repeated "r" times, then is should be added the repetitive factor, denoted as "ρ_k"; in this case, the observation may be written as:

$$y_{ijk} = \mu + \alpha_i + \beta_j + [\alpha\beta]_{ij} + \rho_k + e_{ijk} \tag{4}$$

where $\sum_{k=1}^{r}\rho_k = 0$.

Moreover, we would have to check the following statistical hypothesis,

$$H_R : \text{all } \rho_k = 0,\ k = \overline{1,r} \tag{5}$$

Considering that the repetition is made only in order to reduce the uncertainty of measurement, we use the notations:

T_{ij*} - the sum of the values inside the cell, (i, j);

T_{i**} - the sum of observations for "i^th^" level of the treatment factor (A);

T_{*j*} - the sum of observations for "j^th^" level of the block factor (B);

T_{***} - the sum of all those IJr values;

$\overline{y}_{ij*}$ - the average of observations in the cell (i, j);

$\overline{y}_{i**}$ - the average of observations for "i^th^" level of A factor;

$\overline{y}_{*j*}$ - the average of observations for "j^th^" level of B factor;

$\overline{y}_{***}$ - the average of all those IJr observations.

As a consequence, the statistical hypotheses that must be verified are:

$$H_A : \alpha_1 = \alpha_2 = ... = \alpha_I = 0;\ H_B : \beta_1 = \beta_2 = ... = \beta_J = 0 \tag{6}$$

$$H_{AB} : (\alpha\beta)_{11} = (\alpha\beta)_{12} = ... = (\alpha\beta)_{IJ} = 0 \tag{7}$$

with classical alternatives, of non-equality.

The calculation of the needed quantities is made on the basis of identity (8):

$$\begin{aligned} \sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{k=1}^{r}(y_{ijk} - \overline{y}_{***})^2 &= Jr\sum_{i=1}^{I}(\overline{y}_{i**} - \overline{y}_{***})^2 + Ir\sum_{j=1}^{J}(\overline{y}_{*j*} - \overline{y}_{***})^2 + \\ &+ r\sum_{i=1}^{I}\sum_{j=1}^{J}(\overline{y}_{ij*} - \overline{y}_{***} - \overline{y}_{*j*} + \overline{y}_{***})^2 + \sum_{i=1}^{I}\sum_{j=1}^{J}\sum_{k=1}^{r}(y_{ijk} - \overline{y}_{ij*})^2 \end{aligned} \tag{8}$$

which actually represents the decomposition of total sum of square components involved in expression.

The sums (*SST*) of square deviations, required for determination of scatterings, are thus composed:

$$SST = SS(H_A) + SS(H_B) + SS(H_{AB}) + SSE \tag{9}$$

The degrees of freedom are allocated in accordance with the eq. (10):

$$IJr - 1 = (I - 1) + (J - 1) + (I - 1)(J - 1) + IJ(r - 1) \tag{10}$$

It follows therefore that:

$$MS(H_A) = \frac{SS(H_A)}{I - 1} \tag{11}$$

In order to obtain the simplified expressions, the following notations are made: T_{i*} - the sum of all J observations that belong to "i" treatment; T_{*j} - the sum of all I measurements inside the block "j"; T_{**} - the sum of all IJ experimental values. Thus, the final expressions are:

$$SS(Tr) = \frac{1}{J}\sum_{i=1}^{I} T_{i*}^2 - C \tag{12}$$

$$SST = \sum_{i=1}^{I}\sum_{j=1}^{J} y_{ij}^2 - C \tag{13}$$

$$SS(Bl) = \frac{1}{I}\sum_{i=1}^{J} T_{*j}^2 - C \tag{14}$$

$$SSE = SST - SS(Tr) - SS(Bl) \tag{15}$$

where the term C has the significance: $C = \frac{T_{**}^2}{IJ}$.

Experimental Results and Their Processing by the ANOVA Method

The following components of elasto-plastic composites were taken in the study:

- EPDM rubber and high-density polyethylene, in a 1:1 massic ratio;
- agents against thermal degradation that are specific for the above polymers;
- agents of activation and structuring (during the composite preparation), as zinc oxide, palmitic acid etc.;
- reticulation (vulcanization) accelerators required for elastomer vulcanization, that are denoted in all tables as accelerators No.1,2,3…: tetramethyl thiuram disulphide (1), 2-mercapto benzothiazole (2), 2-2′ dithiobenzothiazole (3), N-cyclohexyl benzothiazole 2-sulphen amide (4), dithio diethyl zinc carbamate (5), diphenyl guanidine (6).

The composites have been obtained by using a Brabender-type kneader, working at 180^0C with 80 rotations per minute, which has enabled the reticulation of elastomer into the melt consisting in the plastic polymer. By using the operating programs of the kneader, the following parameters were determined: induction time (minutes); optimal reticulation (vulcanization) time interval (minutes); vulcanization rate (minutes^{-1}). The six variants experimental results (I – VI) are rows formation organized in table 1.

In the statistical interpretation we have used the statistical software dedicated to ANOVA method to calculate the F-test (F calculated); the level of significance and the coefficient of determination were also computed. The statistical support is shown in table 2.

Table 1. The variation of induction period with accelerators/sulphur ratio

Accelerator	**Accelerator / Sulphur ratio (mass)**			
	0.4	0.7	1.8	8.0
	Induction period, min			
1	0.4	0.7	1.8	8.0
2	1.2	1.1	1.6	1.6
3	1.2	1.3	1.5	1.7
4	1.2	1.8	1.2	1.6
5	1.2	1.4	1.6	1.7

Table 2. Summary of theoretical analysis of variance

Source of variation	**Degrees of freedom**	**Source of squares**	**Weighted sum of squares**	**Statistics (F-test)**
Treatments (A)	$I-1$	SS(H_A)	$MS(H_A)=\frac{SS(HA)}{I-1}$	$F_A=\frac{MS(H_A)}{MSE}$
Blocks (B)	$J-1$	SS(H_B)	$MS(H_B)=\frac{SS(H_B)}{J-1}$	$F_B=\frac{MS(H_B)}{MSE}$
Interaction (AB)	$(I-1)(J-1)$	SS(HBA)	$MS(H_{AB})=\frac{SS(H_{AB})}{(I-1)(J-1)}$	$F_{AB}=\frac{MS(H_{AB})}{MSE}$
Error	$IJ(r-1)$	SSE	$MSE=\frac{SSE}{IJ(r-1)}$	-
Total	$IJ-1$	SST	-	-
Decision	Reject H_A if $F_A > F_{(I-1)(J-1);\,(IJ(r-1));\,\alpha}$			
	Reject H_B if $F_B > F_{(I-1)(J-1);\,(IJ(r-1));\,\alpha}$			
	Reject H_{AB} if $F_{AB} > F_{(I-1)(J-1);\,(IJ(r-1));\,\alpha}$			

In the statistical analysis of carried out experiments the organization was as follows:
(i) the treatments have represented the five types of accelerator, *i.e.* $I = 1.5$;
(ii) the blocks have represented the four values of accelerator / sulphur ratio, *i.e.* $J = 1.4$.

The aim for applying the ANOVA model was to validate the regression model expressed in polynomial equation (16):

$$y = a_o + a_1 x_1 + a_2 x_2 + a_3 x_1 x_2 + \varepsilon \qquad (16)$$

where y is the outcome variable, namely the vulcanization duration; x_1 and x_2 are the two factors of influence and a_0, a_1, a_2, a_3 –the corresponding coefficients. Using the adopted procedure, we could state that the variance of experiment for which F(calculated) is 5.5, significantly higher compared with the variance for the F(tabulated).

The first experiment is testing the interaction for the five accelerators and the rapport between accelerators and sulphur (see table 1).

The experiments had continued with the validation of the dependency among vulcanization time with accelerators/sulphur ratio (experiment II), the variation of vulcanization rate (min^{-1}) with accelerators/sulphur ratio (experiment III), the variation of induction time with various ratios of two accelerators 1 and 2 (experiment IV), the variation of vulcanization time with various ratios of two accelerators 1 and 2 (experiment V) and the last experimental version (VI) which establish the correlation between the variation of vulcanization rate (min^{-1}) with various ratios of two accelerators 1 and 2.

The experimental output is statistical taken to mean in order to identify the significance and to restrain the technical optimal solution. Outputs and statistical indicators calculated are summarized in Table 4.

In the Table 3 the summary model of the statistical interpretation of experiments is presented.

Table 3. The summary model of the statistical interpretation of experiments

No. of Experiment	R	R Square	Adjusted R Square	Standard error of the estimation
I	.783[a]	.613	.541	1.0351
II	**.712[a]**	**.507**	**.414**	**.2826**
III	.653[a]	.426	.319	16.9527
IV	.783[a]	.613	.381	.6940
V	.747[a]	.559	.294	2.1998
VI	.738[a]	.544	.271	15.2424

The results, shown in experiment II, in which was tested the dependency among vulcanization time with accelerators/sulphur ratio, was confirm to be the most accurate as it shows clearly a degree of significance expressed by a lower scattering level, owing to the lowest standard deviation estimated (0.2826). One can appreciate on the basis of the statistical interpretation of data that the most important factor in the rubber vulcanization process studied is represented by the interaction of accelerators and sulphur.

Conclusions

During the laboratory investigation of the obtaining multifunctional composite materials, made from EPDM synthetic rubber and high density polyethylene, the analysis of influence of the some parameters has revealed the following:

- these polymeric materials may have many economic applications and are delivered through a relatively simple technology, in the continuous flow, without emitting noxious and wastes, so that can be integrated in different industry segments;
- the final vulcanization as a separate phase is removed, the crosslinking of elastomer being performed concurrently during its mixing with thermoplastic polymer and filler materials in the presence of different accelerators;
- it is encouraged innovation, because new materials can replace wood, glass, metals etc., making possible the restructuring of traditional industrial activity in some fields.

The experimental results were interpreted statistically by ANOVA method, summarized in table 4. It was concluded that the majority of experiments were programmed correctly. The operating parameters referring to vulcanization time in systems with sulphur and a single accelerator and induction time in systems with sulphur and two accelerators were properly determined. As expected, it was proved the strong interaction between sulphur (vulcanizing agent) and the accelerator. Since the technological systems studied are complex by nature of raw materials, the relationship between them, operating conditions, the ANOVA statistical analysis did not explicitly evidenced optimal manufacturing system, the studied material being obtained in a very wide range, to meet various applications in the economic, social or financial fields.

Table 4. Tests of Between-Subjects Effects

Dependent Variable: Induction Time

Experi-ment	Source	Type III Sum of Squares	df	Mean Square	F	Sig.
I	Corrected Model	16.010[a]	5	3.202	1.582	.229
	Intercept	12.145	1	12.145	6.002	.028
	S (sulphur)	10.632	1	10.632	5.254	.038
	Accelerator	5.378	4	1.345		.627
	Error	28.328	14	2.023		
II	Corrected Model	1.024[b]	5	.205	1.830	.172
	Intercept	72.909	1	72.909	651.117	.000
	S (sulphur)	.017	1	.017	.155	.700
	Accelerator	1.007	4	.252	2.248	.116
	Error	1.568	14	.112		
III	Corrected Model	4002.746[c]	5	800.549	2.795	.059
	Intercept	81066.617	1	81066.617	282.996	.000
	S (sulphur)	659.823	1	659.823	2.303	.151
	Accelerator	3342.923	4	835.731	2.917	.060
	Error	4010.422	14	286.459		
IV	Corrected Model	3.587[d]	3	1.196	2.269	.198
	Intercept	37.556	1	37.556	71.265	.000
	S (sulphur)	2.032	1	2.032	3.855	.107
	Accelerator	1.556	2	.778	1.476	.314
	Error	2.635	5	.527		
V	Corrected Model	35.449[e]	3	11.816	3.053	.130
	Intercept	262.205	1	262.205	67.742	.000
	S (sulphur)	26.240	1	26.240	6.779	.048
	Accelerator	9.209	2	4.604	1.190	.378
	Error	19.353	5	3.871		
VI	Corrected Model	1798.422[f]	3	599.474	3.997	.085
	Intercept	81.664	1	81.664	.545	.494
	S (sulphur)	1140.850	1	1140.850	7.607	.040
	Accelerator	657.571	2	328.786	2.192	.207
	Error	749.834	5	149.967		

a. R Squared = .361 (Adjusted R Squared = .133)
b. R Squared = .395 (Adjusted R Squared = .179)
c. R Squared = .500 (Adjusted R Squared = .321)
d. R Squared = .577 (Adjusted R Squared = .322)
e. R Squared = .647 (Adjusted R Squared = .435)
f. R Squared = .706 (Adjusted R Squared = .529)

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Aplicarea analizei varianței în studiul obținerii de materiale polimerice performante

Rezumat

S-a studiat obținerea de materiale polimerice multifuncționale, realizate din cauciuc sintetic tip EPDM (etilen propilen dienmonomer) şi polietilenă de înaltă densitate, în raportul 1:1 (respectiv 50%:50%), în prezență de diverşi acceleratori. Rezultatele experimentale s-au interpretat aplicând un soft statistic dedicat metodei ANOVA. S-a confirmat statistic interacțiunea puternică dintre sulf (agentul de vulcanizare) şi natura acceleratorului. Metoda ANOVA nu a explicitat dar a evidentiat sistemul optim de fabricație deoarece sistemele tehnologice studiate sunt complexe, prin natura materiilor prime, raportul dintre ele, condițiile tehnologice, iar materiale studiate pot fi fabricate într-o gamă foarte largă, pentru a răspunde diverselor solicitări practice, economice, şi sociale.