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Evidence of ionic intermediates in rubber vulcanization detected by on-line electric current measurements in natural rubber/sulfur/tetramethylthiuram monosulfide/zinc oxide and comparison mixtures

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Abstract

The vulcanization of a mixture of natural rubber (NR, *cis*-1,4-polyisoprene), elemental sulfur (S), tetramethylthiuram monosulfide (TMTM) and zinc oxide (ZnO), in addition to simpler systems containing some of these components, was investigated by means of an electrochemical method. A direct-current voltage was applied to the mixtures with two platinum electrodes. The current, e.g. in the range of 10^{-9} A, was recorded during vulcanization. The complicated curves obtained from the mixture containing S, TMTM and ZnO were most likely caused by the superposition of the contributions of different transitory ionic species. Current maxima occurred at the onset of cross-linking and also earlier. The final reaction product zinc dimethyldithiocarbamate (ZnDMTC) also provided some conductivity. For comparison, a reaction involving radical intermediates, the cross-linking of NR with dicumyl peroxide (DCP), was considered. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Vulcanization (curing) of rubbers with sulfur in the presence of sulfur-containing accelerators and other additives is of outstanding interest in relevant industry, especially in the production of automotive tires and various technical rubber articles. It is a major topic in general and in polymer science in connection with the theory of polymer networks and entropy elasticity.

The characteristic chemical modification of rubber during vulcanization is covalent cross-linking. However, the exact mechanism of most vulcanization reactions is still far from being completely understood. Nieuwenhuizen et al. ([1], p. 371) wrote in a review: “It is difficult to come up with an equally old industrial process where yet so much of the chemistry has remained unknown or unclear”.

In many cases it is still a problem to classify the general mechanism of a vulcanization reaction, i.e. if it has a radical, ionic or coordinative mechanism. For example, EPR (ESR) spectra give evidence of radical intermediates in the case of thiuram disulfide accelerators [2], whereas ionic reactions have been discussed in the presence of amine accelerators, zinc oxide or zinc dithiocarbamates [3,4]. It has even been proposed that radicals, ions, radical ions and so on, may occur in the same vulcanization process simultaneously or one after the other. Some vulcanization processes ‘may be a mixture of radical, ionic and polar (or concerted) reactions’ ([1], p. 402). Direct experimental evidence of ionic intermediates in vulcanization mixtures might be helpful to aid such discussions.

We recently described an investigation method in which the electrical conductivity of rubber mixtures during vulcanization, caused by reaction intermediates and products, can be measured on-line [5]. A prerequisite for the applicability of this method is that the initial mixture to be investigated should be free from electrically conducting additives or impurities, especially from conductive fillers such as carbon blacks. The principle of this method is the application of a DC voltage to the reacting vulcanization mixture under pressure, using a special thermostatted mould with chemically inert electrodes (e.g. platinum electrodes). The

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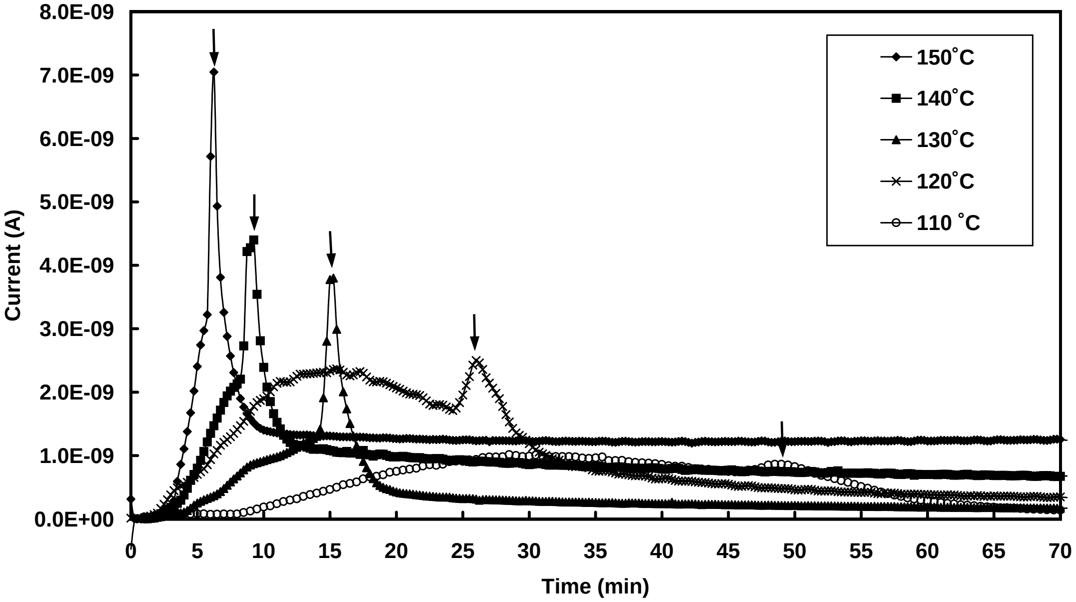

Fig. 1. Reaction of a mixture of NR, S, TMTM and ZnO: investigation by means of electric current measurements from 110 to 150°C, maxima *P* marked with arrows.

resulting electric current is measured with a sensitive ammeter and recorded quasi-continuously as a function of vulcanization time. The curves obtained are characteristic of the composition of the reaction mixture, the vulcanization reaction under investigation and the reaction conditions. They are a kind of 'fingerprint' of the vulcanization process. As far as we know, Ref. [5] describes the first application of this investigation method in vulcanization chemistry. The simplest possible explanation for the electrical conductivity, obtained in the experiments, is the formation of ions.

The experimental example in the previous paper [5] was the 'sulfurless' vulcanization of NR with tetraethylthiuram disulfide and ZnO. The current passed through a maximum (only one) which was reached after a well-defined time. The time to reach the maximum decreased as the reaction temperature increased. With a voltage of 5.0 V, the current maximum at 150°C was, for example, in the nanoampere range.

The vulcanization of NR with S, TMTM and ZnO is considered in the present investigation.

$(CH_3)_2N–CS–S–CS–N(CH_3)_2$ TMTM

2. Experimental

2.1. Substances

NR (pale crepe) was purified by Soxhlet extraction with acetone for 3 days, dried and masticated on a laboratory mill which was also used for the combining of reactants. S (as applied in rubber industry), ZnO (Fluka 96479) and dicumyl peroxide (DCP, Aldrich 32,954-1) were used as received. TMTM (Perkacit TMTM-grs-3 mm, Hazeldonk, NL) was recrystallized from a boiling water/ethanol mixture (3:1, v:v), m.p. 107–108°C. Zinc dimethyldithiocarbamate, $[(CH_3)_2N–CS–S]_2Zn$ (ZnDMTC, Fluka 96480, pract.), was purified by recrystallization from boiling chloroform.

2.2. Vulcanization and DC measurements

A detailed description of the experimental set-up, including a discussion of this method and possible complications (e.g. polarization effects) can be found in Ref. [5].The reaction was performed in a thermostatted two-part aluminum mould which was placed between the platens of a heating press. The mould containing the sample was placed under a pressure of 20 kN. The reaction mixture (ca. 0.25 g) was positioned between the two electrodes which consisted of circular discs made of platinum foil (diameter of 1.47 cm). The electrodes were located in an insulating hollow ceramic cylinder with an inner diameter of 1.47 cm which was coated with a thin Teflon layer. The distance between the electrodes was 0.12 cm. As a consequence, the rubber mixture sample (vulcanizate) was a cylinder with a diameter of 1.47 and a height of 0.12 cm.

A DC voltage of 5.0 V was applied to the platinum electrodes. The current measurements were made with an ammeter from Keithley Instruments Inc., Cleveland (OH, USA), model picoammeter 487/voltage source. The computer software Test Point 3.3 from Capital Equipment Corp., Billerica (MA, USA) was used to design an application program for carrying out real-time measurements and data acquisition.

In principle, the specific resistance of the sample can be calculated from the voltage applied, the current data and the

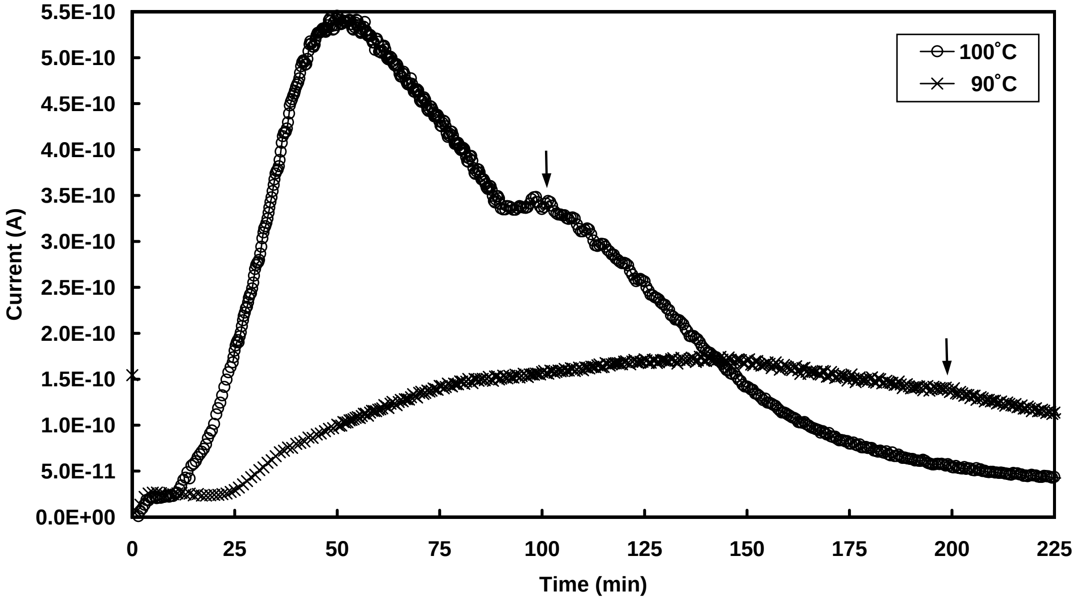

Fig. 2. Reaction of a mixture of NR, S, TMTM and ZnO: investigation by means of electric current measurements at 90 and 100°C, maxima *P* marked with arrows.

dimensions of the sandwich-like arrangement of electrode/vulcanizate/electrode. However the calibration of the measurement arrangement proved to be difficult and the absolute value of the specific resistance was unnecessary for the intended evaluation of the measurements. For this reason, the data given are the directly measured current values.

All curves are the average of three measurements. No correction was made for the time needed to heat the mould to the desired reaction temperature (about 2.5 min at 150°C).

2.3. Vulcametry

The vulcameter was a Monsanto Rheometer 100. For principles of vulcametry see Ref. [6]. In these measurements also no correction was made for the time needed to heat the sample to the reaction temperature.

3. Results and discussion

3.1. NR/S/TMTM/ZnO

A mixture (in parts by weight) of NR (100), S (4.0), TMTM (1.5) and ZnO (2.0) was vulcanized. Fig. 1 shows the DC curves obtained for vulcanization temperatures from 110 to 150°C. The current is mainly in the nanoampere range. There is at least one inflection point in the ascent of the curves at 130, 140 and 150°C. In all cases, a sharp maximum *P* appears (marked with an arrow). A second flatter maximum *Q* exists at lower temperatures which can be seen for temperatures 120 and 110°C. The complicated curves can be interpreted as a superposition of the contributions of different ions. In Fig. 2, the curves for 90 and 100°C demonstrate that maximum *Q* is, in this case, higher than maximum *P* which at a temperature of 90°C is only a small bulge in the curve. This peak is better recognizable in single curves than in the mean of three measurements, which is depicted here. Both curves have an induction period, this is about 23 min at 90°C.

These kinetics need further investigation. It has been previously supposed that at the beginning of this vulcanization process S reacts with TMTM to form tetramethylthiuram disulfide (TMTD) [7].

$$\text{TMTM} + \text{S} \rightarrow (\text{CH}_3)_2\text{N–CS–S–S–CS–N}(\text{CH}_3)_2 \quad \text{TMTD}$$

The TMTD is supposed to be the actual vulcanization agent [8]. Assuming this starting reaction to precede the actual vulcanization process, it is not astonishing that the curves in Figs. 1 and 2 are more complicated than those obtained for the vulcanization with a thiuram disulfide [5].

The times required to reach the maxima *P* and *Q* were determined from 90 to 150°C with temperature intervals of 2.5°C (Fig. 3). Especially maximum *P* (solid curve) was determined with a good reproducibility.

In Fig. 4, the cross-linking reaction was measured by vulcametry [6]. The vulcameter curves are plotted as a function of time. The time of maximum *P* is marked with an arrow. It is clearly shown that maximum *P* is at the end of the induction period of vulcanization, either before the rise of the vulcametric curves begins (below about 140°C) or at the beginning of this rise. Maximum *P* seems to be related to a species that is present just before cross-linking commences, but which decreases once significant cross-linking has occurred.

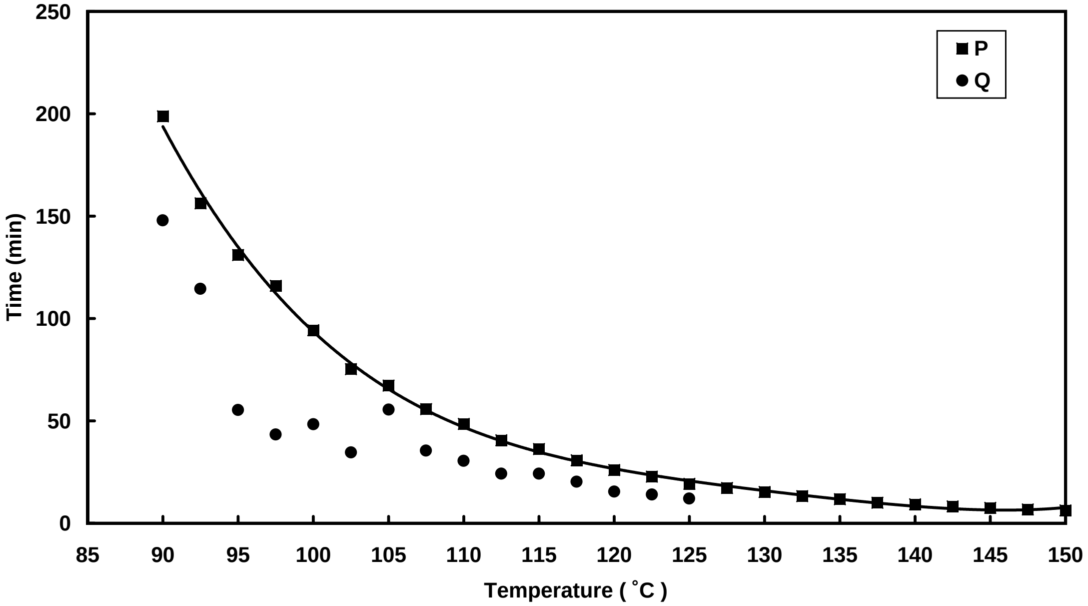

Fig. 3. Reaction of a mixture of NR, S, TMTM ZnO: maxima *P* and *Q* obtained by means of electric current measurements.

3.2. NR/S/TMTM

It is well-known that the system NR/S/TMTM does not give usable rubber vulcanizates. The addition of ZnO is required for the formation of sufficient amounts of cross-links.

The mixture (in parts by weight) consisted of NR (100), S (4.0) and TMTM (1.5). Fig. 5 shows that a current in the nanoampere range is obtained even in the absence of ZnO. Surprisingly, ZnO is not necessary for the formation of ions. The curves have lower maxima than those in Figs. 1 and 2, and the overall shape of the curves differs. Also for a given temperature, the maxima occur after longer reaction times in comparison with the maxima in Fig. 1, for example approximately 56 min at 130°C compared with 15 min for maximum *P* in Fig. 1. Other maxima are 96.5 min at 120°C and 203.5 min at 110°C (not shown in Fig. 5). It is thought that the ions observed result from the reaction of S with TMTM.

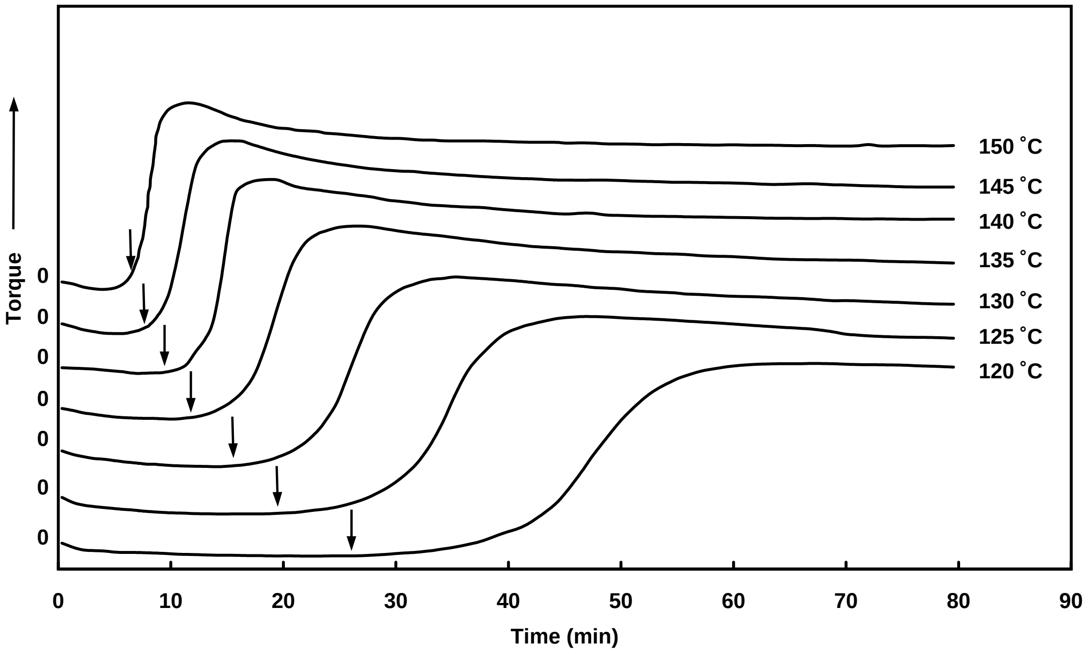

Fig. 4. Reaction of a mixture of NR, S, TMTM and ZnO: vulcametric measurements, the arrows indicate the position of maxima *P* in the investigation by means of electric current measurements.

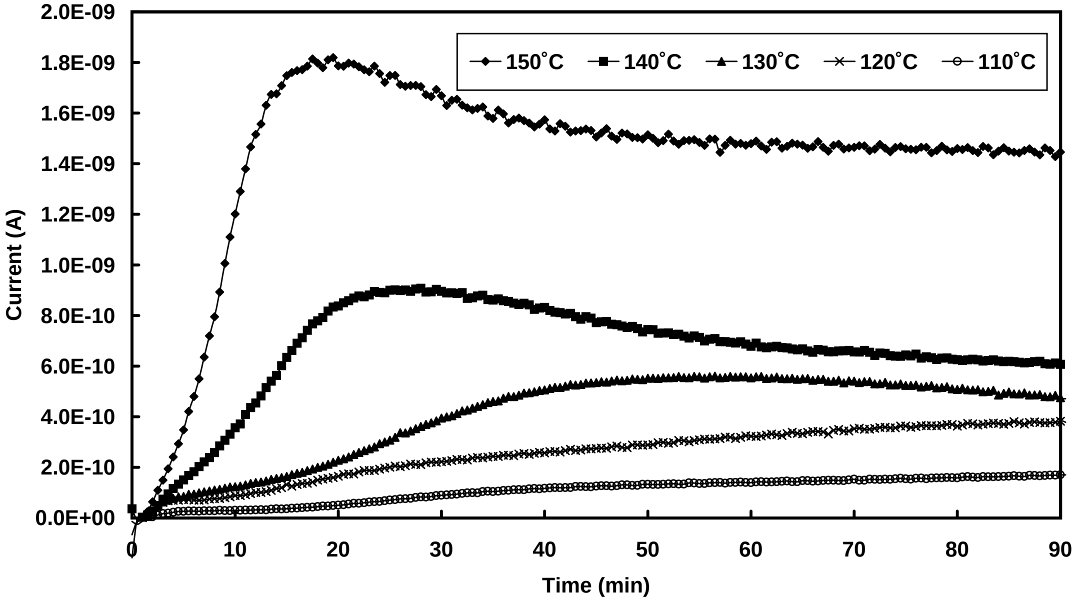

Fig. 5. Reaction of a mixture of NR, S and TMTM, investigation by means of electric current measurements.

3.3. Comparison with other reaction mixtures

A disadvantage of using conductivity measurements in vulcanization investigations is that the mixtures are multi-component systems and there is superposition of various conductivity contributions. It could be useful therefore to compare these results with those obtained from mixtures of other compounds with a simpler composition. The results of all systems, investigated at 150°C and a reaction time of 90 min (this was sufficient for obtaining an approximately constant value of the current) are listed in Table 1. The current values for NR/S/TMTM and NR/S/TMTM/ZnO are in the range of 10^{-9} A.

ZnDMTC is a reaction product of the system NR/S/TMTM/ZnO [8]. The current obtained with NR/ZnDMTC is in the range of 10^{-10} A. It is to be expected that ZnDMTC contributes to the final conductivity in Figs. 1 and 2 at long reaction times.

NR mixtures containing TMTM without S had a lower conductivity than with S. The current values for NR/TMTM/ZnO and NR/TMTM are in the range of 10^{-10} A. The presence of ZnO has only a minor influence. These results confirm former observations [9,10] that there is only a negligible reaction between TMTM and ZnO in the absence of sulfur. The mixture NR/S had a rather low conductivity in the range of 10^{-11} A. Previously a current of about 10^{-11} A was found [5] for NR without additives.

The lowest conductivity observed in our present experiments (see Table 1) was found for the mixture NR/DCP. Peroxides such as DCP cause effective cross-linking via a purely radical mechanism. The reaction begins with a thermal homolytic cleavage of the peroxide.

$$C_6H_5C(CH_3)_2\text{–O–O–}C(CH_3)_2C_6H_5 \rightarrow 2\ C_6H_5C(CH_3)_2\text{–}O^{\cdot}$$

These low-molecular-weight radicals remove hydrogen atoms from the polymer and the polymer radicals recombine under cross-linking. The kinetics of this reaction sequence were already elucidated in the 1960s [11].

It seems reasonable to compare the other results presented in Table 1 with those obtained from the NR/DCP mixture. If the reactions in NR/DCP are considered to be non-ionic, then the reactions in the mixture NR/S also have to be considered non-ionic. The currents measured for NR/S/TMTM and NR/S/TMTM/ZnO are a factor of about 10^2 higher than those for NR/DCP. This provides evidence of transitory ionic species in the mixtures NR/S/TMTM and NR/S/TMTM/ZnO. Free ions should also exist in the mixture NR/ZnDMTC at 150°C. Some ions should also be formed in the mixtures NR/TMTM and NR/TMTM/ZnO at 150°C.

Table 1
Reactions of various additives in NR at 150°C, electric current measurements, values after 90 min reaction time (experimental conditions see text and Ref. [5], voltage 5.0 V)

Components	Parts by weight[a]	Current (A)
NR/S/TMTM	100/4.0/1.5	1.43×10^{-9}
NR/S/TMTM/ZnO	100/4.0/1.5/2.0	1.26×10^{-9}
NR/ZnDMTC	100/3.1	3.95×10^{-10}
NR/TMTM/ZnO	100/1.5/2.0	1.56×10^{-10}
NR/TMTM	100/1.5	1.30×10^{-10}
NR/S	100/4.0	3.82×10^{-11}
NR/DCP	100/2.7	2.78×10^{-11}

[a] 4.00 g (125 mmol) S; 1.50 g (7.20 mmol) TMTM; 2.00 g (24.58 mmol) ZnO; 3.06 g (10.0 mmol) ZnDMTC; 2.70 g (10.0 mmol) DCP.

4. Conclusions

On-line investigations of vulcanization processes of rubbers are mostly carried out by cross-linking measurements (vulcametry), spectroscopy (IR, NMR), calorimetry (DSC) or by the measurement of dielectric properties. The type of electric current measurements described here belongs to this group of real-time investigation methods. Current measurements give direct evidence of ions in the rubber mixture. Complementary investigation methods are required because DC measurements cannot give evidence of uncharged or radical components in the mixture.

The current curves are related to the vulcanization kinetics. Two maxima were found in the system NR/S/TMTM/ZnO. They occur at the onset of cross-linking and also earlier during the scorch period corresponding to the formation of transitory ionic species at these stages. One maximum dominates at the higher cure temperatures, while the other dominates at the lower temperatures. Complicated current curves point to systems with a number of different ions.

The purely radical cross-linking of rubbers with dicumyl peroxide is a suitable reaction for comparison with cross-linking via ionic intermediates.

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