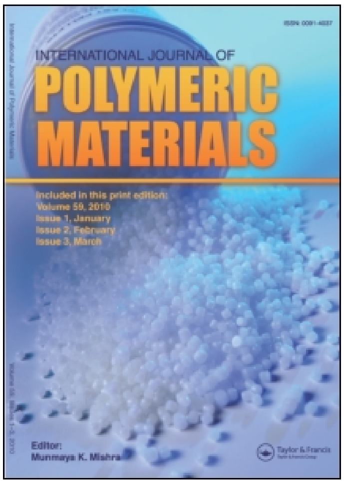

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Vulcanisation of Liquid Thiokol Based Sealants by Manganese Dioxide

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NMR and EPR methods were used to analyse structural and kinetic processes of vulcanisation of industrial liquid thiokols with manganese dioxide (MnO_2). We have established how the different compositions of batches of industrial MnO_2 affect the cure rate and density of chains forming molecular nets within the sealant. We have shown influence of structure and localisation of Mn^{4+} ions (as part of MnO_2) on the mechanism of liquid thiokols vulcanisation, which depending on vulcanisation conditions could go through adsorption–desorption processes of thiokol cure, or through mercaptide links formation. The latter then oxidised by the excess of MnO_2 or eliminated under influence of sulphur of with thermal vulcanisation.

Keywords: Thiokol; MnO_2; time of nuclear relaxation; density of nets chains; vulcanisation time

INTRODUCTION

It is known [1, 2] that the individual characteristics of MnO_2 batches (*i.e.*, % of MnO_2, its distribution, activity and the presence of impurities) have a considerable effect on kinetic parameters of vulcanisation and final qualities of thiokol-based sealants (TS). It has also been previously established [3], that MnO_2 could be non-homogenous in composition and contain Mn^{4+} ions of different activities. This generally affects the cure rate of industrial TS. Here we studied the

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*Corresponding author.

relationship between MnO_2 composition and concentration and the cure rate of industrial TS.

METHODS

MnO_2 parameters and characteristics as described in Minkin *et al.*, 1994 [1]. The method of measuring nuclear spin–spin relaxation T_2 in the process of thiokol vulcanisation previously described in Minkin 1997 [4]. Thiokols HVB-2 (3.9% SH-group content) and type 1 (2.8% SH-group content). All industrial thiokols were of TY 38.50309-93 standards. EPR spectra were recorded on radiospectromere JES-1MEX with λ = 3,2 cm. Densities of vulcanite nets were measured as in Cluff *et al.*, 1960 [5].

RESULTS AND DISCUSSION

The quality of MnO_2 used has a considerable influence on the cure rate. Analysis of T_2 change rate in vulcanisation process (Fig. 1) shows that with the increase of vulcanising agent concentration the transverse relaxation period finishes earlier. This is linked to the increase of vulcanising agent concentration above the optimum (CO-efficient of

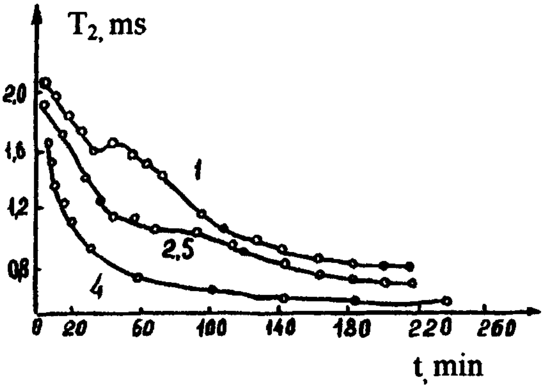

FIGURE 1 Dependence of nuclear spin–spin relaxation time T_2 from the time of vulcanisation of HVB-2 thiokol by MnO_2 of non-homogenous composition (values on the graphs indicate excess coefficient of vulcanising agent *n* against stecheometry).

excess against stechiometry $n = 2-2.5$), which leads to increased rate of vulcanisation and more defects in the net [2–4]. When concentration of vulcanising agent is below the optimum ($n < 2{,}5$), kinetics of the reaction show two distinct phases of vulcanisation: during beginning of the first phase T_2 drops rapidly and then plateaux; during the second phase further change of T_2 time observed–after end of plateaux and until constant level of T_2 reached, when vulcanisation reaction of polysulfide oligomers (PSO) ends.

The observed on Figure 1 two periods of vulcanisation when concentration of vulcanising agent below optimum ($n < 2, 5$), achieved when Mn^{4+} ions in the MnO_2 possess different activity, which is due to distortion of local internal symmetry in MnO_2 [4]. This differential localisation of Mn^{4+} ions was confirmed by investigation of parameters of EPR spectra at different temperatures. Figure 2 demonstrate a typical EPR spectra of vulcanising agents which have different activity of Mn^{4+} ions in dependence of type of link with their metal ligand.

During the first phase, characterised by the higher rate of vulcanisation, more active Mn^{4+} ions of vulcanising agent are involved (narrow component of EPR spectrum), which have weaker links with the crystal field of ligand. This type of Mn^{4+} ions characterised by strong deviation from octahedral symmetry and have weaker covalent links with six neighbouring oxygen atoms. Hence during the first stage

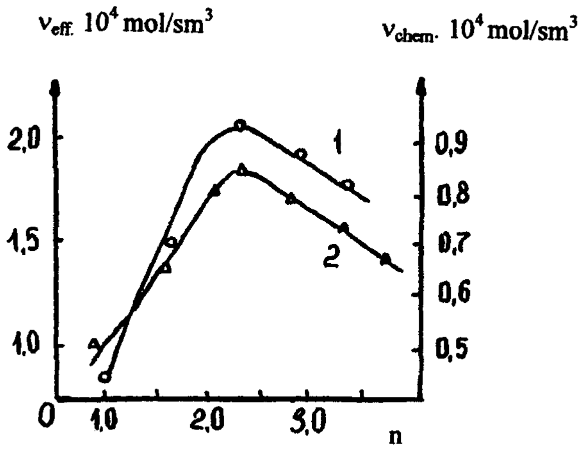

FIGURE 2 Appearance of MnO_2 EPR spectra ($T = 290°K$) a. MnO_2 with different mobility and localisation of Mn^{4+} ions; b. MnO_2 of homogenous composition.

oligomers oxidation happens at high rate. Then, when high activity Mn^{4+} ions used up, the rest of the Mn^{4+} ions of the vulcaniser, which linked stronger to the neighbouring atoms of oxygen and participating in bigger conglomerates, start to participate in vulcanisation process. During that time process of PSO vulcanisation starts to slow down.

As the concentration of vulcanising agent increases, the amount of higher activity Mn^{4+} ions increases and at the optimum concentration of MnO_2, which equal two times excess of necessary according to the reaction equation, the second stage of the kinetic reaction disappears. Vulcanisation process under this condition described by one smooth kinetic curve. It is noted that with optimal MnO_2 concentration most effective oligomer construction is observed (Fig. 3) and the density of chains in the net reaches maximal value [2].

Some industrial batches of MnO_2 have definite differences in activity and localisation of Mn^{4+} ions, however sometimes such batches are more homogenous (Fig. 2). When they are of the latter quality, the vulcanisation of PSO doesn't have two phases and described by a single smooth kinetic curve with different concentration of vulcanising agent.

It is conceivable that vulcanising agent which has homogeneously localised Mn^{4+} ions cure thiokols through adsorption–desorption mechanism [2], during which no mercaptide links formed. In cases,

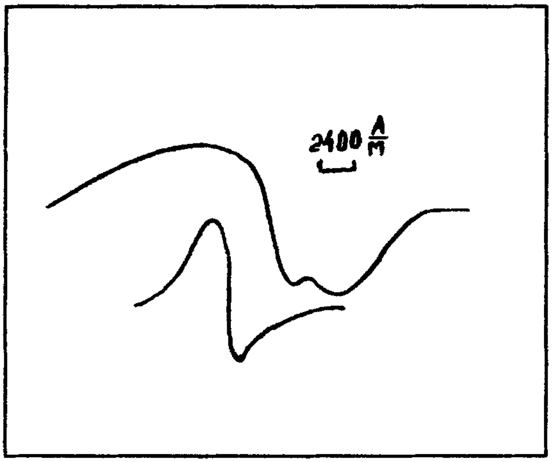

FIGURE 3 Dependence of the density effectives (1) and chemical chains of the net from the concentration of oxidant *n* (MnO_2).

when vulcanising agent has areas which differ in Mn^{4+} localisation and activity (in non-homogenous MnO_2), mechanism of vulcanisation could be described as in the scheme below:

$$2{\sim}R-SH+MnO_2 \rightarrow {\sim}R-S-S-R{\sim}+MnO+H_2O$$
$$2{\sim}R-SH+MnO \rightarrow {\sim}R-S-Mn-S-R{\sim}+H_2O$$

Initially mercaptide links are formed, which are then oxidised by MnO_2 excess:

$${\sim}R-S-Mn-S-R{\sim}+MnO_2 \rightarrow {\sim}R-S-S-R{\sim}+2MnO$$

or eliminated under thermal vulcanisation or under influence of sulphur:

$${\sim}R-S-Mn-S-R{\sim} \xrightarrow{T^0} {\sim}R-S-R{\sim}+MnS$$
$${\sim}R-S-Mn-S-R{\sim} \xrightarrow{S} {\sim}R-S-S-R{\sim}+MnS$$

It is likely that both types of reaction take place and their prevalence dependent on the composition of MnO_2 used (Fig. 4).

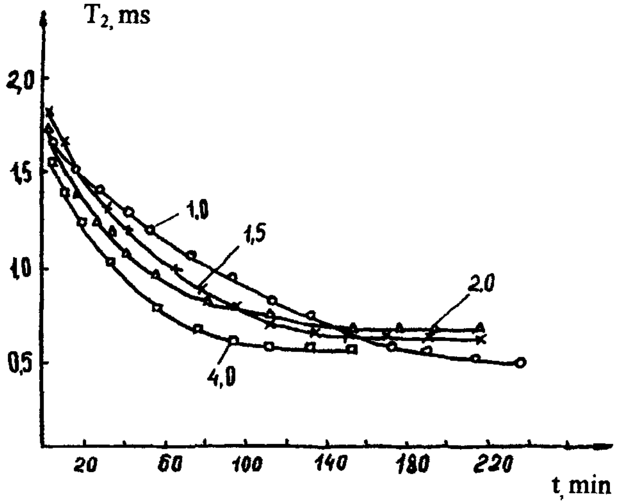

FIGURE 4 Dependence of spin–spin relaxation time T_2 from the time of thiokol vulcanisation by MnO_2 of homogenous composition. The values on the graph are the coefficients of the vulcanising agent n excess.

The effect of structure and localisation of Mn^{4+} in MnO_2 on the rate of cure nets of chains density of forming thiokol-based sealants was studied. A possible mechanism of vulcanisation of sealant with non-homogenous MnO_2 is suggested.

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