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Polymer 43 (2002) 1649–1655

polymer

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Mechanistic approach to the curing of carboxylated nitrile rubber (XNBR) by zinc peroxide/zinc oxide

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Received 20 April 2001; accepted 12 November 2001

Abstract

The crosslinking of carboxylated nitrile rubber (XNBR) with a special preparation based on zinc oxide/zinc peroxide (Struktol ZP1014) is studied. It is shown that ionic species, by metallic salts formation, and covalent crosslinks, by zinc peroxide decomposition, are formed. The complete process can be empirically split in two contributions, with mathematical modeling rendering a satisfactory fit to experimental data. However, infrared and calorimetric analyses support the contribution of at least three mechanisms to the torque build-up: a very fast ionic species formation process by the initial zinc oxide present; covalent crosslinks and additional ionic species formation coming from zinc peroxide decomposition and contributing at all times from the beginning but decaying with time; and a third, not yet determined, contribution that accounts for the torque increment at long times. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: XNBR; Curing; Mechanism

1. Introduction

For several years, the crosslinking of carboxylated nitrile rubbers (XNBR) with zinc oxide, zinc oxide/zinc peroxide, and mixed curing systems, in order to obtain ionic type elastomers, and the properties of the vulcanized rubbers, have been studied in our laboratory.

The salt crosslinkages are characterized by high tensile, self reinforcement, hardness, tear resistance, good abrasion resistance and high compression set properties (and rapid stress relaxation or poor stress retention), plasticity at elevated temperatures, and poor flexure.

Zinc oxide is a very effective ionic promoter agent and yields vulcanizates with one of the highest tensile strength [1]. These metal oxide vulcanizates are characterized by instability under stress, high hysteresis, and high permanent set. Limitations of zinc oxide vulcanizates of carboxylic elastomers have been scorchiness, poor flex properties, high compression set and high durometer hardness. In spite of this zinc oxide remains the predominantly employed material for salt crosslinkage of carboxylic elastomers.

Combinations of crosslinks through the carboxyl groups with those derivable from other parts of the molecule by sulfur, peroxide or similar agents have yielded vulcanizates superior to those obtainable with either crosslinking system alone [2,3].

When mixed curing systems are employed, the peroxide cure has shown to have a less deleterious effect on the tensiles of the metal salt cures than was observed with sulfur systems. Zinc peroxide is used to reduce scorch problems that arise with zinc oxide. At the same time, it promotes a high ultimate state of cure (coated ZnO reduces scorch [4] but significantly reduces ultimate state of cure [5]).

By a choice of the balance of the two types of crosslinkages, it is possible to design vulcanizates to meet better specific application requirements than can be done with either type crosslinkage alone.

Although zinc peroxide preparation usually enters the XNBR curing systems, a literature search shows a lack of studies about XNBR crosslinking with zinc peroxide alone. With this work, we pretend to partially fill this gap. The results reveal that crosslinking, measured as torque build-up, does not correspond to a simple mechanism, as already anticipated by the shape of the rheometer curves. We applied a mathematical treatment to divide the process in the least possible number of contributions and then, with the help of other formulations and several characterization techniques, we tried to find out the origin of these empirical contributions.

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PII: S0032-3861(01)00734-0

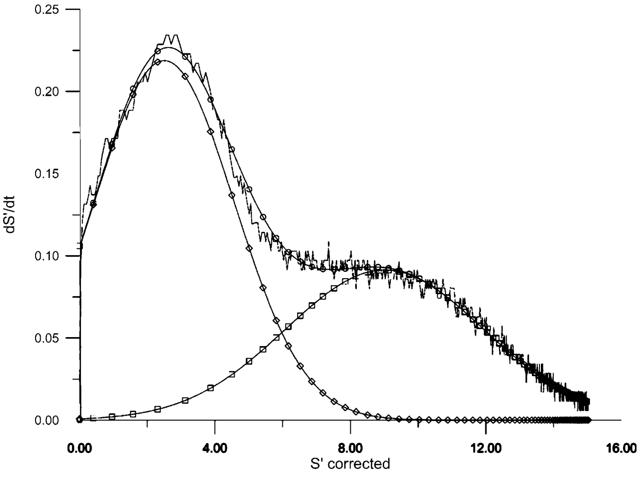

Fig. 1. Fitted curves for the experimental dS'/dt versus S' data obtained for the compound XNBR 100/Struktol 20 at 160 °C (—) experimental curve; (◇) first gaussian; (□) second gaussian; (○) sum of gaussians.

2. Experimental

Blends were prepared in a laboratory cylinder mixer with a friction ratio of 1:1.2, refrigerated by cold water. Formulations studied were: polymer, 100; crosslinking agent, variable; stearic acid, 1.

The carboxylated nitrile rubber used was Krynac 7.40, with an acrylonitrile content of 27%, 7% carboxylic groups content and a Mooney viscosity of 40. The conventional nitrile rubber used was Krynac 2750, with an acrylonitrile content of 27% and a Mooney viscosity of 50. Both polymers were supplied by Polysar (Barcelona, Spain).

The crosslinking agents in this study were pure zinc oxide, rubber grade, and zinc peroxide, in a special preparation with the trade name Struktol ZP1014, supplied by Schill & Seilacher (Hamburg, Germany). Struktol ZP1014 has a specific gravity of 2.3 g cm^{-3}, and a content of 50% of active compounds (29% zinc peroxide and 21% zinc oxide), 30% of inorganic dispersants and 20% organic dispersants.

Vulcanization was followed at different temperatures in a Monsanto rheometer, model MDR 2000E, with an oscillation arch of 1°. Elastic (S') and viscous components (S'') were registered, and for the mathematical calculations, corrected values of S' (subtraction of minimum torque value) were employed.

The fitting of the curves was done using the software PeakFit v.3.11 from Jandel Scientific Software, and the numerical integration using the software Kaleidagraph v.3.0 from Abelbeck Software.

DSC analysis was performed in a Perkin Elmer instrument, model DSC7, at a rate of 10° min^{-1} and a constant dry nitrogen purge.

Infrared spectra were taken in a Perkin Elmer FT-IR Spectrum One instrument using a Perkin Elmer Universal ATR Sampling Accessory. Sixteen scans at 4 cm^{-1} resolution were signal averaged for each spectrum.

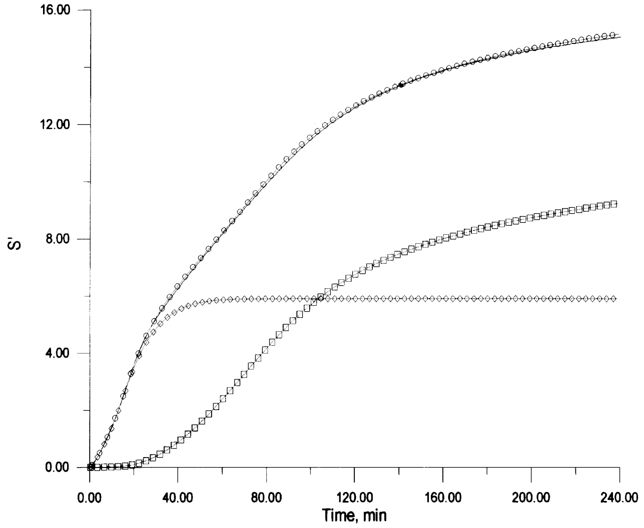

Fig. 2. Experimental data and integral curves fitted for the compound XNBR 100/Struktol 20 at 160 °C. Symbols as in Fig. 1.

3. Results and discussion

3.1. XNBR crosslinked with zinc peroxide

In a first stage, the vulcanization curve at 160 °C of a sample of XNBR with 20 pphr of Struktol ZP1014 (equivalent to 10 pphr of active compounds) was analyzed. In order to get some qualitative information on the reactions taking place on the vulcanization reaction, we tried to fit the curve with the least number of simple equations possible. The goal is to find a simple mathematical model, in principle without mechanistic significance able to describe the different contributions to the curve. Although it could be tried to fit the S' curve directly, it was decided to use the data in differential form because in this way, the changes in the curve are more easily visualized and the fitted results are more precise. As the abscissa parameter sometimes *time* and others S' was chosen at our convenience.

The curve did not follow any simple n order equation nor an equation corresponding to an autocatalytic process. In Fig. 1, the representation of dS'/dt versus S' can be seen. The curve has two maxima, which can be assumed as the concurrence of two different vulcanization processes, and the best fit corresponded to two gaussian curves (the fit was better using S' than t as the abscissa variable). These two gaussians and the corresponding sum curve are also represented in Fig. 1.

The integrated curves and the corresponding sum are depicted in Fig. 2, with the latter representing the experimental data adequately. The mathematical analysis allow us to split the rheometer curve into two contributions: a very fast process that reaches a plateau and a slower process that progressively builds up the torque and does not reach a plateau within the time of the test. We do not pretend to give extra significance to the shape of the curves and the possibility of division of the crosslinking process in two

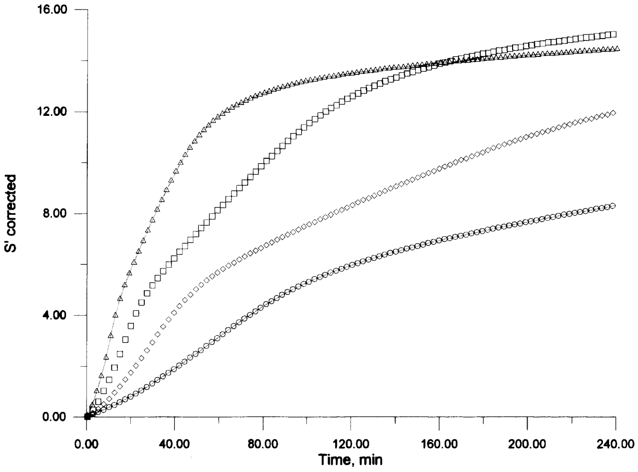

Fig. 3. Vulcanization curves for compound XNBR 100/Struktol 20 at different temperatures. (○) 140 °C; (◇) 150 °C; (□) 160 °C; (△) 170 °C.

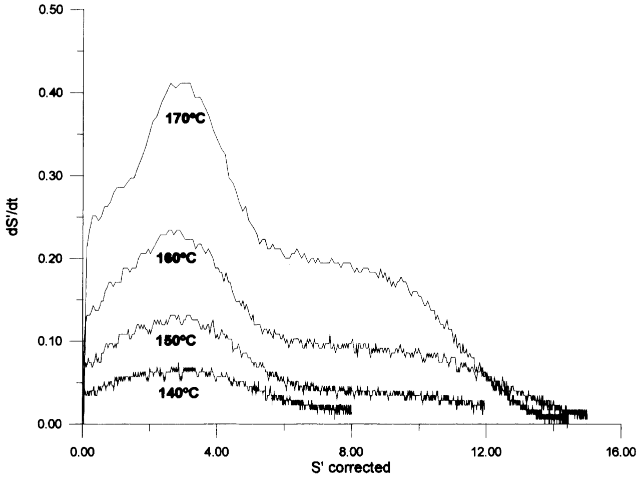

Fig. 4. Differential curves (dS'/dt versus S') for compound XNBR 100/Struktol 20 cured at different temperatures.

differentiated contributions is the only conclusion we can truly derive.

As already indicated, the peroxide used as crosslinking agent is a mixture of zinc peroxide and zinc oxide. Therefore, it is logical to think that the first contribution is due to the reaction of zinc oxide with the carboxylic groups of the rubber to give ionic crosslinks, a reaction that it is well-known and takes place at a very high rate producing scorch problems [5], and that the second contribution is due to the reaction of the zinc oxide generated in the decomposition of the peroxide plus possibly additional covalent crosslinking produced by the radicals generated during the decomposition. No other secondary reactions are expected during zinc peroxide decomposition, as it has been shown that on heating at 20–400 °C, zinc peroxide gives ZnO and O with no other phase transitions observed [6].

3.2. Temperature effect

In Fig. 3, the corrected vulcanization rheograms of the previous formulation at different temperatures can be seen. At 170 °C, the torque reached is lower than for 160 °C, which could be due to some change in the crosslinking mechanism with respect to lower temperatures. When they are represented in differential form (Fig. 4, dS'/dt versus S'), it is found that, if multiplied by a certain proportionality constant, the first maximum superpose whereas the second do not superpose. The curves fit well to the sum of two gaussians (fitted parameters in Table 1), and the sum of their integrated curves to the experimental data. The integrated curves are again consistent with two contributions: the first supposedly coming from the zinc oxide (Fig. 5), with reaches similar torque in the plateau (taken into account the errors of the mathematical manipulation) as it should be because the content is always the same in the sample, and with the rate dependent only on the temperature; and the second, supposedly from the peroxide (Fig. 6), with the rate dependent not only on the temperature.

Table 1
Gaussian parameters as a function of temperature

T (°C)	Amplitude		Peak		Width	
	Gauss-1	Gauss-2	Gauss-1	Gauss-2	Gauss-1	Gauss-2
140	0.065	0.015	2.65	9.5	2.06	2.45
150	0.126	0.035	2.51	9.17	2.19	2.59
160	0.218	0.091	2.50	9.01	2.07	2.92
170	0.384	0.181	2.66	8.71	2.21	2.13

3.3. Concentration effect

We studied the effect of active compounds content on the curing behavior. In Fig. 7, the rheograms for the formulations with 6, 8, 10 and 12 parts of active compounds (12, 16, 20 and 24 parts of Struktol), cured at 150 °C, are shown. The

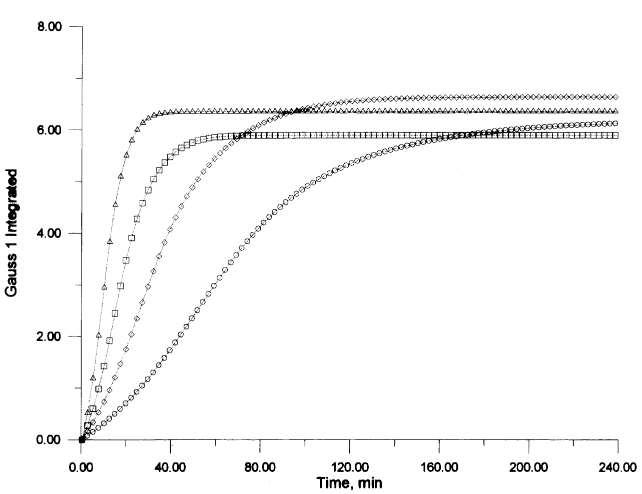

Fig. 5. Integrated curves of the first contribution to the torque for the compound XNBR 100/Struktol 20, cured at different temperatures. Symbols as in Fig. 3.

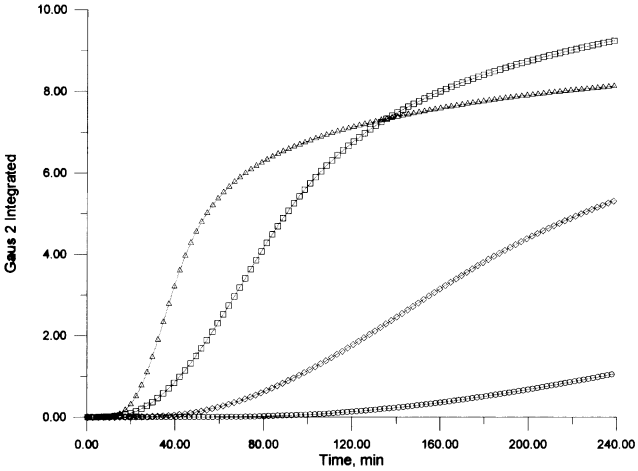

Fig. 6. Integrated curves of the second contribution to the torque for the compound XNBR 100/Struktol 20, cured at different temperatures. Symbols as in Fig. 3.

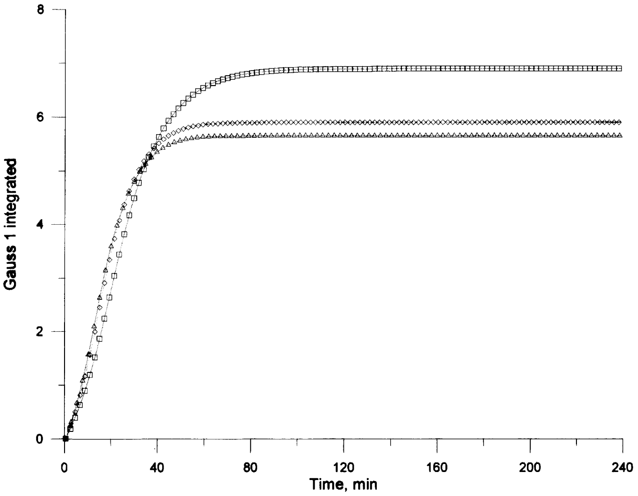

Fig. 8. Integrated curves of the first process for compounds XNBR 100/ Struktol (16, 20 and 24 parts) cured at 160 °C. Symbols as in Fig. 7.

differential curves, $\mathrm{d}S'/\mathrm{d}t$ versus S', present again two maxima (except for six parts, where the second maximum is not defined), but in this case, the first one is shifted to lower S' and the second to higher S' when the zinc peroxide content is increased. The same previous fitting procedure was applied and the results were good although some discrepancies arise at the end of the fitted curve.

When the integrated curves of the separated processes are represented together, some interesting results were yielded. The individual curves of the processes have the same shape and differentiate in a proportionality constant, which implies that the rate and the process is the same for all contents. But in the first process (Fig. 8), it can be noticed that, contrary to expected, if the process is related to zinc oxide-carboxylic groups reaction the torque reached is lower when Struktol content increases (because of the lack of the second maximum, the curve with 6 parts is not taken into account). The torque in the second process follows the normal behavior and increases as expected. No explanation was found for the behavior of the first process that it was expected to increase with Struktol, and therefore zinc oxide, content increase. The process, where the particles containing zinc oxide dispersed in the matrix are supposed to form the links on the surface of the particles giving rise to multifunctional crosslinking sites, that increase their functionality and at the same time reduce M_c between crosslinks when reaction proceeds, simply do not follow an addition rule when tried to relate with torque.

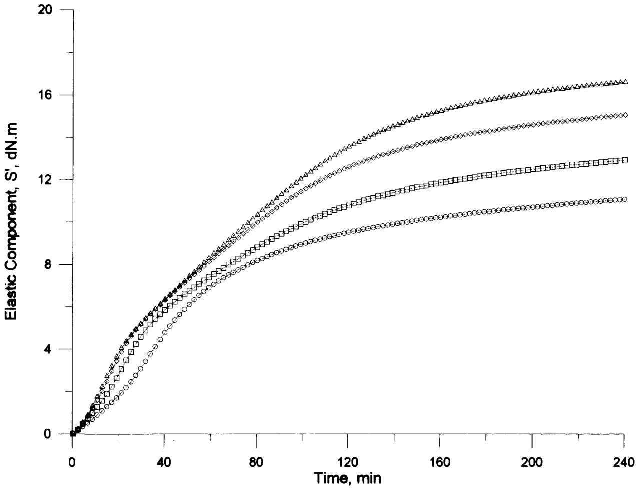

Fig. 7. Rheograms for compounds XNBR 100/Struktol ((○) 12, (□) 16, (◇) 20 and (△) 24 parts), cured at 150 °C.

3.4. XNBR crosslinked with zinc oxide

XNBR compounds were formulated with pure zinc oxide in order to clarify that the first process on the curing of compounds with Struktol is related to zinc oxide reaction.

In Fig. 9, the curves for a compound with four parts of ZnO cured at 110, 130 and 150 °C are displayed. This time, fitting procedure was done for the differential curves $\mathrm{d}S'/\mathrm{d}t$ versus t, because they rendered better results. A single maximum is found and the integrated curve adequately represent the experimental curve except at the end of the growth in the curve: whereas the simple gaussian fitted reaches a plateau, the real process continues with a small steady growth with time (Fig. 9). We think this could be due to the improvement on the ordering on the ionic species that slowly increases the torque with time, and is independent of the first fast process, due to the formation of the ionic species. For the Struktol compounds, where we suppose some covalent crosslinking is achieved in the second process, leading to an immobile covalent network, this phenomenon will be less evident.

The facts that, in this system only a maximum appears and the curing rate is even faster that for the first process in the curing of Struktol compounds, and furthermore, the level of the torque achieved is roughly similar to the torque achieved for the first process of the compound with 20 parts of Struktol (equivalent to approximately 4.2 parts of zinc

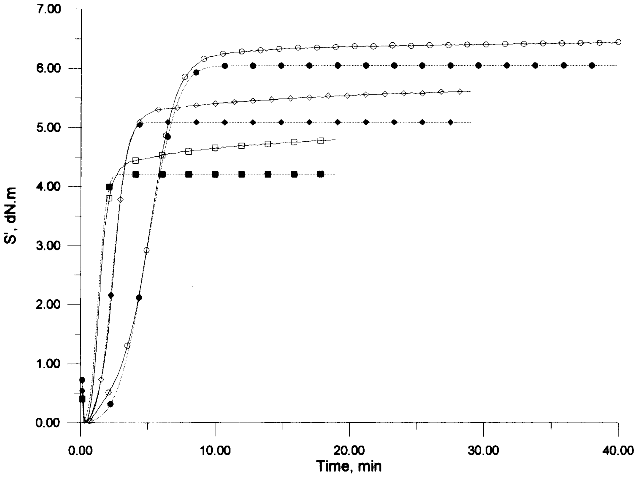

Fig. 9. Real and fitted rheometer curves for compound XNBR 100/ZnO 4 cured at different temperatures. (○, ●) 110 °C; (◇, ◆) 130 °C; (□, ■) 150 °C. Empty symbols, experimental curve; full symbols, fitted curve.

oxide) supports the first process as been due to zinc oxide reaction.

The effect of temperature is the reverse to Struktol compounds. In this system, with only ionic species formed, the torque reached decreases with the increase in temperature. This is the usual behavior of ionomers. However, at this point, we should remark that whereas the structure of the ionic species in a ionomer is composed of ionic pairs, multiplets and clusters, in this ionic system, the crosslinks (or at least most of them), as already forwarded, are multifunctional sites where the ionic bonds with a range of strengths are located on the surface of the dispersed particles. The rise in temperature will break the weaker bonds and others will remain stable, producing a system that, for example at 150 °C, still reaches a torque value. The transition found by Ibarra and Alzorriz [7,8] and other authors [9,10] by the DMTA technique at approximately 80–120 °C will be related to the breaking of certain ionic bonds, but others still remain holding the sample that, in the references cited, up to 150 °C do not suffer any catastrophic drop in mechanical properties.

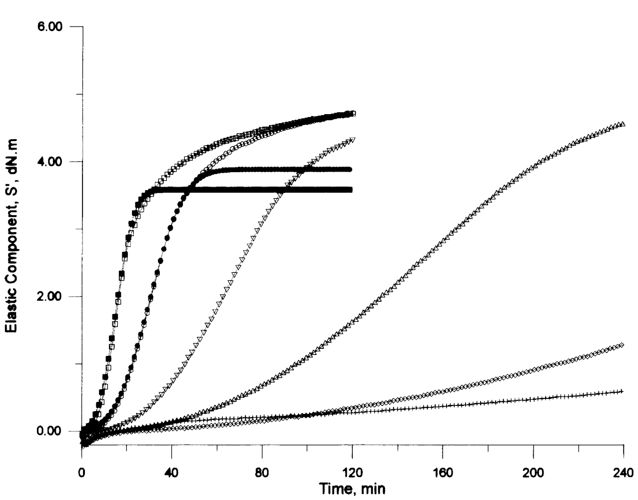

Fig. 10. Real and fitted (only for 190 and 200 °C is shown) rheometer curves for compound NBR 100/Struktol 20 cured at different temperatures.(+) 150 °C; (◇) 160 °C; (△) 170 °C; (▽) 180 °C; (○) 190 °C; (●) fitted 190 °C; (□) 200 °C and (■) fitted 200 °C.

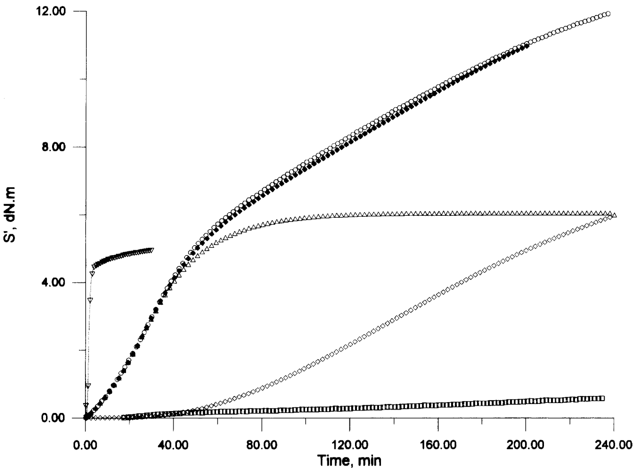

Fig. 11. Curves for the systems (▽) XNBR + ZnO; (○) XNBR + Struktol (and its splitting in two processes: (△) first; (◇) second and (◆) sum), and (□) NBR + Struktol cured at 150 °C.

3.5. NBR crosslinked with zinc peroxide

These formulations aimed to prove that the second process in XNBR + Struktol compounds was related to peroxide crosslinking. Since there are no carboxylic groups present in NBR, ionic crosslinks are not possible, and crosslinking, if any, can only be of the covalent type from the radicals produced by the zinc peroxide.

In Fig. 10, the rheograms of the system NBR 100/Struktol 20 at different temperatures can be found. In the differential curves (dS'/dt versus t), from 170 °C a single maximum is found, and the integrated curves fit quite well except the last part of the curve. As for the system XNBR + ZnO, after the calculated curve reaches a plateau, the experimental curve continues a slower steady growth (Fig. 10).

The important findings in this system are that covalent crosslinking is produced and the decomposition rate for the peroxide is lower than for XNBR. It seems that carboxylic groups in XNBR induce peroxide decomposition giving crosslinking at lower temperatures.

For comparison purposes, in Fig. 11, the curves for the systems XNBR + ZnO, XNBR + Struktol (and its splitting in two processes), and NBR + Struktol are drawn.

3.6. Infrared and calorimetric analyses

These two techniques were used to find further evidences to support the separation of the crosslinking on the XNBR + Struktol system in two processes.

In Fig. 12, several IR spectra taken from a sample of XNBR + 20 parts of Struktol (no stearic acid was added

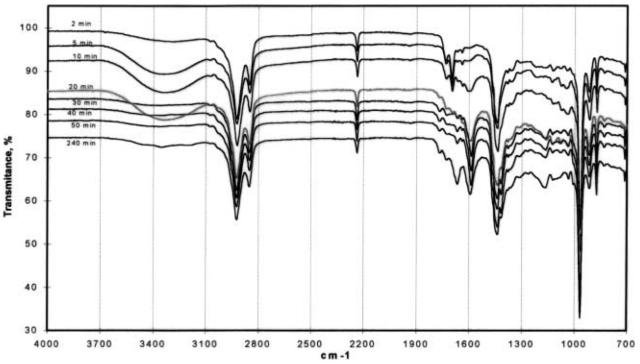

Fig. 12. Infrared spectra of the compound XNBR 100/Struktol 20 cured at 150 °C for different times.

in this formulation to avoid interferences in the carbonyl region) cured at 150 °C for different times on the rheometer chamber are stacked. As it can be seen, distinctive changes are produced during reaction. The peak at approximately 1698 cm^{-1}, related to carboxylic groups, disappears and some other new peaks (1667, 1590 and a shoulder at 1417 cm^{-1}) appear. A broad band centered around 3350 cm^{-1} appears and disappears during the run. This band is ascribed to water generated during reaction between ZnO and –COOH with posterior release. In Fig. 13, the height in absorbance measured at 3347, 1698 and 1588 cm^{-1}—band at 1588 cm^{-1} could be assigned to the carbonyl stretching vibration of zinc carboxylated salt [11]—and ratioed with the absorbance measured at 2932 cm^{-1} (taken as internal reference) is represented. It is clear that after 30 min, the carboxylic groups have been consumed, carboxylate groups have been formed and the water has been released, in other words, ionic species formation has been already taken place. If we look at Fig. 11, this compares well with the initial fast torque build-up due to the first process, and therefore proves that this process is related to the ionic species reaction.

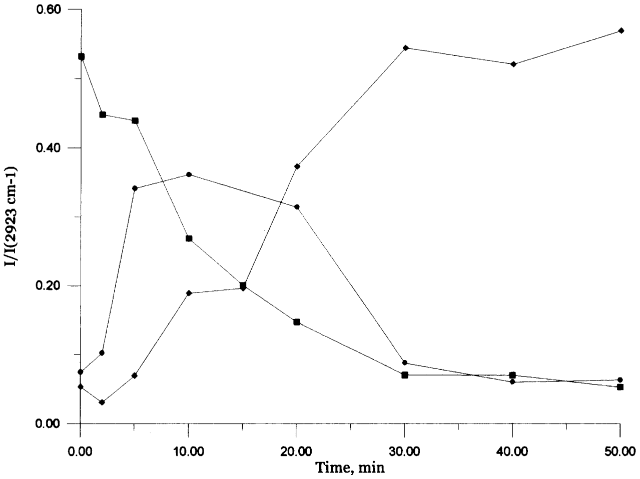

Fig. 13. Plot of the ratioed peak height for several absorptions at different times (●) 3347 cm^{-1}; (■) 1698 cm^{-1}; (◆) 1588 cm^{-1}.

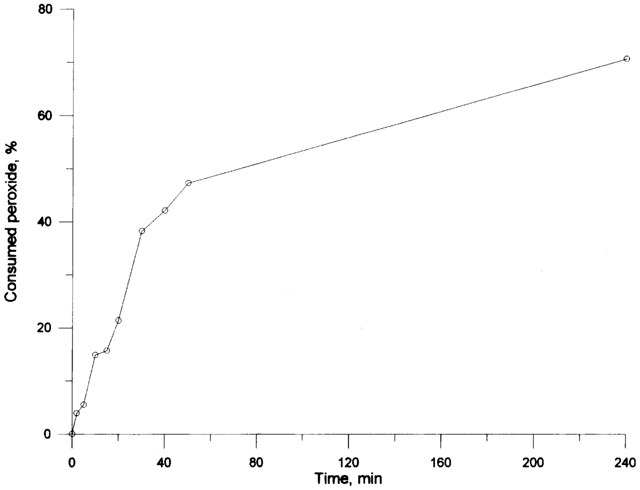

Fig. 14. Decomposition of zinc peroxide as measured by DSC.

The same samples were analyzed for thermal transitions. In dynamic DSC runs, a reaction exotherm was found. The heat of the exotherm, related to the heat evolved during zinc peroxide decomposition, was measured and converted to conversion data. From the representation of these data, Fig. 14, it becomes clear now that covalent crosslinking from peroxide do not suffice to explain the torque build-up due to the second process. Half the peroxide is consumed within the first 50 min of reaction and by this time, the first process has almost decayed and the second process is starting, and after three more hours, the torque has doubled, thanks to the second process with only a further 20% decomposition of the initial amount of peroxide.

Although peroxide crosslinking still can be a minor contribution, another explanation has to be found for the main contribution to the second process. In the IR spectra at long times, a new peak at around 1667 cm^{-1} has developed. This new absorption is practically absent at 50 min reaction and therefore its apparition is coincident with the torque build-up during the second process. The species related to this peak, that could be, for instance, a transformation of the original ionic bonds to other stronger bonds, are the possible responsible of the second process.

4. Conclusions

The curing behavior of XNBR with Struktol, which contains a mixture of zinc oxide and zinc peroxide, at different temperatures and concentrations was studied. Rheometer curves can be split in two contributions that allow an empirical mathematical description of the crosslinking with good accuracy.

The results on the curing behavior of XNBR/ZnO compounds and the infrared results support the conclusion that the first, very fast, process is mainly due to the formation of ionic species from the reaction between ZnO and polymeric carboxylic groups.

Curing behavior of NBR/Struktol compound is quite different from the XNBR/Struktol behavior. A much slower rate is achieved at the same temperature, which could be due to a catalytic effect of the carboxylic group on the zinc peroxide decomposition.

Calorimetric analysis proves that the second mathematically derived process is definitively not due to the progress on zinc peroxide decomposition. This decomposition takes place from the very beginning and its contribution to the torque is larger during the early stages of the vulcanization, adding to the process of ionic species formation.

The curing behavior is the sum of at least three contributions: a very fast ionic species formation coming from the initial zinc oxide present, peroxide crosslinking (covalent plus ionic species formed by the zinc oxide generated) contributing to the torque at all times and decaying with time, and a third contribution, not yet identified, that from infrared results could be related to the ionic species.

Acknowledgements

We are indebted to the CICYT (MAT 98/0905) for the financial support.

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