

Effect of Temperature on the Crosslink Densities of Nitrile Rubber and Carboxylated Nitrile Rubber with Zinc Peroxide

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Received 5 March 2001; accepted 12 December 2001

ABSTRACT: We studied the crosslinking of conventional nitrile rubber with metal peroxide at varying temperatures. Crosslink density, measured by swelling in the solvent until equilibrium, and the reaction rate increased with temperature, suggesting that crosslinking is a function of peroxide decomposition. At a specific reaction time, some peroxide remained in the unreacted form in the final product. This was not observed when the reaction temperature was sufficiently high to achieve total decomposition of the peroxide

(190–200°C). When a carboxylated nitrile rubber was crosslinked, the same results were obtained. However, in this case, exclusively ionic or a combination of ionic and covalent crosslinks were generated, depending on the vulcanization temperature used. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 335–340, 2002

Key words: nitrile rubber; carboxylated nitrile rubber; zinc peroxide; crosslinking; elastomers; DSC

INTRODUCTION

Crosslinking of carboxylated nitrile rubber (XNBR) with metal oxide produces ionic structures, which brings about a significant increase in the material's physical properties, even with no filler, in comparison to those obtained by conventional vulcanization with sulfur accelerators.^{1–3} Zinc oxide is usually used as a crosslinking agent to obtain ionic elastomers, although its use does entail several drawbacks, the most important of which is its high trend to scorch.

To reduce this limitation, zinc peroxide has been used instead of zinc oxide. This was incorporated in a diluted form into the masterbatch with conventional nitrile rubber (NBR) in a proportion of 50/50 (Krynac PA 50),⁴ which produced the same results with regards the material's properties.

Since the first appearance of commercial preparations of zinc oxide, such as Struktol ZP 1014, this chemical has been used as a crosslinking agent, and several related aspects, such as the influence of the level of crosslinking agent,⁵ reaction time,⁶ and acid group content on the elastomeric matrix,⁷ have been studied. Nevertheless, in the literature, its use as a sole crosslinking agent has not been described, although it has been used in combination with other sulfur accelerators.⁸

In the vulcanization curves of the XNBR/Struktol ZP1014 mixtures recorded by the Monsanto MDR 2000E rheometer (Akron, OH), we observed, for all the samples studied, that the vulcanization rates did not fit a simple reaction curve but appeared to obey complex kinetics; this is currently being studied in our laboratory.

In this study, we also wanted to establish whether, during vulcanization, in addition to the more evident ionic structures, covalent bonds were also produced between the chains, which involved bonds with the radical produced by peroxide decomposition.

A XNBR and a NBR with the same viscosity and acrylonitrile content as XNBR were used as elastomeric matrices. The Struktol ZP1014 preparation was used as the crosslinking agent.

EXPERIMENTAL

The NBR we used corresponded to a copolymer of acrylonitrile–butadiene, with an acrylonitrile–butadiene content of 27% and a Mooney viscosity of 50 (Krynac 2750), and was supplied by Bayer (Levenskufen, Germany).

XNBR was a Krynac 7.40, with an acrylonitrile content of 27% and with 7 mol % carboxylic groups, and was supplied by Polysar.

Struktol ZP1014 was used as a crosslinking agent and was supplied by Schill-Seilacher (Hamburg, Germany); it had specific weight of 2.3. Struktol ZP 1014 is an easy product to incorporate. It is composed of a mixture of ZnO/ZnO₂ (approximately 50 wt %) in a ratio of 1 : 1; the other half is composed of organic and inorganic dispersion agents.

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Contract grant sponsor: CICYT, through the MAT 98-0905 Programme.

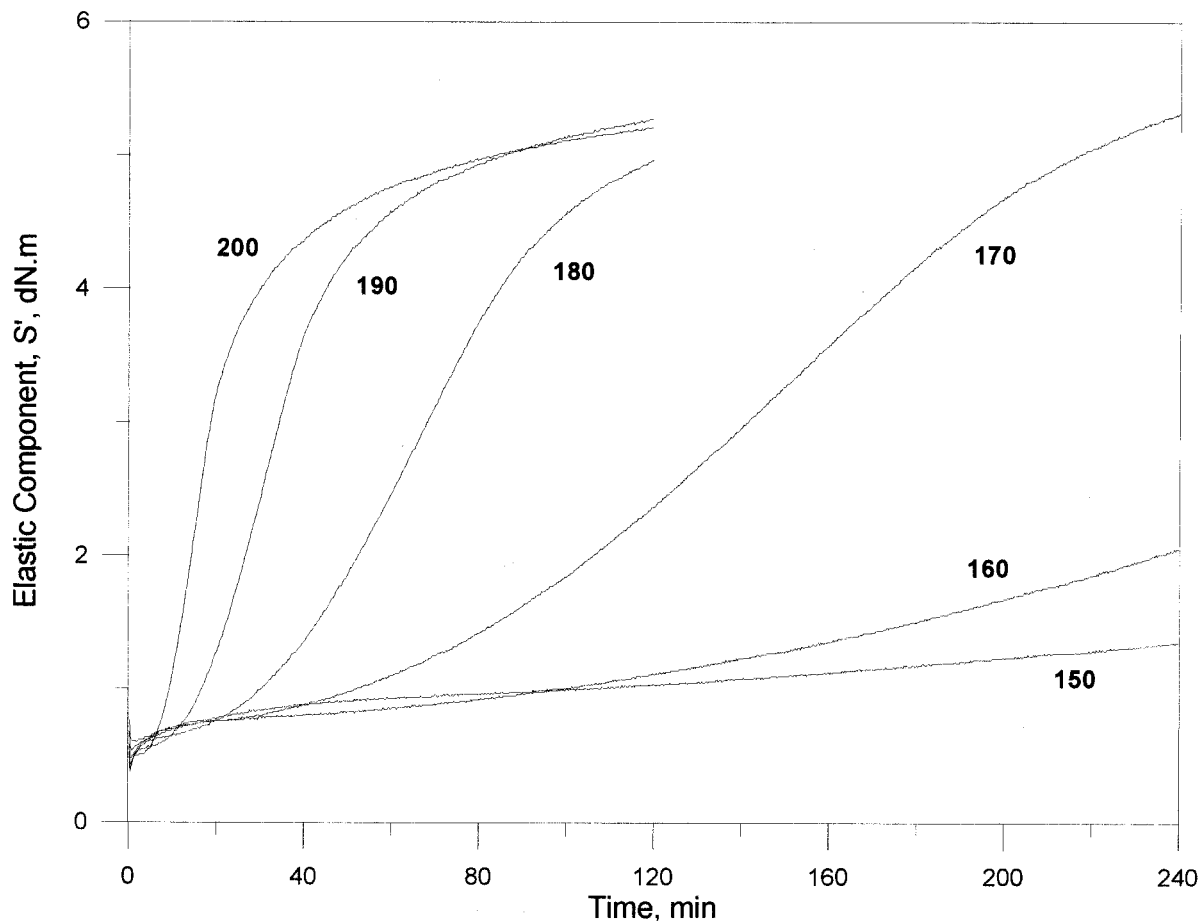


Figure 1 S' (dN m) as a function of temperature in the NBR/Struktol ZP1014 compound.

The mixture was prepared in a laboratory cylinder mixer, 25 cm in length with a friction ratio of 1 : 1.12 (Gumix, Barcelona, Spain). The cylinders were maintained at a cool temperature with cold circulating water for the whole mixing time.

Vulcanization curves were obtained with a Monsanto MDR 2000E rheometer, which was used at variable temperature with an oscillation arch of 1° .

For the thermal analysis, a PerkinElmer differential scanning calorimeter (model DSC7) (Norwalk, CT) was used at a heating rate of $5^\circ\text{C}/\text{min}$.

We determined the crosslink density (ν) of the vulcanized products was determined by measuring swelling at equilibrium and using benzene as a solvent at a temperature of 30°C and an immersion period of 7 days. ν (mol/cc) measured by swelling at equilibrium were calculated with the Flory–Rhener equation:⁹

$$\nu(\text{mol/cc}) = \frac{-[\ln(1 - \nu_r)] + \nu_r + \chi\nu_r^2}{V_s(\nu_r^{1/3} - \nu_r/2)}$$

where ν_r is the fraction in volume of the swollen rubber at equilibrium, χ is the parameter of polymer–solvent interaction, and V_s is the molar volume of the solvent. The value of parameter χ used was 0.49.

RESULTS AND DISCUSSION

NBR (Krynac 2750)

Figure 1 represents the vulcanization curves of the mixture based on Krynac 2750 (100 parts in weight) and Struktol ZP1014 (20 pcc, which corresponds to 10 pcc of the crosslinking agent ZnO/ZnO_2) at different temperatures.

At the lowest temperature, 150°C , the change in the elastic component of the pair of forces (S') with time up to 240 min remained almost parallel to the abscissa, which means that the variation in ν of the polymer at this temperature either did not exist or was very small. As expected, at this same temperature, NBR, which has no acid groups in its structure, did not form crosslinks. As the temperature increased to 160°C , in the first stages this parallelism with the abscissa was maintained, but as the reaction temperature increased, so did the S' value, reflecting an increase, although only a small one, of ν , as measured by the increase in the pair of forces.

As the temperature continued to rise, a drastic change was observed in the rheometric curves such that, from 170 to 200°C , the differences in the pair

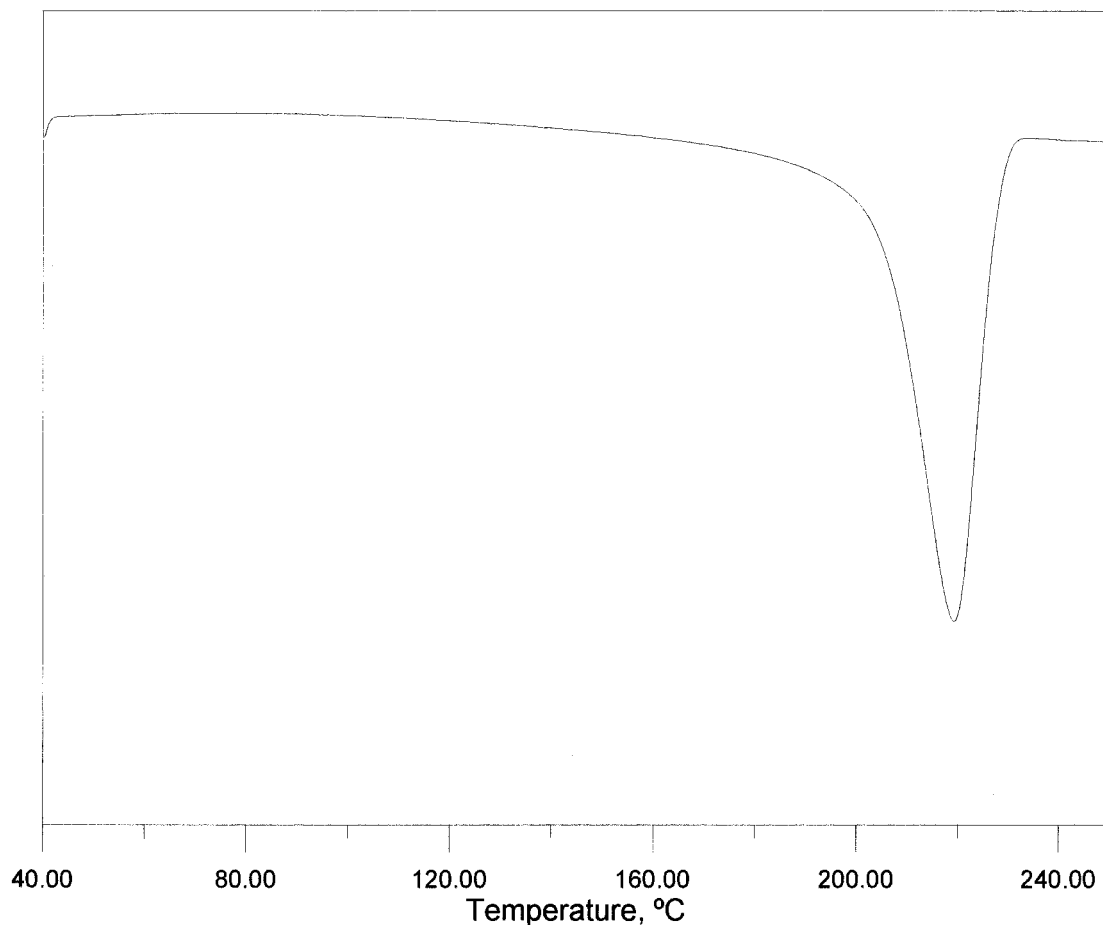


Figure 2 DSC results for the pure crosslinking agent (Struktol ZP1014).

were considerable, and there was a pronounced rise in ν .

Because the polymer lacked groups capable of forming metal salts with the peroxide to produce ionic crosslinks, the increase in ν observed above a specific temperature must have been related to the decomposition of the metal peroxide, probably involving the formation of free radicals capable of crosslinking the polymeric chains.

Figure 2 shows the differential scanning calorimetry (DSC) results of the pure Struktol ZP1014, in which only one transition was observed, which corresponded to the decomposition of the metal peroxide. This had a maximum decomposition rate at around 220°C. At lower vulcanization temperatures, almost no peroxide decomposition occurred, but as the temperature rose, approaching that of maximum decomposition, and the reaction times increased, decomposition started to take place, and crosslinking occurs.

The determination of crosslinking, by techniques of swelling at equilibrium, of the final vulcanization products at different temperatures and the different corresponding reaction times (240 min for those vulcanized at 150, 160, and 170°C and 120 min for the

other temperatures), demonstrated a considerable increase with rising vulcanization temperature, as shown in Table I. However, independently of the value of ν , the most important occurrence was that above a specific temperature, NBR crosslinked with metallic peroxide, and the rate of this increased with temperature.

If this crosslinking involved a radical, it should have been inhibited or delayed by the presence of radical-capturing compounds such as hydroquinone. Figure 3 shows the vulcanization curves at 200°C of a mixture to which hydroquinone was added (4 pcc) and also of the normal mixture. Indeed, for the mixture supplemented with hydroquinone, crosslinking was, to some

TABLE I
 ν by Swelling

Temperature	V_r	$\nu \times 10^4$ (mol/cc)
160	0.055	0.028
170	0.117	0.187
180	0.118	0.194
190	0.145	0.336
200	0.153	0.383

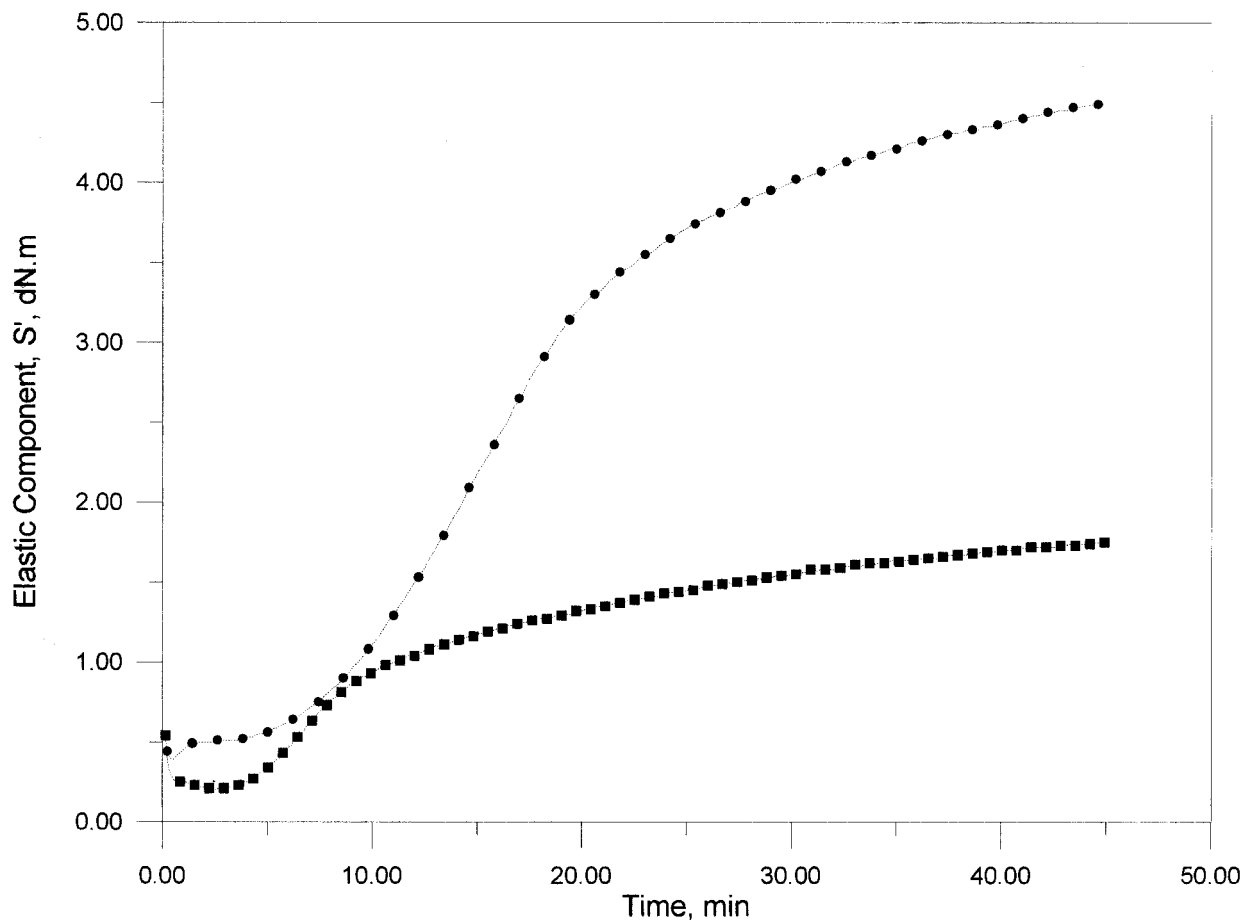


Figure 3 Vulcanization curves at 200°C of (●) the NBR/Struktol compound and (■) NBR/Struktol/hydroquinone.

degree, inhibited, which resulted in a reduction in S' , that is, a reduced ν .

As we observed, crosslinking at 160°C was minimal and could only have been due to the radicals produced by peroxide decomposition, which was very limited at this temperature. This suggests that the final product contained undecomposed peroxide. At temperatures above 170°C, where a reasonable amount of crosslinking took place, there should have been no peroxide in the final product. Figure 4 shows the DSC results corresponding to the final vulcanization products at 160 and 190°C. At the former temperature, after 240 min of reaction time, there was a transition that by its position, could correspond to peroxide decomposition; that is, it was displaced to a higher temperature than that of pure peroxide. In contrast, the curve corresponding to the higher temperature did not present any transition after a shorter reaction time (120 min).

XNBR

XNBR, which presents free carboxylic groups in its structure is, therefore, capable of forming metallic salts in the presence of the metal oxide or peroxide, generating ionic crosslinks. Figure 5 shows the vulca-

nization curves and S' at two temperatures, 150 and 200°C, of a mixture of XNBR and Struktol ZP1014.

As expected, a higher vulcanization rate was observed at the higher temperature and greater pair values. If the pair values were compared at the same temperature with those obtained in the vulcanization of NBR (Fig. 1), as expected these were higher for the XNBR at all the reaction rates because in this case, ionic associations were formed, which gave rise to crosslinks.

Therefore, if NBR can form crosslinks via the decomposition of the metal peroxide, this same decomposition would take place during the vulcanization of XNBR, provided that the temperature was high enough for this to occur.

Figure 6 shows the DSC results of the vulcanized products at 160 and 200°C generated from XNBR. There was evidence of peroxide decomposition at the lowest temperature; that is, after 240 min of reaction there was still peroxide in the final vulcanized product. However, at the higher temperature, there was no sign of this, implying that the peroxide had completely decomposed during vulcanization.

Hence, depending on the vulcanization temperature selected, crosslinking with zinc peroxide in the form of

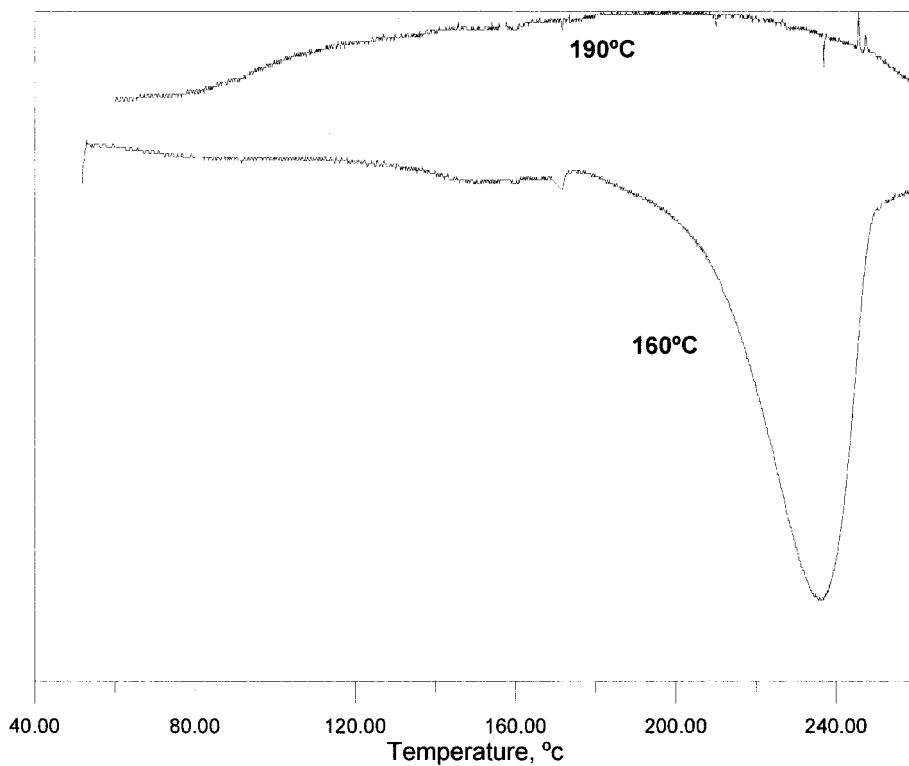


Figure 4 DSC results for the final vulcanizates at 160 and 190°C of the NBR/Struktol compound.

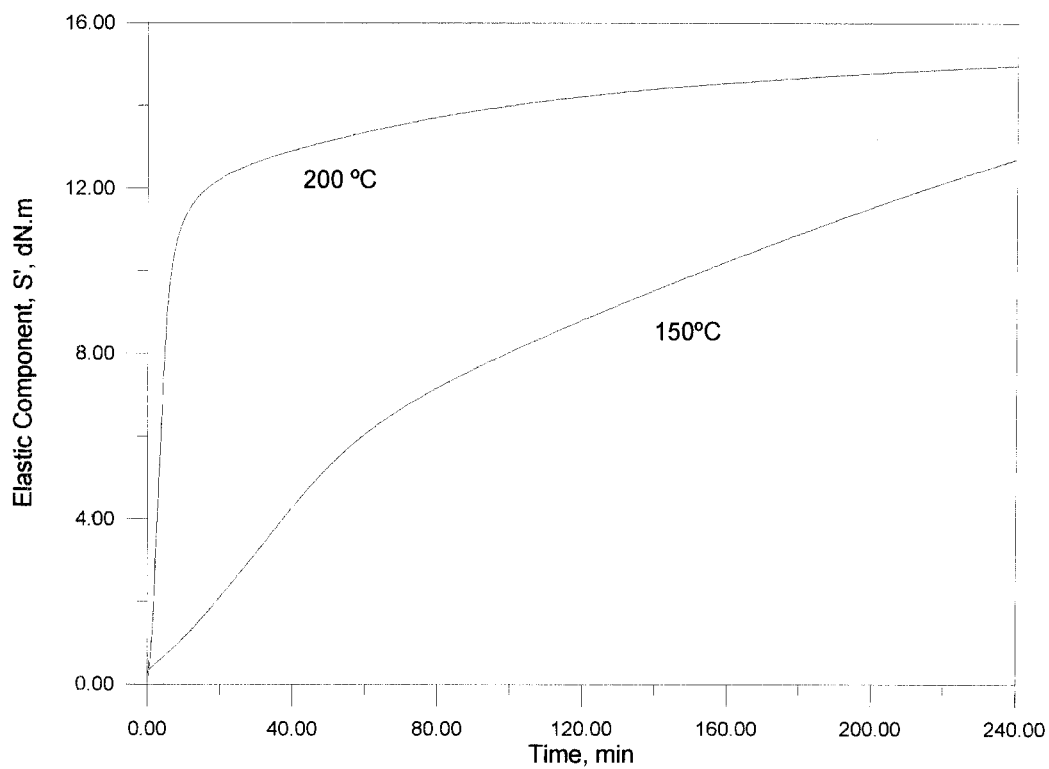


Figure 5 Vulcanization curves of the XNBR/Struktol compound at 150 and 200°C.

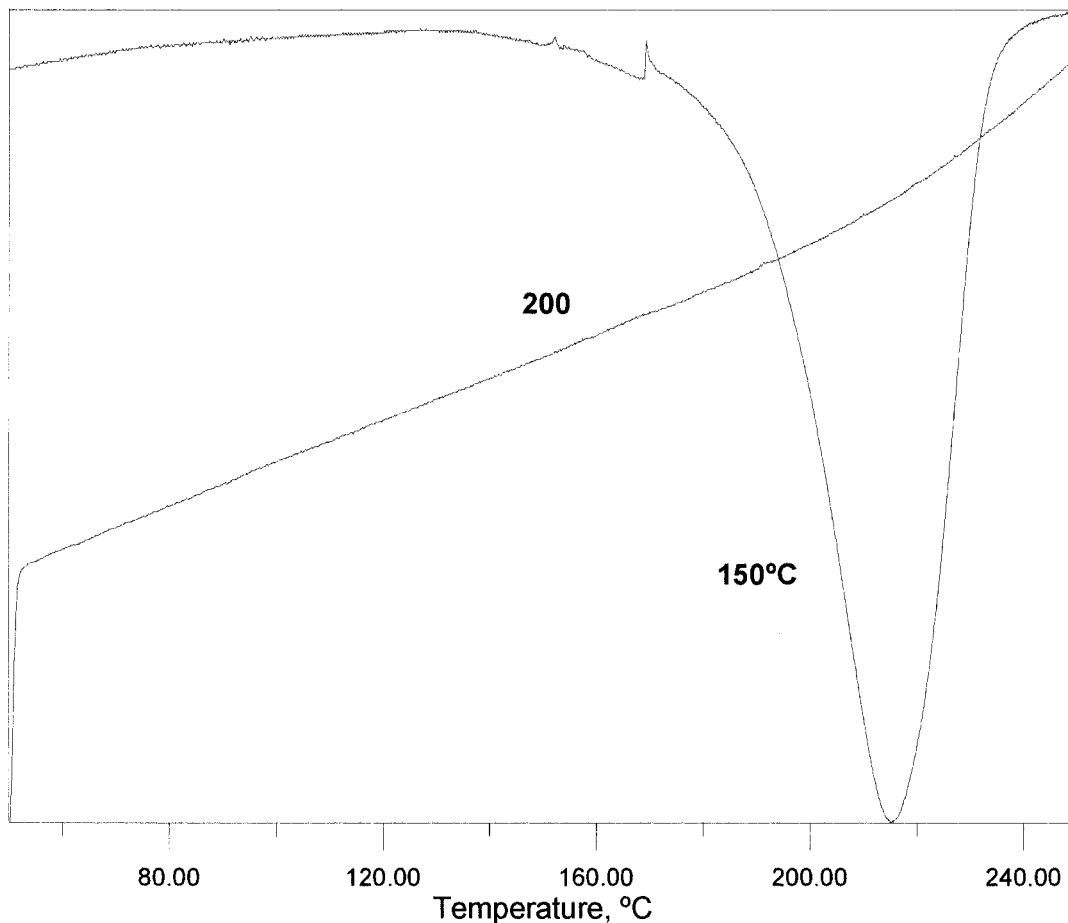


Figure 6 DSC results for the final vulcanizates at 160 and 200°C of the XNBR/Strukol compound.

the Struktol ZP1014 preparation, can give rise to exclusively ionic structures or, at higher temperatures, can also generate other kinds of crosslinks made possible by peroxide decomposition.

CONCLUSIONS

The results reported here demonstrate the possibility of crosslinking NBR with the zinc peroxide in the Struktol ZP1014 preparation. These crosslinks can only be obtained via peroxide decomposition and, therefore, must have a covalent character. The crosslink density varies as a function of temperature, with higher densities corresponding to higher temperatures.

In the crosslinking between XNBR and zinc peroxide, both ionic and covalent crosslinks are generated, and the proportion of each one depends on the reaction temperature selected.

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