Processing and Statistical Analysis of the Experimental Data Resulted from EPDM Rubber Grafting and Crosslinking with Accelerated Electrons in the Presence of TMPT

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This paper deals with the ethylene-propylene-terpolymer rubber (EPDM) crosslinking and grafting by use of accelerated electrons (AE) beams in the presence of a multipurpose monomer such as trimethylolpropane-trimethacrylate (TMPT). Physico-mechanical characteristics of the samples irradiated with various AE doses were compared with those of the sample obtained by classical crosslinking in the presence of peroxides. The resulting data were subjected to processing and statistical analysis to show the reliability of the EPDM crosslinking and grafting by means of AE. Based on the experimental data, the single factorial regression models for the assessment with a 95 % probability of rubber blend characteristics with different irradiation doses were established.

Keywords: EPDM, crosslinking, radiations, regression model, estimation of variables

In the world, the first patent on the rubber curing by use of ionizing radiations was granted to Dunlop Rubber Co. LTD in 1956 [1]. Since that year the use of ionizing radiations in the polymer field has been investigated by many researchers [2-5], resulting in modern, environmentally friendly, quick crosslinking and/ or grafting methods for polymers. Due to the great number of advantages [6-8] resulting from application of such processes, implementation of ionizing irradiation plants for polymer crosslinking and/or grafting has been proved to be highly efficient and the investment has been paid off in a short time.

This paper deals with the ethylene-propylene-terpolymer rubber (EPDM) crosslinking and grafting by use of accelerated electrons (AE) beams in the presence of a multipurpose monomer such as trimethylolpropane - trimethacrylate (TMPT). Physical - mechanical characteristics of the samples irradiated with various AE doses were compared with those of the sample obtained by classical crosslinking in the presence of peroxides. The resulting data were subjected to processing and statistical analysis to show the reliability of the EPDM crosslinking and grafting by means of AE.

Experimental part

Raw materials

EPDM rubber (Nordel 4760) (70 % ethylene and 4.9% ENB), multipurpose monomer such as trimethylolpropane-trimethacrylate (TMPT DL 75), and benzoyl peroxide (Perkadox 14-40B) as vulcanizing agent for the control blend.

Blends were prepared on a laboratory electrically heated roller mill. The blend constituents were added in the following sequence and amounts: EPDM (100 p) and TMPT (3p). Process variables: temperature 70 ± 5^{o}C, friction 1:1.1, and total blending time 7 min. Plates required for physico-mechanical tests were obtained by pressing in a hydraulic press at 100^{o}C, covered thereafter with a polyethylene film and irradiated with accelerated electron (AE) beam generated by the ALIN-10 electron accelerator.

The major value in AE irradiation is the ‘absorbed dose’ (D) [9] that means the ‘amount of energy absorbed by the unit mass of the irradiated material’, and is measured in J/kg. The unit of measure for the absorbed dose is the gray (Gy); 1 Gy = 1 J/kg; 10 KGy = 1 Mrad. Iradiation doses used in trials were in the 2 – 24 Mrad range.

The control blend was prepared similarly with the experimental ones with the following specifications: 8 phr of dibenzoyl peroxide as vulcanizing agent was added, and the blend crosslinking was achieved in a hydraulic press at 160^o; the best vulcanization time (18') was measured by means of Monsanto Rheometer.

Hardness, in Shore A, was measured by means of a hardness tester. Tensile strength was measured by means of a Schopller 500 strength tester. Dumb bell test specimens were used in tensile strength tests, and sleeve test specimens were used in tear strength tests. Test specimens were cut off from plates of 150 . 150 . 2 mm by means of an automatic punching die.

Statistical processing of data was performed in the SPSS version 13. It was aimed at explaining the relationship between the resulting variable (analyzed blend characteristic) and causal independent variable – beam current based on a mathematical relation known as regression model. Statistic models are applied to enable predictions of the future states based on information resulting from the previous states. They deal certainly with a prediction based on probable statistic elements, accompanied by some risks assumed previously to this prediction process [10].

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Selection of adequate single factorial regression models and testing of their validity are carried out in several stages [11].

Stage 1. Plotting the relationship between the effect variable and independent variable by means of point cloud. Based on such plots the suggested functions revealing the relationship in the best way were selected.

Stage 2. Application of dispersion analysis test ANOVA to test the model validity. Such a test involves the calculation of the following variation types:

$\sum_{i=1}^{n}(y_i - \bar{y})^2$ means the total variation and is noted SST; (1)

$\sum_{i=1}^{n}(y_i - \hat{y}_i)^2$ means the remanent variation and is noted SSE; (2)

$\sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2$ means the variation explained based on the regression and is noted SSR (3)

where:

y_i = experimental values;

$\hat{y}_i$ = values adjusted based on the regression model;

$\bar{y}$ = the mean of the experimental values.

If the variation explained by the observed value spreading because of the factorial variable, according to the analyzed regression model, is larger than the spreading of the same values because of the hazard the model is considered to be valid. To test this statistic assumption the Fischer ratio calculated by the relation below was used.

$$F_{calc} = \frac{\sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2}{k} \Bigg/ \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{n-k-1} \quad (4)$$

where:

k is the number of factorial variables in the model;

n - the number of observations.

Where the plot has suggested more regression functions, the test of the dispersion analysis was performed for each of them and the models where the F ratio values have no statistical significance were given up.

Stage 3. Testing the significance of the regression model parameters. Only judging a model as valid based on the dispersion analysis test is not conclusive. Every regression model parameter has to have a statistic significance for a probability not less than 0.95. Tests for parameter significance were performed by means of the Student test (5), considering a trial number less than 30.

$$t_{calc} = \frac{b_i - \beta_i}{s_{b_i}} \quad (5)$$

where:

β_i is the parameter i of the single factor regression model (if assuming that it has no statistic significance its value is considered 0);

b_i is the parameter i estimator for the regression model obtained from the experimental data;

s_{b_i} = standard deviation of the b_i estimator.

During the experimental data analysis the models with parameters without statistical significance have been given up.

Stage 4. Computing the determination coefficient R^2. This means to find out the ratio of the variation given by the regression model to the total variation of the effect variable being analyzed.

$$R^2 = \sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2 \Big/ \sum_{i=1}^{n}(y_i - \bar{y})^2 \quad (6)$$

Where more regression models were validated during the previous stages, the model with the highest determination coefficient (R^2) value is to be selected.

Stage 5: Assessing the values of the analyzed characteristics. The values of the analyzed characteristics for various irradiation doses were estimated based on every validated regression model. The obtained values have fallen in the confidence intervals presumably guaranteed (based on the relation 7).

$$\hat{y}_D - t_{\alpha/2;n-k-1} \times s_{\hat{y}_D} \le y_D \le \hat{y}_D + t_{\alpha/2;n-k-1} \times s_{\hat{y}_D} \quad (7)$$

where:

y_D is the estimated value of the characteristic based on the regression model for a given irradiation level D;

s_{yD} - the standard value calculated from the relation 8;

$t_{\alpha/2;\ n-k-1}$ - the value calculated for the Student distribution based on the safety level α (it was assumed to be 0.05 as the result guarantee with 95 % probability was intended);

df=n-k-1 - the number of freedom degrees where n is the number of observations and k is the number of causal variables (there is a single independent variable here: irradiation dose).

$$s_{\hat{y}_D} = \sqrt{\frac{SSE}{n-k-1}\left[1 + \frac{1}{n} + \frac{(D-\bar{D})^2}{\sum_i^n (D_i - \bar{D})^2}\right]} \quad (8)$$

where:

D is the irradiation mean dose;

$\sum_i^n (D_i - \bar{D})^2$ - the total variation of the independent variable (irradiation dose).

Results and discussions

The physico-mechanical characteristics of blends based on EPDM and TMPT crosslinked with peroxides are taken as reference values and presented in table 1.

Table 1

REFERENCE CHARACTERISTICS

Ref. No.	*Characteristic*	*Control blend*
1	Hardness, °ShA,	64
2	Breaking strength , N/mm^2	2.1
3	Elongation at break, %	127
4	Elongation set, %	5
5	Tear strength, N/mm	13.5

When analyzing the experimental data, a distinct processing was carried out for every characteristic, trying to validate a model revealing the way such characteristics are changed based on the AE irradiation dose. The validation of the regression models has involved the four stages referred to above.

Hardness of EPDM and TMPT blends crosslinked and grafted by means of accelerated electron beam against the irradiation dose is presented in figure 1. Experimental value spreading has suggested a relationship as a second degree curve between the two variables. Equation for the validated regression model is the following:

$$y_{(x_i)} = 60{,}617 + 0{,}602 \cdot x_i - 0{,}022 \cdot x_i^2 \quad (9)$$

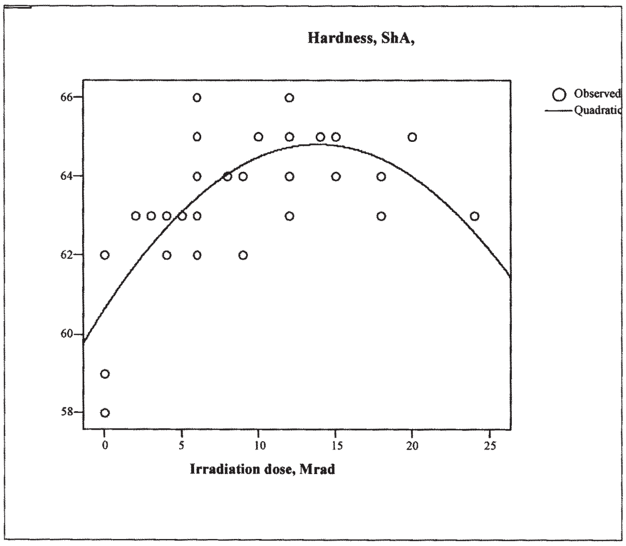

Fig. 1. Changes in the hardness according to the iradiation doses

The value of the determination coefficient (R^2) is 0.547 suggesting that the regression model has explained 54.7 % of this characteristic variation.

According to this model, the blend hardness has increased by sample irradiation, reaching a maximum value of 64.7 ShA corresponding to an irradiation of 13.98 Mrad, and afterwords the characteristic value has decreased.

To obtain the best value for the characteristic, close to 64^o ShA obtained by crosslinking with peroxides the blend is recommended to be irradiated with accelerated electron beam of 8 – 15 Mrad.

Breaking resistance for the EPDM and TMPT blends crosslinked and grafted by means of the accelerated electron beam against the irradiation dose is presented in figure 2. The experimental value spreading has suggested an exponential relationship as a second degree curve. Both models were validated after having the dispersion analysis test ANOVA and parameter significance test performed.

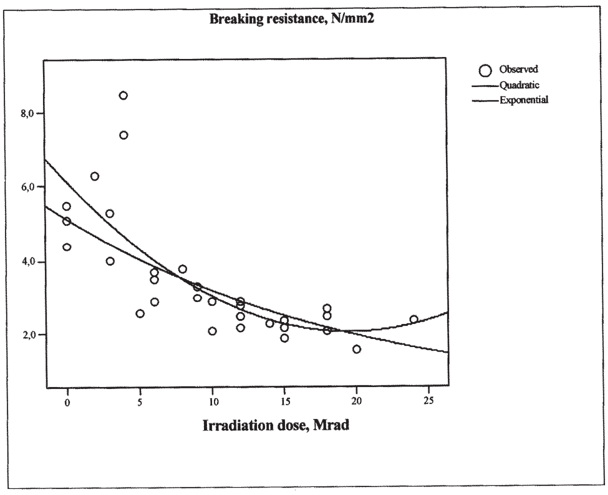

Fig. 2. Changes in breaking resistance according to the irradiation dose

Having analyzed the characteristics of the two regression models, the exponential model was chosen for the characterization of the relationship between breaking strength and beam current as the value of the determination coefficient R^2 is higher (55.3 as compared to 50.7), and the standard error of the estimations is lower (0.287 as compared to 1.292).

Equation for this model is:

$$y_{(x_i)} = 5,133 \cdot x_i^{(-0,048)} \quad (10)$$

Breaking strength value has decreased as the beam current has increased. The blend is recommended to be subjected to an irradiation with accelerated electron beam not exceeding 10 Mrad to obtain values of this characteristic higher than in samples crosslinked by means of peroxides. The plot of the two variables has revealed high values of the breaking strength at low beam current that decrease afterwards.

Elongation at break for the EPDM and TMPT blends crosslinked and grafted by means of the accelerated electron beam against the irradiation dose is presented in figure 3. Spreading of the experimental values has suggested a relationship between the two variables as a second degree curve. The validated model is revealed by the following relation:

$$y_{(x_i)} = 949,478 - 95,086 \cdot x_i + 2,721 \cdot x_i^2 \quad (11)$$

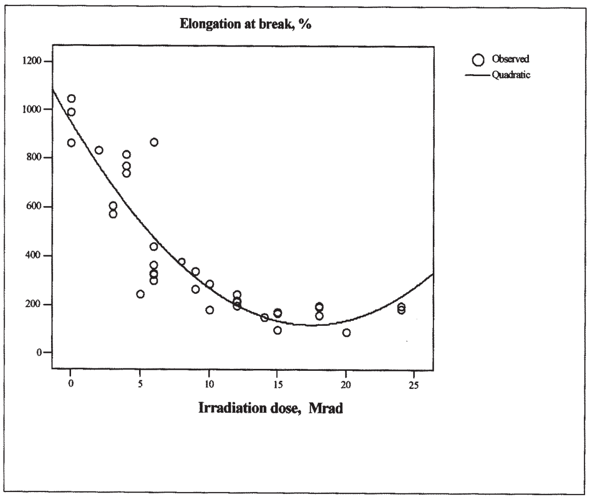

Fig. 3. Changes in the elongation at break according to the iradiation dose

There is a strong relationship between the accelerated electron beam current and elongation at break (correlation ratio of 0.905) and variation explained by the investigated regression model stands for 91.9 % of the total changes in the analyzed characteristic.

According to the model equation, the least value for the elongation at break is achieved when irradiating the blend with 17.5 Mrad. Obtaining a value above 200 % for this characteristic is aimed based on how the crosslinked blend is used. Therefore, a beam current less than 15 Mrad is recommended.

Elongation set for the EPDM and TMPT blends crosslinked and grafted by means of the accelerated electron beam against the irradiation dose is presented in figure 4. The experimental value spreading suggests an exponential relationship between the two variables. The validated model has explained 70.4 % of the analyzed variable changes (R^2 = 0.704) and is expressed by the following equation:

$$y_{(x_i)} = 93,339 \cdot x_i^{(-0,159)} \quad (12)$$

As the crosslinking is aimed at obtaining an elongation set as low as possible, a beam current not less than 4 Mrad is recommended to be used.

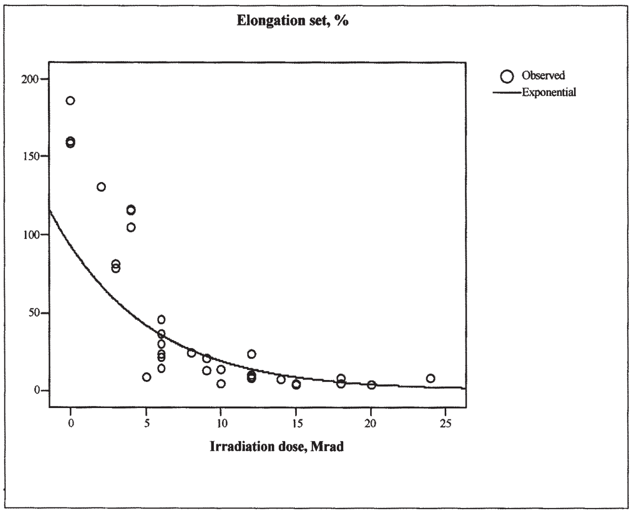

Fig.4. Changes in the elongation set according to the iradiation dose

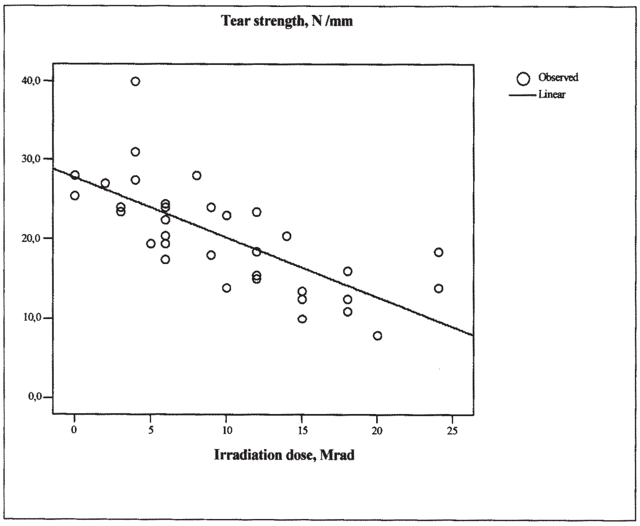

Fig. 5. Changes in the tear strength according to the iradiation doses

Tear strength for the EPDM and TMPT blends crosslinked and grafted by means of the accelerated electron beam against the irradiation dose is presented in figure 5. The experimental value spreading suggests a reverse linear relationship between the two variables. The validated linear regression model has explained 53.6 % of the analyzed variable changes.

$$y_{(x_i)} = 27,773 - 0,755 \cdot x_i \qquad (13)$$

Tear strength decreases as the beam current increases. To obtain values for this characteristic comparable with those of the samples crosslinked with peroxides the blend is recommended to be subjected to a beam current not exceeding 10 Mrad.

The plot of the two variables has revealed higher values for the tear strength for the lower beam current and a decreasing trend thereafter.

100% modulus for the EPDM and TMPT blends crosslinked and grafted by means of the accelerated electron beam against the irradiation dose is presented in figure 6. The experimental value spreading suggests a second degree curve relationship between the two variables.

The parameters estimated based on the employed model are significantly different from 0 and changes explained by the model have exceeded the remanent one (the Fisher ratio is 30.639 and the significance level is close to 0). The validated model has explained 69.4 % of this variable spreading and is expressed by the following equation:

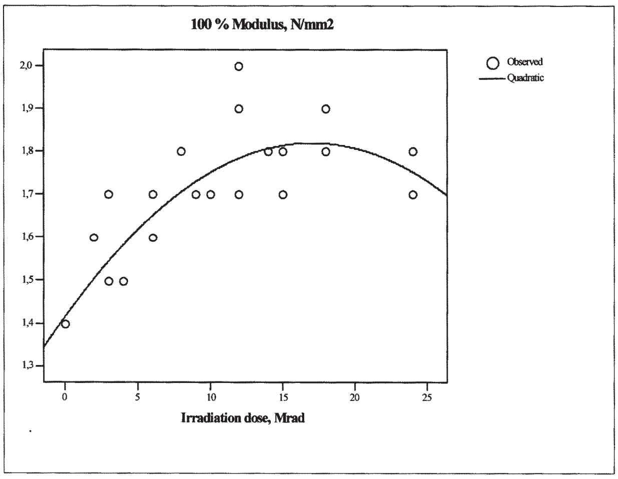

Fig.6. Changes in the 100% modulus according to the iradiation doses

$$y_{(x_i)} = 1,414 + 0,04761857 \cdot x_i - 0,0013965 \cdot x_i^2 \qquad (14)$$

According to this model, by the sample irradiation procedure the values for this characteristic are increased, reaching the highest value of 1.94 N/mm^2 for an irradiation of 17 Mrad, and thereafter are decreased.

Table 2
ESTIMATED CHARACTERISTICS OF THE EPDM AND TMPT BLENDS FOR DIFFERENT ACCELERATED ELECTRON BEAN IRRADIATION DOSES

Characteristic	6 Mrad		8 Mrad		10 Mrad		12 Mrad		15 Mrad	
	Estimated value	Limit error	Estimated value	Limit error	Estimated value	Limit error	Estimated value	Limit error	Estimated value	Limit error
Hardness, ShA,	63,44	±2,44	64,03	±2,44	64,44	±2,43	64,67	±2,44	64,7	±2,46
Module 100 %, N/mm^2	1,67	±0,18	1,73	±0,18	1,79	±0,17	1,85	±0,18	1,91	±0,18
Breaking strength, N/mm^2	4,71	±0,59	4,65	±0,59	4,6	±0,59	4,56	±0,59	4,51	±0,6
Elongation at break, %	476,92	±81,14	362,93	±81,08	270,72	±81,02	200,27	±81,16	135,41	±81,78
Elongation set, %	70,2	±1,43	67,06	±1,42	64,72	±1,42	62,87	±1,43	60,68	±1,44
Tear strength, N /mm	23,24	±9,74	21,73	±9,71	20,22	±9,7	18,71	±9,72	16,45	±9,79

Based on the validated regression models (9-14), the values of the investigated characteristics of the blends for irradiation doses (D) of 6, 8, 10, 12 and 15 Mrad were assessed. The limit errors enabling the assessment based on the confidence interval were calculated from relation (7) with a probability of 95%. Results are presented in table 2.

Conclusions

The examination of physico-mechanical characteristics based on the irradiation dose has revealed the following: (a) the changes of characteristics with the increase in the AE doses have revealed the EPDM crosslinking and grafting; (b) the physico-mechanical characteristics of the blends have shown either unchanged or lower values because of an advanced crosslinking occurring in the blend and elastomer decomposition reactions; (c) in production some adequate values of the characteristics are aimed depending on the end use of the blends based on EPDM and TMPT. Establishing the regression models enables the expected blend properties to be estimated for an irradiation dose to control thus the product quality.

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