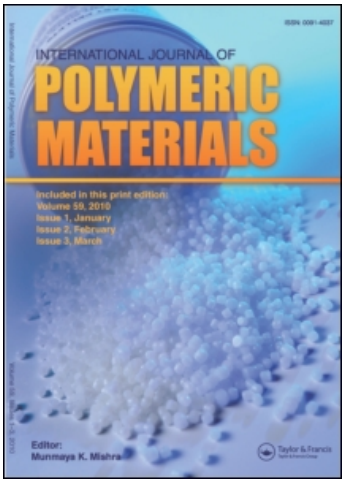

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Manganese Dioxide Structural Influence on Polysulfide Oligomers Cure Speed

Y. N. Khakimullin[a]; V. S. Minkin[a]; A. A. Idyatova[a]; Y. V. Minkina[a]; R. A. Deberdvaev[a]; G. E. Zaikov[b]
[a] Kazan State Technological University, Kazan, Russia [b] Institute of Biochemical Physics, Moscow, Russia

To cite this Article Khakimullin, Y. N. , Minkin, V. S. , Idyatova, A. A. , Minkina, Y. V. , Deberdvaev, R. A. and Zaikov, G. E.(2000) 'Manganese Dioxide Structural Influence on Polysulfide Oligomers Cure Speed', International Journal of Polymeric Materials, 47: 2, 373 — 378
To link to this Article: DOI: 10.1080/00914030008035072
URL: http://dx.doi.org/10.1080/00914030008035072

Intern. J. Polymeric Mater., 2000, Vol. 47, pp. 373–378
Reprints available directly from the publisher
Photocopying permitted by license only

Manganese Dioxide Structural Influence on Polysulfide Oligomers Cure Speed

Y. N. KHAKIMULLIN [a], V. S. MINKIN [a], A. A. IDYATOVA [a], Y. V. MINKINA [a], R. A. DEBERDYAEV [a] and G. E. ZAIKOV [b,*]

[a] *Kazan State Technological University, 68 Karl Marx St., Kazan Russia, 240015;*
[b] *Institute of Biochemical Physics, 4 Kosygin St., Moscow, Russia, 117334*

(Received 2 May 1999)

Characteristics of vulcanisation process of industrial polysulfide oligomers (PSO) by MnO_2 were studied. Influence of activity of MnO_2 industrial batches on parameters and EPR line forms of vulcanising agents were ascertained. The influence of cure speed on physical and mechanical properties of two sealants Y-30 M and AM-05 were analysed. It was established that activity of Mn dioxide used primarily influenced speed of cure but not the deformation, durability or hardness of final product.

Keywords: Thiokol; MnO_2 form and width of EPR lines; rate of vulcanisation; adhesion; durability

1. INTRODUCTION

Studies of the influence of MnO_2 structure on the cure rate of PSO are currently the subject of great interest. Vulcanising pastes used in PSO curing often have different activities, which is primarily due to activity of MnO_2 [1, 2]. During PSO vulcanisation lengthening of the chains, their occasional joining with oxidation of end thiokol groups of linear chains and long-chained branches are observed during synthesis of oligomers. At the same time decrease of molecular mobility of

*Corresponding author.

macromolecules and linked to it time of nuclear spin-spin relaxation T_2 are observed. The latter decreases [3, 4] until it reaches a particular minimal level, which changes in direct correlation with the density of vulcanisator nets and is a reliable structural kinetical parameter in analysis of liquid thiokols vulcanisation and based on them compositions.

2. METHODS

Structure and activity of different industrial batches of MnO_2, which used for PSO vulcanisation were investigated. Characteristics and structural parameters of MnO_2 industrial batches are shown on the Table I.

Methods of measuring time of spin-spin relaxation T_2 in the process of PSO vulcanisation as in Avero-Antonovitch *et al.*, 1974 [4]. Thiokols of type 2 (SH-group content 1.9%) and type 1 (SH-group content 2.8%), of TY 38.50309.93 standard, EPR spectra recorded on radiospectrometer JE-1 MEX with $\lambda = 3.2$ cm.

3. RESULTS AND DISCUSSION

EPR spectra of MnO_2 industrial batches shown in Figure 1. In all cases EPR spectra of MnO_2 and vulcanising pastes base on them show absorption signal brought about by Mn^{4+} ions. G-factor values, width and form of resonance lines are within the published values for MnO_2 and Mn^{4+} in glass and polymers [5, 6]. Increase in width of EPR lines is due to covalent link of Mn^{4+} ions with oxygen atoms, which has electron state ($3d^3$) as are Cr^{3+} and V^{2+} [5, 6]. Maximal width of the

TABLE I Characteristics and structural parameters of MnO_2 industrial batches

Industrial batch	*Composition MnO_2*	*Width of EPR lines δH, Gs (±0,2) (290°K)*	*g-factor (±0,001)*	*Form of the lines*
1.	80	560	1,956	complex
2.	78,2	1890	1,953	simple
3.	76,8	narrow component – 620 wide – 2013,2	1,956	complex
4.	82,7	1556,3	1,954	simple

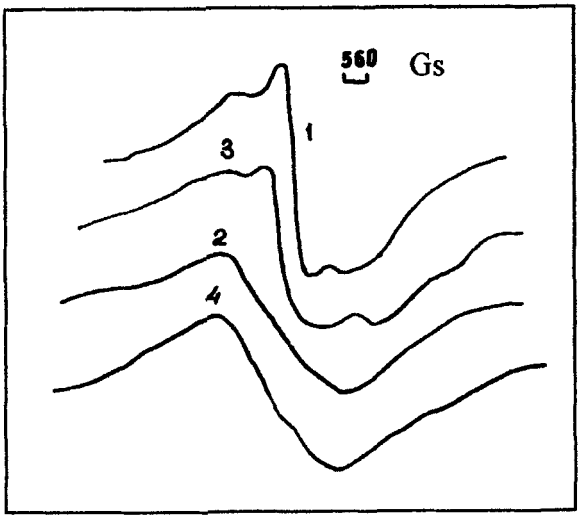

FIGURE 1 EPR spectra of industrial MnO_2 batches (numbers on the spectra correspond to the numbers of industrial parties in Tab. I).

resonance line δH was observed for the samples 2 and 4 in the Table I. Complex form of EPR lines especially characteristic of samples 1 and 3. It is noted that parameters of MnO_2 and vulcanising pastes on their base spectra have similar tendencies of resonance line changes, however the width of resonance lines for vulcanising pastes much lower due to the presence in them of plastificators (dibutylphtalate). As the quantitative criterion of MnO_2 activity we used the width and form of resonance line of EPR spectra, as those parameters well correlated with the activity and the distribution character of Mn^{4+} atoms in the oxidant.

After comparing the data from Table I and Figures 1 and 2, it is clear that observed differences in the activity and ion localisation of the oxidant do influence the kinetics of PSO vulcanisation. Figure 2 shows kinetic curve of the industrial thiokol type 1 vulcanisation with MnO_2 (samples 1, 2). The activity of the sample 1 almost two times higher than the activity of the sample 2. The effective constant of the vulcanisation rate ($k_1 \cdot 10^3 \, min^{-1}$) for the sample 1 is 3,7, whereas for the sample 2 is 7, 8. The oxidant activity shows also in industrial thiokol batches, which have different molecular weight (Fig. 3).

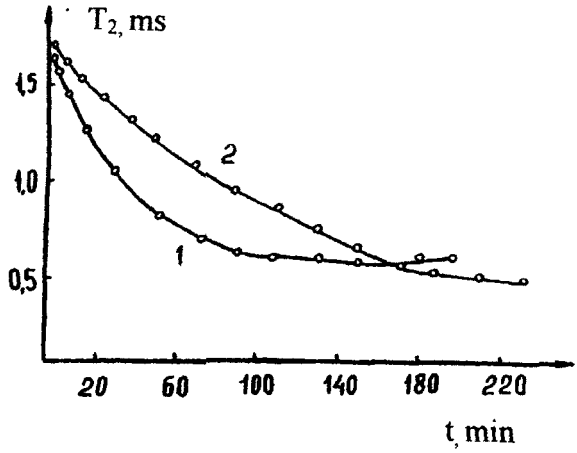

FIGURE 2 Kinetics of industrial liquid thiokols of type 1 vulcanisation by industrial MnO_2 batches of different activity (samples 1 and 2 from Tab. I).

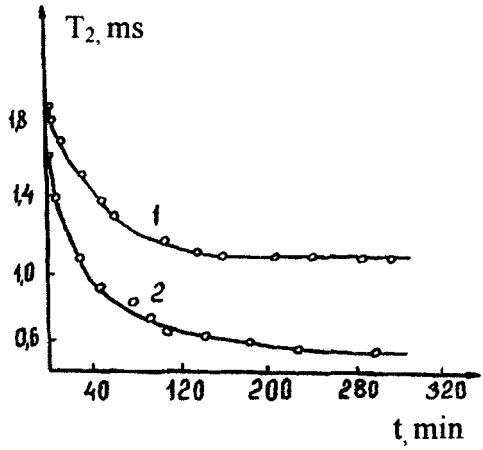

FIGURE 3 Kinetic of industrial liquid thiokols of type 1 (line 1) and type 2 (line 2) vulcanisation by industrial MnO_2 batches (sample 1, Tab. I).

This direct correlation between changes of EPR line width and the activities of industrial vulcanising agents noted for all the studied MnO_2 batches. The vulcanising agents with the line width of equal or less than 600 – 700 Gs show reasonably high activity in reaction of PSO

vulcanisation. Oxidants with the width value of over 1000 Gs characterised by low values of kinetic parameters.

Active batches of MnO_2 have complex form of EPR lines, which is due to the presence of Mn^{4+} ions of different activity (Fig. 1). In practice, wide anisotropic line of Mn^{4+} ions absorption represented by intensive narrow component of the spectrum of which in MnO_2 could reach 20–25% of the all Mn^{4+} ions. Therefore, despite large width of EPR lines of industrial MnO_2 batches their activity is relatively high due to the presence of highly mobile Mn^{4+} ions (narrow component of the spectrum) of quite high concentration, which have crucial influence on the rate of PSO oxidation at the early stage of liquid thikol vulcanisation (as observed for the samples 1 and 3).

Analysis of the acquired structural parameters allowed to estimate the activity of industrial MnO_2 batches in PSO reaction of vulcanisation before the actual vulcanisations.

Different activity, localisation and concentration of mobile Mn^{4+} ions in a vulcanisation process. The rate determines the length of life of thiokol-based compositions. To confirm the above assumptions we studied influence of cure rate on the qualities of 2 types of sealants Y-30M(compounds 1,2) and AM-05 (compounds 3,4), differing from each other by the nature of a filler (technical carbon P-803 and chalk correspondingly) and E-40 as part of AM-05 compositions. To cure compositions 1 and 2 MnO_2 (sample 1, Tab. I), and to cure compositions 2 and 4 MnO_2 (sample 2, Tab. I). The sealants cure was during 48 hours at 70°C.

From the data shown in the Table II, it is possible to conclude that the activity of MnO_2 primarily influence rate of cure (half-life, hardness Shore A after 24 and 48 hours), and practically do not influence deformation and durability or eventual hardness. Even during high

TABLE II Qualities of thiokol-based sealants acquired under different cure rates

No.	Sealant	*Half-life, min*	*Conditional durability during time of break, Mpa*	*Relative lengthening, %*	*Adhesion with duralumin, kH/m*	*Shore's hardness A*		
						24h,	*48h,*	*336h*
1.	Y-30M	10	2,87	275	–	48	51	56
2.	Y-30M	420	2,51	275	–	31	38	54
3.	AM-05	12	0,82	460	1,88	–	–	–
4.	AM-05	510	0,81	510	2,50	–	–	–

rates of cure (half-life 10–12 min.) no defective structures formation has been observed, which reduces durability.

It is necessary to notice some improvements of the sealant AM-05 adhesion to duralumin with higher half-life. This could be explained by improvement of condition for contact formation on the boarder between sealant -duralumin Therefore, as the result of the study we found that it is possible to predict activity of MnO_2 in vulcanisation of liquid thiokols by its EPR spectrum. The examples demonstrated that the activity of MnO_2 primarily influence the rate of sealants cure.

References

[1] Minkin, V. S. *et al.* (1981). High molecular weight compositions, series B, **23**(8), 593–96.
[2] Minkin, V. S. *et al.* (1994). *Moscow International Conference on Rubbers*, pp. 98–105.
[3] Minkin, V. S. *et al.* (1973). High molecular weight compositions, series B, **15**(1), 24–26.
[4] Averco-Antonovitch, L. A. *et al.* (1974). High molecular weight compositions, series A, **16**(8), 1709–1713.
[5] Altshuler, C. A. and Kosurev, B. M. (1972). EPR of compound of intermediate groups, Moscow Science, p. 262.
[6] Kuska, H. and Rogeres, M. (1970). EPR of compound of intermediate groups, Moscow Science, p. 82.