

Evidence of Ionic Components in Vulcanization Mixtures by Means of Electric Current Measurements: Investigations with Natural Rubber/Sulfur/Zinc Bis(dimethyldithiocarbamate) and Comparison Mixtures

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ABSTRACT: Continuous low-level current (CLLC) measurements for detecting ionic species in the course of vulcanization reactions were applied to investigate the vulcanization of a mixture of natural rubber (NR), sulfur (S), and zinc bis(dimethyldithiocarbamate) (ZnDMTC). A dc voltage was applied to the reaction mixture in a special vulcanization mold and the current (e.g., in the range of 10^{-9} A) was measured. Temperature-dependent current maxima were found after reaction times t_{\max} . The simplest explanation is that transitory ionic species occur during vulcanization. An activation energy (E_a) = 116.4 kJ/mol, similar to that obtained in previous chemical investigations, was determined from the decrease of t_{\max} with increasing temperature. The maxima corresponded to reaction times where a strong increase of polymer crosslinking was observed, as measured using vulcametry. For comparison, dc measurements were carried out with the corresponding mixture without elemental sulfur (NR/ZnDMTC) and mixtures containing zinc stearate (ZnST) instead of zinc bis(dimethyldithiocarbamate) (NR/S/ZnST and NR/ZnST). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2206–2212, 2000

Key words: natural rubber; sulfur vulcanization; ionic components; zinc bis(dimethyldithiocarbamate); electric current measurements

INTRODUCTION

The chemistry of rubber curing is known to be complicated and the exact mechanism of most reactions is not yet satisfactorily elucidated. This is evident for the vulcanization with elemental sulfur (S) in the presence of accelerators.¹ In many cases, it is even difficult to decide if a vulcanization reaction has a radical, ionic, or coordinative mechanism or if intermediates of various types occur simultaneously.

As a contribution to the solution of this problem, we recently described an electrochemical investigation method (as far as we know, new in this field) to provide evidence of ionic intermediates during vulcanization using continuous low-level current (CLLC) measurements.² The reaction mixture was positioned between two platinum electrodes in a two-part mold which was under the pressure of a thermostatted heating press. Applying a constant dc voltage, the current was recorded quasi-continuously during the whole vulcanization time. Current maxima occurred and could be explained with the occurrence of ionic species.

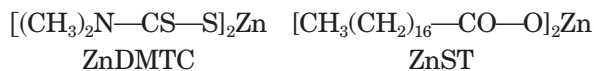
Our previous investigations were carried out with natural rubber (NR, *cis*-1,4-polyisoprene)

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mixtures. They did not contain electrically conductive additives such as carbon black, as this was thought to facilitate evidence of ionic species during vulcanization. Investigation examples were NR/tetraethylthiuram disulfide/ZnO,² NR/S/tetramethylthiuram monosulfide/ZnO,³ NR/S/2-mercaptobenzothiazole/ZnO/stearic acid,⁴ and simpler mixtures. Under the given experimental conditions (e.g., between 130 and 150°C), the expected dc current maxima for transitory ionic species were found in the range of 10^{-9} A.

In the present article, investigations with the vulcanization accelerator zinc bis(dimethyldithiocarbamate) (ZnDMTC) were performed. The mixture NR/S/ZnDMTC, which is an industrial vulcanization system, was investigated using dc current measurements. In addition, vulcametric investigations (concerning kinetics of crosslinking) were carried out. Current measurements were also performed with a corresponding mixture without S, namely, NR/ZnDMTC. Other comparison mixtures containing zinc stearate (ZnST) instead of ZnDMTC, namely, NR/S/ZnST and NR/ZnST, were also investigated:



ZnDMTC and ZnST provide electric conductivity to NR, which is to be expected if free low-molecular-weight ions are present. The electric current measured increases with the temperature. Possible reasons are the increases in dissolution of the ion-producing substances, in the degree of dissociation, and in the ion mobility.

EXPERIMENTAL

Materials

NR (pale crepe) was purified by Soxhlet extraction with acetone for 3 days, then dried and masticated on a laboratory mill. S, as applied in rubber industry, was used as received. ZnDMTC (Fluka, Buchs, Switzerland, No. 96480), mp 248–250°C, was dissolved in boiling chloroform under reflux for purification. The solution was filtered and cooled to -10°C for recrystallization.

ZnST (Aldrich, Steinheim a.A., Germany, No. 30,756-4) had a mp of 128–130°C. An attempt of further purification by recrystallization from boiling toluene was not successful. For ZnST, melting points between 120 and 140°C have been pub-

lished.^{5,6} Commercial ZnST usually contains the zinc salt of palmitic acid and some excess of zinc oxide.⁵ These foreign substances do not interfere with the investigations performed.

Vulcanization and CLLC Measurements

A detailed description of the experimental setup was published recently.² The reaction mixture (ca. 0.25 g) was vulcanized in a hollow ceramic cylinder (internal diameter 1.47 cm). The electrodes were circular discs (diameter 1.47 cm) made of platinum foil with a thickness of 0.025 cm. The insulating ceramic cylinder was positioned in a two-part aluminum mold, which was placed under the pressure (20 kN) of the platens of a laboratory heating press. The electrodes were thereby pressed to the reaction mixture. This sandwichlike arrangement produced cylindrical rubber samples with a diameter of 1.47 cm and a height of 0.12 cm.

During vulcanization, a dc voltage of 5.0 V was applied to the electrodes. Current measurements were made with a sensitive ammeter (487 Picoammeter/Voltage Source from Keithley Instruments Inc., Cleveland, OH).⁷ It was found that polarization effects were negligible.²

A computer program for carrying out real-time measurements and data acquisition was designed using commercial software (Test Point 3.3 from Capital Equipment Corp., Billerica, MA). The data given are the directly measured current values. The absolute values of the specific resistance (which can be calculated from the voltage applied, the current, and the dimensions of the arrangement electrode/vulcanizate/electrode using some kind of calibration) are unnecessary for the intended evaluation of the measurements. The current curves shown are the average of three measurements. The times t_{max} needed for reaching the curve maxima were satisfactorily reproducible in all cases.

The time for heating the mold from room temperature to the desired reaction temperature (e.g., 150°C) was about 2.5 min. A correction for this heating time was only made in the determination of the t_{max} values of Table I and the Arrhenius plot in Figure 3.

Vulcametry

A Monsanto Rheometer 100 was used. In the measurements shown in Figure 4, no correction was made for the time needed to heat the sample in

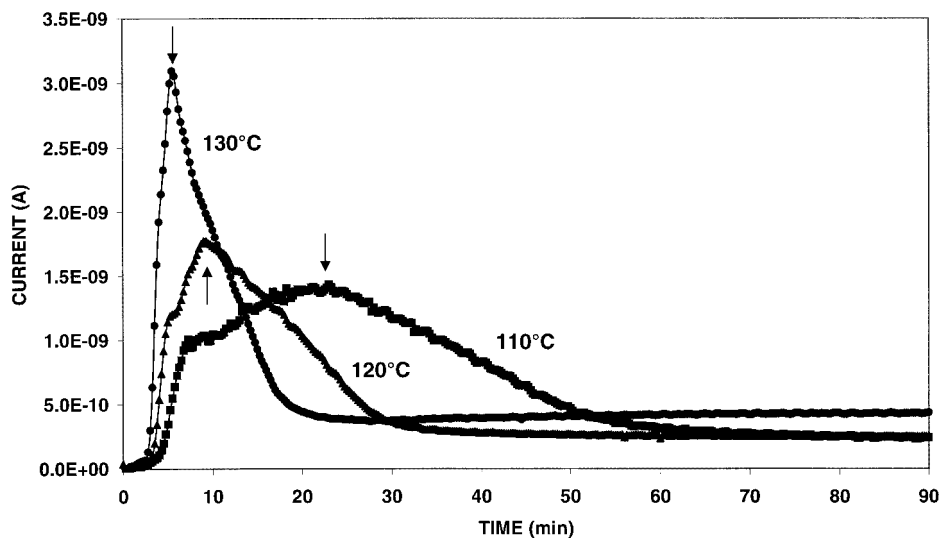


Figure 1 Mixture of NR, S, and ZnDMTC: investigation using electric current measurements from 110 to 130°C; maxima *P* are marked with arrows.

the vulcameter to the reaction temperature. For principles of vulcametry, see ref. 8.

RESULTS AND DISCUSSION

Vulcanization of the Mixture NR/S/ZnDMTC

The results for a mixture of 100 g of NR, 4.0 g (125 mmol) of S, and 3.085 g (10.0 mmol) of ZnDMTC are shown in Figure 1 (reaction temperature 110–130°C) and Figure 2 (80–100°C). The curves pass

through maxima *P*, which are marked with arrows in Figures 1 and 2. The times t_{\max} for reaching maxima *P* are listed in Table I; the values are corrected by subtracting 1.5 min to compensate for the lower reaction rate during the heating period. At a short reaction time, a step is found in the curves for 110 and 120°C and a second maximum for 80 to 100°C. The curves demonstrate that different ions exist in the reaction mixture which pass through maxima at well-defined different times.

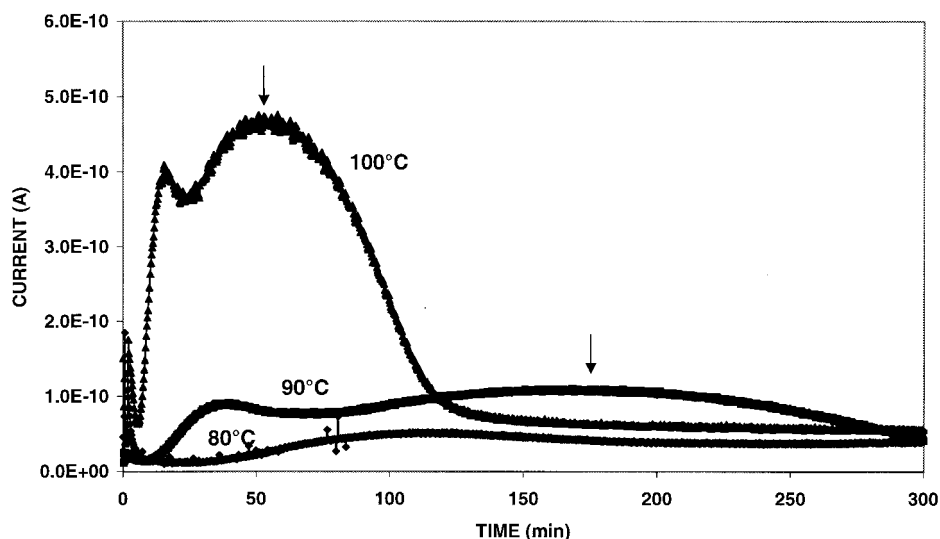


Figure 2 Mixture of NR, S, and ZnDMTC: investigation using electric current measurements from 80 to 100°C; maxima *P* are marked with arrows.

Table I Electric Current Measurements: Mixture of 100 g of NR, 4.0 g (125 mmol) of S, and 3.085 g (10.0 mmol) of ZnDMTC

T ($^{\circ}\text{C}$)	t_{\max} (min)
130	4.0
120	7.8
110	21.3
100	51.0
90	176.5
80	494.5

t_{\max} at different temperatures (see text).

The experimental activation energy (E_a) of a chemical reaction is generally calculated from the temperature dependence of the rate constants. However, if the rate constants of the reaction are unknown, times t_x with an equal conversion x can be used for the determination of E_a . It was discussed previously that under certain preconditions E_a can be determined from the decrease of t_{\max} values with increasing temperature.^{2,9} In Figure 3, the reciprocal t_{\max} values of Table I are plotted logarithmically against the reciprocal absolute temperature. An E_a value of approximately 116.4 kJ/mol was obtained. This is a reasonable value for chemical reactions. Scheele and Birghan obtained a value of $E_a = 122.2$ kJ/mol for this type of vulcanization under other reaction conditions.¹⁰

The crosslinking of the mixture used in the investigation of Figures 1–3 was measured by vulcametry.⁸ It is shown in Figure 4 that at maximum P (marked with arrows) about half of the crosslinking has already taken place. Therefore, maximum P can be attributed to ions which are directly involved in crosslinking. Their concentrations decrease when substantial crosslinking has occurred. Concerning the connection between the appearance of the current maxima (i.e., ion maxima) and the crosslinking reaction, the results are similar to those obtained with the above-mentioned other vulcanization systems.^{2–4}

One problem to be solved is whether the ions are really intermediates of the vulcanization process. Ions could exist in equilibrium with nonionized species, with only the nonionized species participating in the reaction. When the concentration of the nonionized species decreases due to its reaction, so will the ion concentration. Another remaining problem is the possible role of small amounts of water present in the starting rubber or formed in the course of the reactions which will influence the electric current.

Complementary Investigations

For comparison, CLLC measurements with ZnDMTC in the absence of sulfur were carried out. A mixture of 100 g of NR and 3.085 g (10.0 mmol) of ZnDMTC was investigated. The results for 120–140 $^{\circ}\text{C}$ are shown in Figure 5. No maxima are

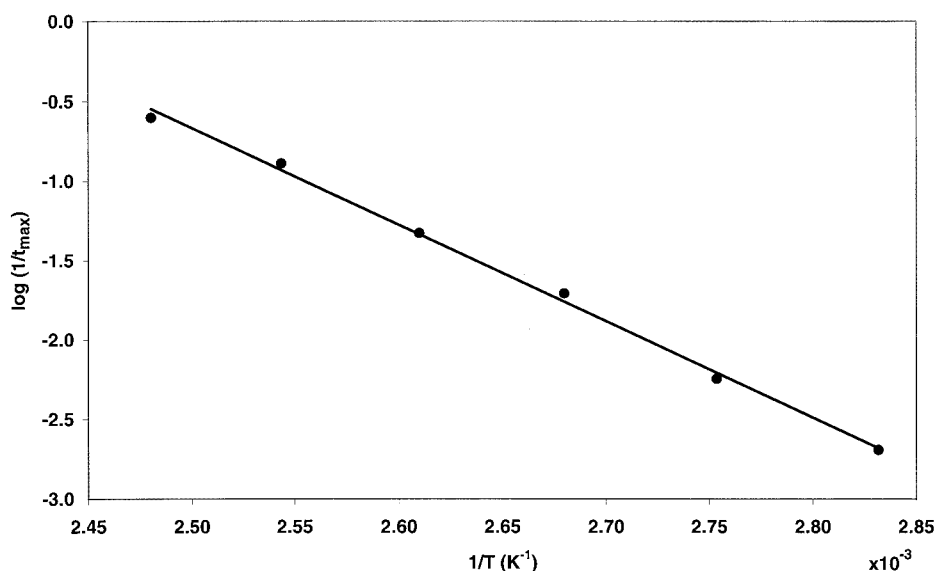


Figure 3 Determination of the experimental activation energy (E_a) from the data in Table I.

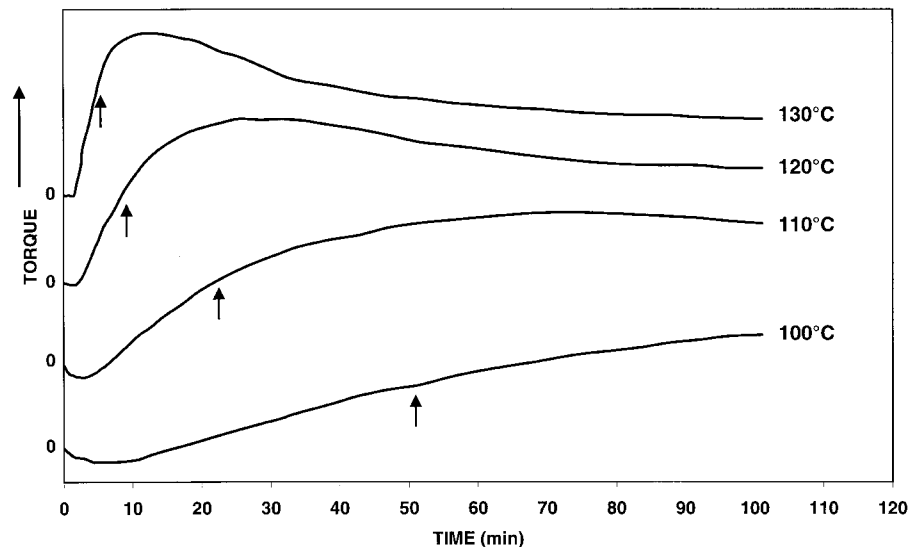


Figure 4 Mixture of NR, S, and ZnDMTC: vulcammetric measurements; the arrows indicate the position of the maxima P in the investigation using electric current measurements.

observed in contrast to Figures 1 and 2. The increase in current with the time can be explained with an increasing dissolution of the ZnDMTC in the rubber and/or a gradual thermal decomposition of the ZnDMTC.^{11,12} The dissolved products are thought to dissociate to low molecular weight ions, causing additional conductivity. The current values for the mixture NR/ZnDMTC obtained after 90 min are listed in Table II.

Figure 6 shows measurements for a mixture of 100 g of NR, 4.0 g (125 mmol) of S, and 7.40 g (11.7

mmol) of ZnST. At first sight, the curves seem to have maxima (marked with circles) at low reaction times. However, the time needed to reach these maxima does not increase with decreasing temperature, as in Figures 1 and 2. For higher temperatures (140 and 150°C), there is a remarkable decrease of the current to a value of 2×10^{-10} A. A possible explanation for this observation is that Zn^{2+} ions are removed from the ion equilibrium by the formation of insoluble products (ZnS and zinc mercaptides). It is well known

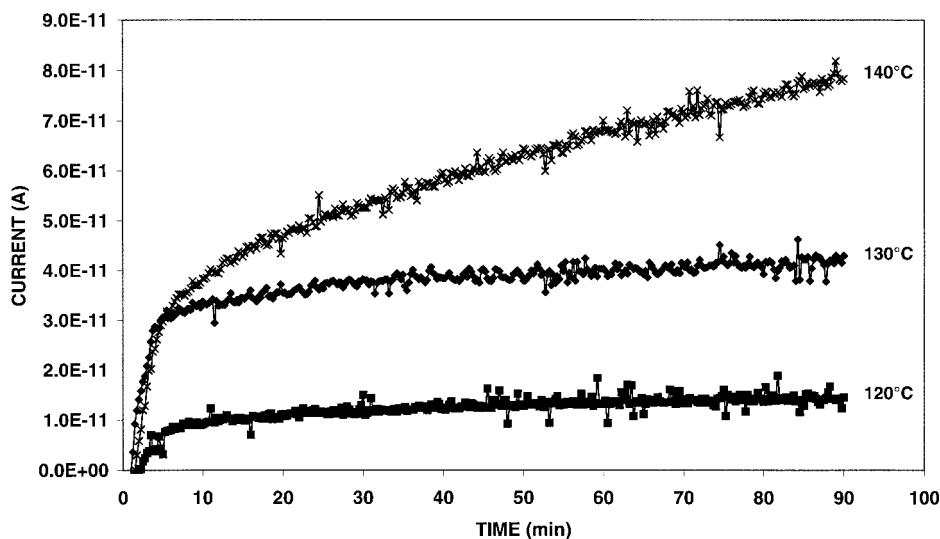


Figure 5 Mixture of NR and ZnDMTC: investigation using electric current measurements from 120 to 140°C.

Table II Electric Current Measurements: Mixture of 100 g of NR and 3.085 g (10 mmol) ZnDMTC at Different Temperatures After 90 Min Reaction Time

T ($^{\circ}\text{C}$)	Current (A)
160	1.38×10^{-9}
150	3.95×10^{-10}
140	7.83×10^{-11}
130	4.30×10^{-11}
120	1.45×10^{-11}
110	6.81×10^{-12}

that rubber mixtures containing S and zinc compounds result in vulcanizates with a substantial content of ZnS.¹³ An interesting question arises as to the fate of the stearate residue. The formation of stearic acid is probable. There are observations in the literature that free stearic acid is formed from ZnST or similar salts during sulfur vulcanization.^{14,15} In additional experiments, we found that the electric current obtained for a mixture of 100 g of NR and 3.33 g of stearic acid was rather low (about 1.5×10^{-10} A after 90 min at 150°C).⁹

The behavior of a mixture of 100 g of NR and 7.40 g (11.7 mmol) of ZnST was investigated between 90 and 150°C (see Fig. 7). The current values for a given temperature are in all cases higher than for NR/ZnDMTC (compare Fig. 5). As

in Figure 6, the curves seem to have maxima (marked with circles) at low reaction times and the time to reach these maxima does not increase with decreasing temperature. There is a kind of peculiarity between 110 and 130°C ; for example, the current value found for 110°C is higher than for 120°C after 15 min and longer times, although, in all other cases, the current increases with increasing temperature. A possible explanation for this irregular behavior can be based on the fact that ZnST melts in this temperature range. We carried out differential scanning calorimetry (DSC) investigations with the NR/ZnST mixture.⁹ A strong endothermic peak was found between 110 and 130°C , which can be attributed to the melting of ZnST.

CONCLUSIONS

Reactions in vulcanization mixtures containing ZnDMTC were often described with mechanisms including ionic reactions.¹ We applied CLLC measurements for the investigation. If transitory ionic species occur during vulcanization, the method used should give electric current maxima and the time to reach these maxima should be temperature-dependent.²⁻⁴ They are found only for the investigations with NR/S/ZnDMTC, but not with mixtures NR/S/ZnST. This corresponds to the fact that ZnDMTC is used in the rubber

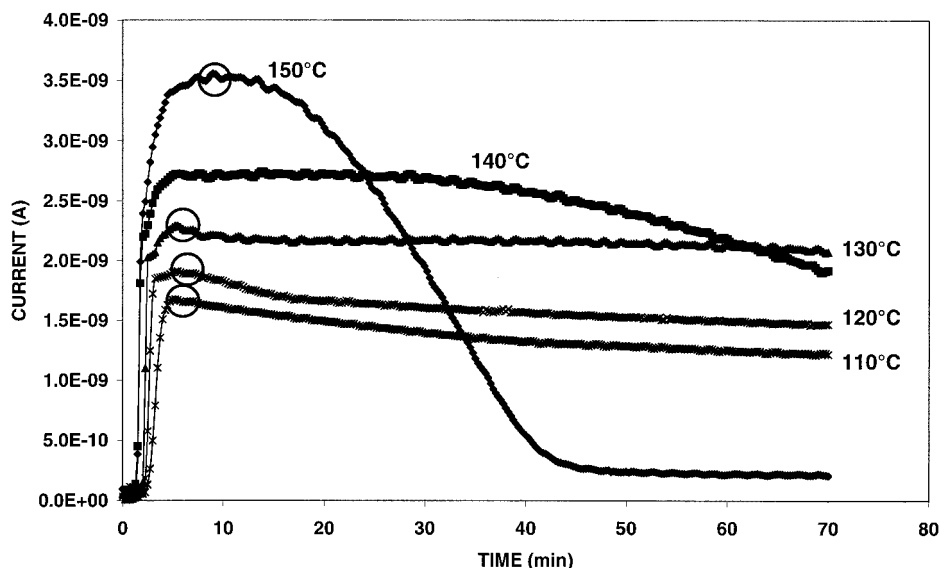


Figure 6 Mixture of NR, S, and ZnST: investigation using electric current measurements from 110 to 150°C .

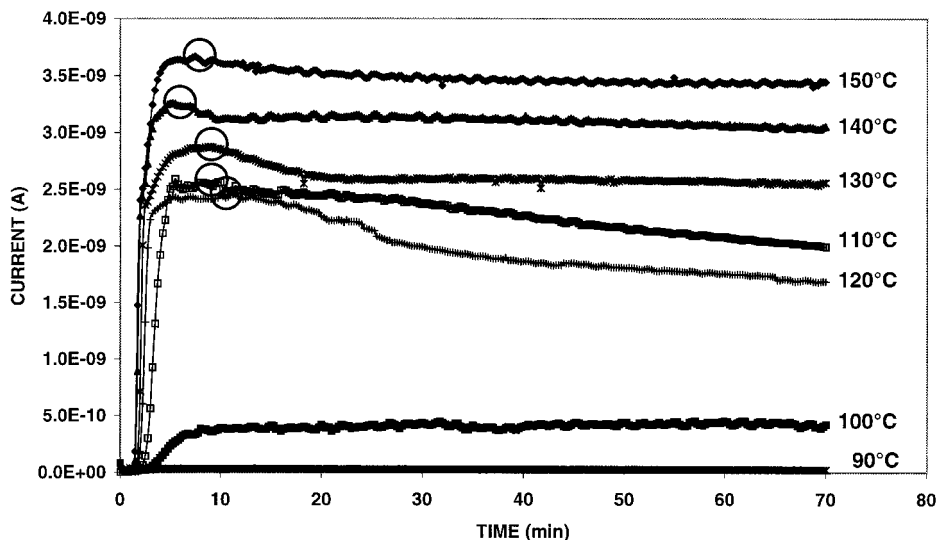


Figure 7 Mixture of NR and ZnST: investigation using electric current measurements from 90 to 150°C.

industry as an “ultra-accelerator” of vulcanization, while ZnST is only used as an activator together with various accelerators.¹⁶

The dc measurements of the type described give a kind of “fingerprint” for the behavior of vulcanization mixtures. They provide a picture of the kinetics of vulcanization reactions where ions are involved. A general difficulty in the interpretation is that the current values are the result of a superposition of different ion contributions and do not provide identification of single ionic species. Furthermore, dc measurements can only give evidence of ionic species and not of the uncharged or radical components in the mixture. For these reasons, complementary investigation methods are required. Notwithstanding these restrictions, the electrochemical investigation method used here is thought to have great potential with respect to gaining insight into vulcanization reactions.

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