Mathematical characterization of values of rheological variables during the networking reaction of rubber mixtures based on SBR

E Seliga[1], O Bošák[1], S Rusnáková[2], S Minárik[1] and M Tóth[3]

[1] Department of Physics, Institute of Materials, Faculty of Materials Science and Technology SUT, J. Bottu 25, 917 24 Trnava, Slovakia
[2] Department of production engineering, Faculty of technology, Thomas Bata University in Zlin, Nad Stráněmi 4511, 760 05 Zlín, Czech Republic
[3] FLEXOPRINT, s. r. o., Bystrická cesta 69, 034 01 Ružomberok, Slovakia

E-mail: emil.seliga@stuba.sk, ondrej.bosak@stuba.sk, rusnakova@ft.utb.cz, stanislav.minarik@stuba.sk, toth@flexoprint.sk

Abstract. The article presents an analysis of cross-linking reaction using measurements of time dependencies of torque at constant temperature from the range 100 up to 200 °C. The measured results obtained on sample based on styrene - butadiene (SBS) prepared in the laboratory show the behaviour which can be well described by equations of chemical reactions of first-order kinetics. It is possible mathematically describe significant constants of the kinetics of networking reaction (induction period, reaction rate coefficient) by the solution of differential equations and by mathematical approximation. Constants are exponentially dependent on the temperature of vulcanization, while dependencies are Arrhenius like. Math description allows describe the progress of the vulcanization reaction also in the temperature range outside of the monitoring interval, i.e. in the area of extremely long times required for the realization of the cross-linking reaction.

1. Introduction

Elastomers used in production of divers gaskets, tires, insulant claddings etc. belong among meaning group of technical materials. These materials gain their properties in vulcanization process. Fundamentals of vulcanization process are based on generation of three-dimensional network by origin of cross-linking bonds among linear chains of rubber [1]. Generally, the process of vulcanization predominantly influences the final properties of rubber and course of this process can be influenced by compounds in vulcanization system (kind of rubber, vulcanization reagent insuring creation of cross-linking bonds, accelerator for acceleration and shortening of process of cross-linking bonds creation and activator for initialization of cross-linking bonds creation). Others compounds insuring properties of incoming vulcanizers can be divided on fillers, antidegradation reagents and additional compounds (colorants, retarders of combustion and etc.). Production of vulcanizers of rubber mixtures is most often realized at constant increased temperature. Mentioned procedure of cross-linking creation is well described mathematically [1,2]. In technical practice number of crosslinking bonds can be observed by means of values of mechanical variables increasing [2].

Presented contribution is oriented on determination and experimental approval of mathematical formula describing vulcanization process at linear increasing temperature. Laboratory prepared mixture based on styrene-butadiene rubber (SBR) was prepared for experimental approval.

2. Experiment

Experimental work has been carried out on laboratory prepared rubber mixture based on SBR with a simple vulcanization system with vulcanization reagent based of sulphur. The blending of the mixture composition showed in table 1 was realized on double- roller.

Table 1. Composition of the tested rubber mixture

Components	pphr
SBR Rubber Buna VSL 5025-0	100.0
Vulcan C-72 R	8.0
ZnO	3.0
Sterin III	1.0
Dusantox IPPD	1.0
Sulfenax CBS	1.5
Sulphur	1.5
Total	116

In view of the fact that the number of cross-links resulting from the process of vulcanization increases growth of mechanical properties, rheological measurements have been used in the case of the mixture. Torque values required to create a constant value of shear deformation 0,5° were measured [3]. Measurements were carried out by means of the device D-MDR 3000 MonTech. Two types of measurements have been realized. The first type of measurement was carried out at a constant temperature from the range 100°C to 200°C. The temperature interval was chosen with a view to a typical vulcanization temperature of mixture based on SBR rubbers. Measuring time intervals were 4 hours for temperatures (100°C – 120°C), 3 hours for temperatures (130°C – 150°C) and 2 hours for temperatures (150°C – 200°C). Time dependences of the torque at a constant temperature was the result of the experiment. Measurements of temperature dependence of torque at linear increasing temperature with constant heating rate 0.2°C/min; 0.4°C/min; 0.6°C/min; 0.8°C/min; 1.0°C/min; 2.0°C/min; 3.0°C/min; 4.0°C/min; 5.0°C/min; 7.0°C/min; 10°C/min were the second type of experiment [4].

3. Determination of the formula describing the vulcanization process at linear increasing temperature

In General, the process of vulcanization realized on a rubber mixture is observable at a constant temperature by a characteristic time dependence of torque. This dependence can be divided into three parts: I - induction stage II- cross-linking stage and III-stage of additional reactions. In the induction stage the chemical preparation of the mixture on the networking process, which follows in the cross-linking stage is realized. In the third stage, depending on the type of rubber, it can be realized further networking (a), the number of links may not be changed (b) or cross-links reduction can be occurred (c).

Figure 1. Schematic view of the vulcanization curve (time dependence of the torque).
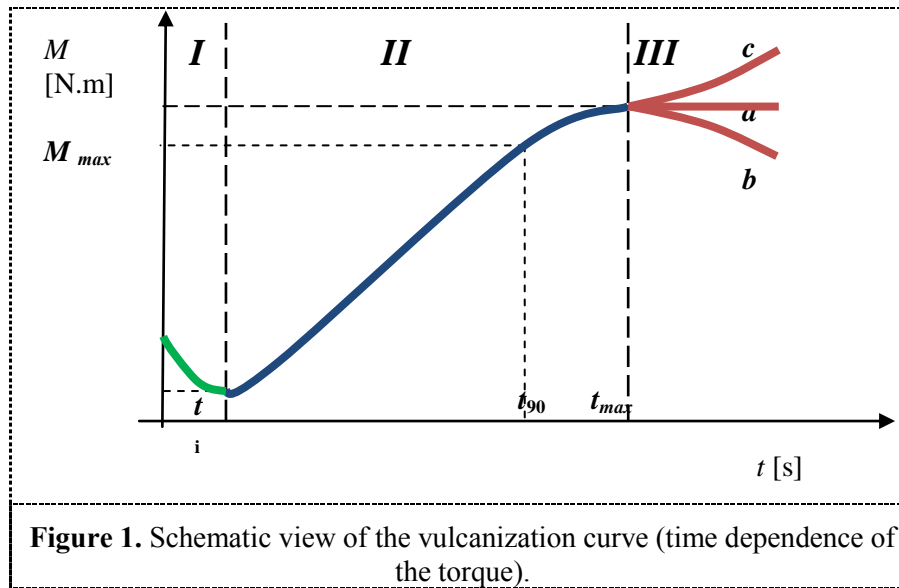
For a mathematical description of networking (stage II in Figure 1), we can use next equation [5]:

$$M = M_{max} - (M_{max} - M_{min}) \cdot e^{-k(t-t_i)}, \tag{1}$$

where M_{max} represents maximum value of torque, M_{min}, minimum value of torque, k vulcanization rate constant, t_i time of induction period.

Equation (1) is the solution to the differential equation that explains the proportionality between time change of torque and instant value of torque [6]. The vulcanization rate constant k and the time of the induction period t_i are constants in case of measurements at a specific temperature. For this reason, they are not suitable for description of the behaviour of rubber mixtures during networking at linearly increasing temperature. Thermal dependence of induction period can be described as:

$$t_i = e^{-S_2 + \frac{E_2}{RT}}, \tag{2}$$

where S_2 is kinetic constant independent on temperature and E_2 is activation energy of initiation [7]. Thermal dependence of "vulcanization rate" can be described as:

$$k = e^{S_1 - \frac{E_1}{RT}}, \tag{3}$$

where S_1 is kinetic constant independent on temperature and E_1 is activation energy of vulcanisation.

Mentioned kinetic constants (S_1, S_2, E_1, E_2) are independent from the temperature and they allow to describe the kinetics of the cross-linking process during vulcanization. Taking account of both relationships (2), (3) in (1) may be obtained formula:

$$M = M_{max} - (M_{max} - M_{min}) \cdot \exp\left[-e^{S_1 - \frac{E_1}{RT}}\left(t - e^{-S_2 + \frac{E_2}{RT}}\right)\right] \tag{4}$$

and also the rate of the cross-linking reaction in the next form:

$$r_M = \frac{dM}{dt} = e^{S_1 - \frac{E_1}{RT}} \cdot (M_{max} - M_{min}) \cdot \exp\left[-e^{S_1 - \frac{E_1}{RT}}\left(t - e^{-S_2 + \frac{E_2}{RT}}\right)\right]. \tag{5}$$

Relationships (4), (5) provide a description of the vulcanization also in case of temperatures, which cannot be used for the experimental observations (too long or short periods of vulcanization).

Formula for determination of the rate of change of torque was used in the next form:

$$r_M = \dot{M} = \frac{dM}{dt} \ . \tag{6}$$

Considering the time and temperature dependence of torque $M = M(t;T)$ and time dependence of temperature $T = T(t)$ it can be found:

$$\dot{M} = \frac{dM}{dt} = \frac{\partial M}{\partial t} + \frac{\partial M}{\partial T}\left(\frac{dT}{dt}\right) = \frac{\partial M}{\partial t} + \frac{\partial M}{\partial T}\ \vartheta, \tag{7}$$

where ϑ is heating rate, which corresponds to time derivation of temperature:

$$\vartheta = \frac{dT}{dt} \ . \tag{8}$$

Using the relations (5), (7), (8) the temperature dependence of the rate of change of the torque can be written in the form:

$$M = \int_{T_0}^{T} (M_{max} - M_{min})k\left\{1 + \frac{1}{RT^2}\Big[E_1(T-T_0) + \vartheta(E_2 - E_1)t_i\Big]\right\}e^{-k\left(\frac{T-T_0}{\vartheta} - t_i\right)}dT + M_{min} \ , \tag{9}$$

where k and t_i are values of rate constants and time of the vulcanization period, writable by temperature dependencies (relations 0 and 0) by means of constants S_2, E_2 and S_1, E_1**Hiba! A hivatkozási forrás nem található.**. The constant T_0 corresponds to the initial temperature of cross-linking reaction at the linear increasing temperature.

4. Results and discussion

Vulcanization curves i.e. time dependencies of torque in determined temperature range are shown in figure 2. It can be recognized from the figure 2, that only the induction period area and the beginning of cross-linking reaction can be observed at low temperatures (the temperature range 100°C – 130°C). For this reason, we chose the longer period of measurements (4 hours). So it is already possible to observe the whole vulcanization curve at the increasing of temperature.

Figure 2. Time dependences of the torque M measured at the constant temperature from temperature range 100°C – 200°C.
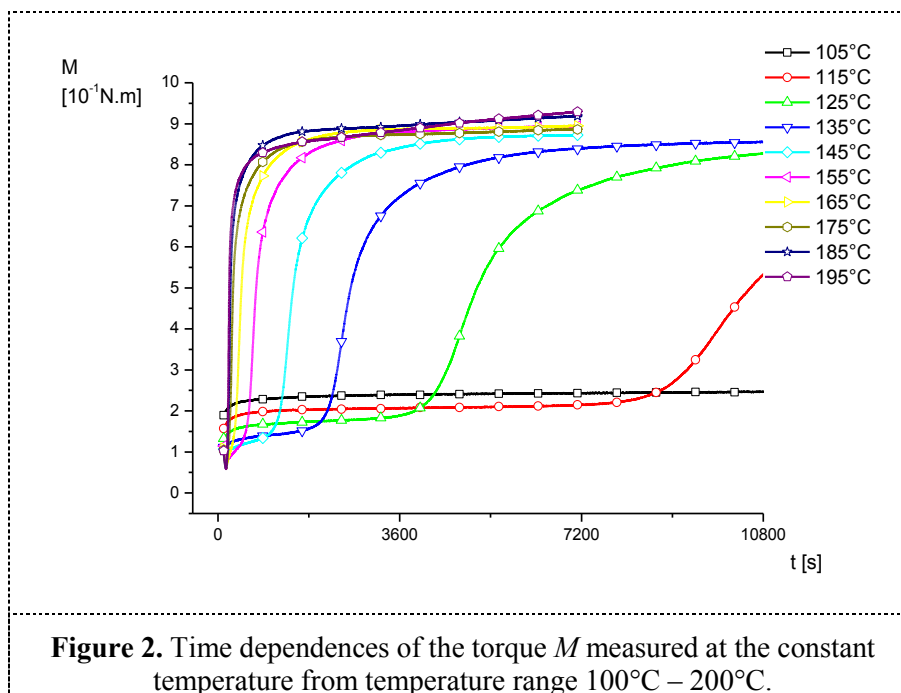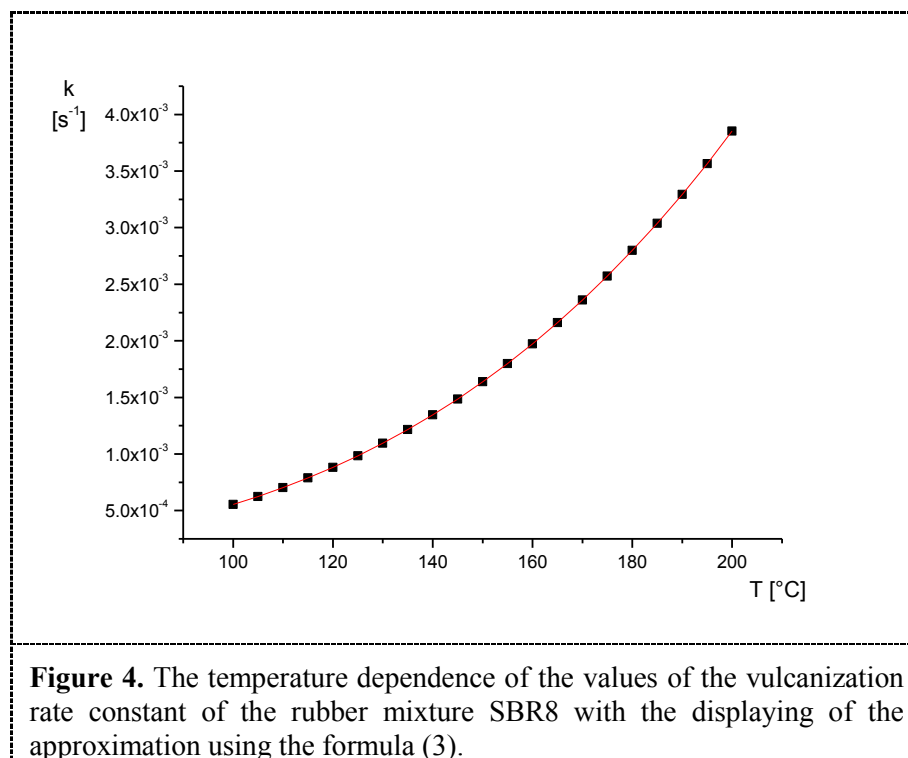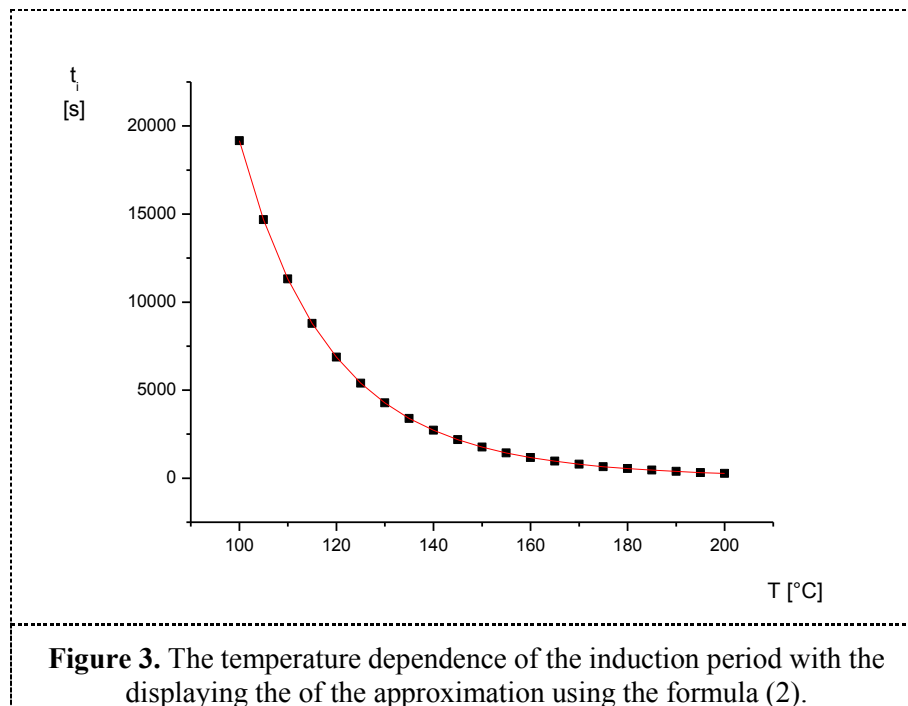
Time dependencies shown in the figure 2 were approximated by non-linear least squares method using formula (1). Values of four constants describing the shape of the vulcanization curve at constant temperature were determined by approximation (table 2)

Table 2. Approximated parameters M_{max}, M_{min}, k, t_i at selected temperatures obtained by nonlinear least-squares method at the formula for time dependence of torque

| T	M_{max}	M_{min}	k	t_i
[°C]	[10^{-1} Nm]	[10^{-1} Nm]	[s^{-1}]	[s]
100	3.99704	0.49189	1.3E-4	18779.08
105	2.68953	2.49577	2.1E-4	12941.58
110	6.9127	1.75399	4.4E-4	14557.63094
115	7.35884	3.22511	4.9E-4	9427.539
120	7.74198	0.31809	6E-4	6662.87541
125	8.39588	3.20519	6.5E-4	4525.968
130	8.02582	6.01818	9.7E-4	4958.79029
135	8.38727	1.35968	0.00116	2049.691
140	8.48268	7.95749	0.0014	3663.10373
145	8.59956	1.89259	0.00194	1206.522
150	8.35191	7.81586	0.002	2091.17697
155	8.80918	1.63488	0.00266	552.5776
160	8.5945	4.80595	0.0025	652.4464
165	8.93491	6.17877	0.00185	661.0386
170	8.76327	5.73496	0.00219	498.7025
175	8.77729	5.61095	0.00262	387.2245
180	8.90283	6.02321	0.00288	383.2369
185	9.0135	6.21982	0.00308	369.0329
190	9.07853	6.25042	0.00343	331.6193
195	8.9259	5.77486	0.00334	299.905
200	9.43829	5.76528	0.00352	263.9531

Rate constant values k and values of time of induction period listed in table 2 are exponentially dependent on the temperature (figure 3, figure 4). Their dependencies are well aproximable by relationships (2) and (3). Values of constants S_1, E_1, S_2, E_2 were determined after the approximation. Values of constants $S_1 = 1,68$ [-] and $E_1 = 28487$ [J.mol^{-1}] were obtained by approximation of the temperature dependence of the rate constant k (3). Values of constants $S_2 = 10,31$ [-] and $E_2 = 62581$ [J.mol^{-1}] were obtained by approximation of the temperature dependence of the time of induction period t_i (2).

Figure 3. The temperature dependence of the induction period with the displaying the of the approximation using the formula (2).

Figure 4. The temperature dependence of the values of the vulcanization rate constant of the rubber mixture SBR8 with the displaying of the approximation using the formula (3).

Non-linear least squares approximation by means of formula (9) was realized using mentioned constants. Example of the measured temperature dependence of torque and also approximation of measured values in the cross-linking area at the temperature increasing 0.8°C/min are shown in figure 5. Decrease of measured values of the torque associated with the change of viscosity at the mixture heating is observable up to temperature 140°C. Significant increase of torque values from the temperature approx. 150°C can be associated with the cross-linking reaction (II. stages of

vulcanization). The same character of the measured dependencies was recorded at all speeds of the heating used in the experiment, 0.2°C/min; 0.4°C/min; 0.6°C/min; 0.8°C/min; 1.0°C/min; 2.0°C/min; 3.0°C/min; 4.0°C/min; 5.0°C/min; 7.0°C/min; 10°C/min. Good agreement between measured data and values obtained by approximation by means of formulas (9) (table 3) can be seen at comparison of values of the cross-linking beginning at linear increasing temperature.
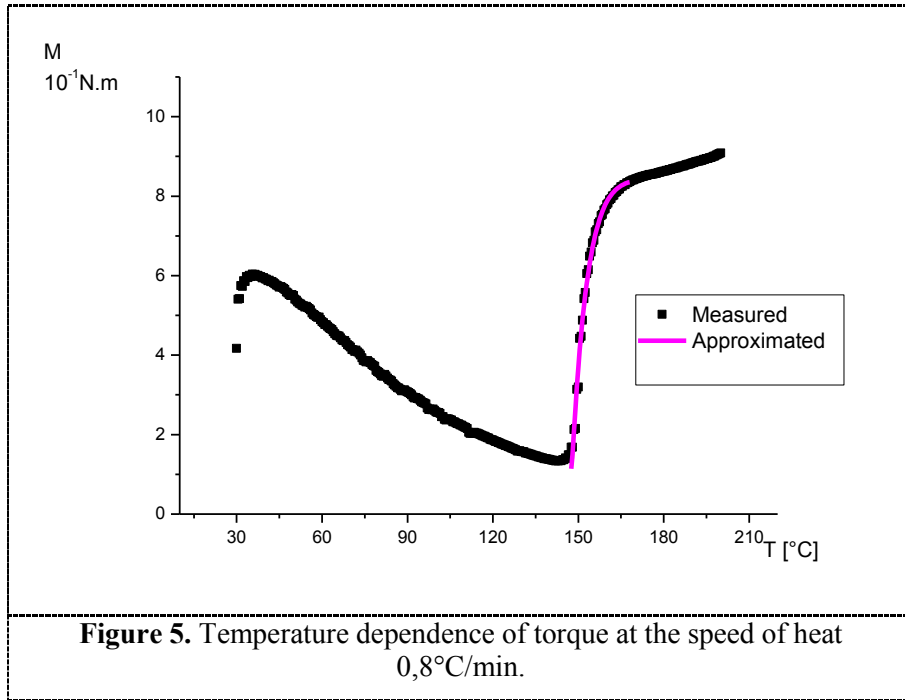
Figure 5. Temperature dependence of torque at the speed of heat 0,8°C/min.

Table 3. Table of values of specific constants M_{min}, a T_0.

Heating rate ϑ [°C.min^{-1}]	Values obtained from the measured dependence		Values obtained by approximation measured dependencies using equation (9)	
	T_0 [°C]	M_{min} [10^{-1} N.m]	T_0 [°C]	M_{min} [10^{-1} N.m]
10.0	180.5	0.558797	179.709	0.559
7.0	177.5	0.556334	177.004	0.556
5.0	172.5	0.67664	171.807	0.674
4.0	170	0.680469	169.271	0.673
3.0	165.5	0.714617	165	0.697
2.0	159	0.83019329	158.626	0.820
1.0	150	1.0354992	149.751	1.135
0.8	148	1.14451	147.731	1.140
0.6	142	1.2401	142.155	1.24
0.4	136.5	1.386896	136.998	1.392
0.2	126.5	1.567274	128.345	1.567

5. Conclusion

Time dependencies of torque during vulcanization can be described by formula (4) in case of laboratory prepared rubber mixture based on SBR with simple vulcanization system. Temperature

dependence of the torque at the linear temperature increasing can be found by means of this formula. This dependence is expressed by (9). Formula (9) well describes the actual measured curves. Constants specifying the beginning of cross-linking during the linear increasing temperature (M_{min}, T_0) obtained from the measured data and from the relation (9) derived by approximation are in good agreement.

References

[1]   Stark W, Jaunich M, Bohmeyer W and Lange K 2012 *Polymer Testing* **31** 904

[2]   Bielinski D M, Stepkowska A 2012 Mechanical properties and friction of rubber vulcanizates: Aspects of crosslink structure *Archives of civil and mechanical engineering* 192-198

[3]   Bošák O, Tóth M, Minárik S and Psota J 2011 Equipments for investigation of non-metallic materials. *XXIV Didmattech 2011 : Problems in teachers education. - Kraków : Instytut Techniki UP* ISBN 978-83-7271-679-8. 63-68

[4]   Milani G, Leroy E, Milani F and Deterre R 2013 *Polymer Testing* **32** 1052

[5]   Goyanes S, Lopez C C, Rubiolo G H, Quasso F and Marzocca A J 2008 *European Polymer Journal* **44** 1525

[6]   Zanchet A, Carli L N, Giovanela M, Brandalise R N and Crespo J S 2012 *Materials and Design* **39** 437

[7]   Leroy E, Souid A and Deterre R 2013 *Polymer Testing* **32** 575

[8]   Young Kee Chae, Woo Young Kang, Joong-Hee Jang and Sung-Seen Choi 2010 *Polymer Testing* **29** 953

[9]   Johns J and Nakason Ch 2011 *Journal of Non-Crystalline Solids* **357** 1816

[10]   Salgueiroa W, Somozaa A, Marzocca A J, Consolati G and Quasso F 2007 *Radiation Physics and Chemistry* **76** 142

[11]   Bošák O, Kalužný J, Preto J, Vacval J, Kubliha M and Hronkovič J 2007 *Polymers for Advanced Technologies* **18** 141