

# Vulcanization of Chlorobutyl Rubber.

## I. The Identification of Crosslink Precursors in Compounds Containing ZnO/ZnCl<sub>2</sub>

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**ABSTRACT:** Chlorinated poly(isoprene-coisobutylene) (CIIR or chloro-butyl) was characterized by Nuclear Magnetic Resonance. Compounds with ZnO, ZnCl<sub>2</sub>, and ZnO/ZnCl<sub>2</sub> were vulcanized in a DSC at a programmed heating rate and isothermally at 150°C in a press. Crosslink densities were determined by swelling and extracted ZnCl<sub>2</sub> analyzed by atomic absorption. ZnCl<sub>2</sub> formation precedes crosslinking, and at equilibrium only 50% of the chlorine in the rubber is extractable as ZnCl<sub>2</sub>. ZnCl<sub>2</sub> promotes crosslinking, and its addition to formulations decreases but does not eliminate the induction period prior to crosslinking. Dehydrohalogenation, which is catalyzed by ZnCl<sub>2</sub> in an autocatalytic process, is accompanied by the formation of conjugated diene butyl on the polymer chain. It is demonstrated that both species, not only ZnCl<sub>2</sub>, are necessary precursors to crosslink formation. Moist ZnCl<sub>2</sub> catalyzes dehydrohalogenation but not crosslinking, while ZnO does not promote either reaction. CIIR can be crosslinked to polybutadiene and to polyisoprene, no induction period applying when ZnCl<sub>2</sub> is present in the formulation, and high crosslink densities develop in blends precipitated from solution. Severe reversion occurs in formulations where there is insufficient ZnO to trap all of the HCl evolved. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2290–2301, 2000

**Key words:** chloro-butyl; vulcanization; ZnO; ZnCl<sub>2</sub>; conjugated diene butyl

## INTRODUCTION

Chlorinated poly(isoprene-coisobutylene) (CIIR of chloro-butyl) can be crosslinked upon heating,<sup>1</sup> the reaction being facilitated by the addition of ZnO, ZnCl<sub>2</sub>, or zinc dimethyldithiocarbamate (Zn<sub>2</sub>(dmtc)<sub>4</sub>).<sup>2–4</sup> Stearic acid is frequently added to commercial formulations. It is generally accepted that reactions leading to the formation of

ZnCl<sub>2</sub> precede crosslinking, the induction period prior to crosslinking being ascribed to the need to form ZnCl<sub>2</sub> that is considered to act as a catalyst for crosslinking via a cationic mechanism.<sup>2–4</sup> In ZnO formulations the ZnCl<sub>2</sub> formed may initially result from reaction of ZnO with HCl formed on thermal dissociation of the allylic chlorine.<sup>2</sup> Conjugated dienes are formed on the polymer chain as a result of HCl evolution, but dienes are not considered to play any role in the crosslinking reaction, other than in HCl evolution permitting the formation of ZnCl<sub>2</sub>.<sup>3,4</sup> Indeed, Kuntz et al.<sup>3</sup> showed that blends of CIIR with a conjugated diene butyl (molecular mass 590,000) crosslinked

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more slowly and gave lower crosslink densities than was obtained with CIIR on its own, and concluded that the formation of conjugated diene butyl is not an essential intermediary in the crosslinking process. However, no data is available on the degree of molecular intermixing achieved in the blends, and the result may not necessarily prove that conjugated diene butyl does not play a role in the reaction: a two-phase blend, in which the conjugated diene butyl phase does not possess functional groups to crosslink to itself, would also result in a lower crosslink density in the blend as a whole. Vukov<sup>4</sup> considered two competitive processes to take place on heating chlorinated model compound 2,2,4,8,8-pentamethyl-4-nonene. The first step was the formation of monomeric conjugated dienes, and this was considered to precede crosslinking, because it produced  $\text{ZnCl}_2$  or  $\text{Zn}(\text{OH})\text{Cl}$ , the catalyst for crosslinking. The reaction was the dominant pathway, and could consume as much as 80% of the starting allylic chloride. Crosslinking, the minor of the two reactions, was considered to proceed via a cationic reaction mechanism. The mechanism put forward did not involve the participation of the conjugated dienes. The cationic mechanism as originally proposed by Baldwin et al.,<sup>2</sup> also showed the  $\text{ZnCl}_2$  initiated cationic reaction to lead to crosslinks without the participation of a conjugated diene butyl precursor. Although it has not been demonstrated, the cationic reaction mechanism implies that  $\text{ZnCl}_2$  containing formulations should crosslink without an induction period.

Baldwin et al.<sup>2</sup> reported that good covulcanization of CIIR with unsaturated rubbers can be effected, although care must be taken in the selection of curatives. Although sulfur and conventional accelerators were included in the formulations, the ability to link CIIR to highly unsaturated rubbers may point to dienes playing a role in the crosslinking process.  $\text{ZnCl}_2$  and conjugated diene butyl are products of the same reaction, dehydrohalogenation, and separation of their roles in the crosslinking process is not easy. Furthermore, stearic acid, which would react with  $\text{ZnO}$  to form zinc stearate, was added to formulations in previous studies,<sup>2</sup> and this would influence the vulcanization reaction.

This article reports on a detailed study of the crosslinking of CIIR compounds with  $\text{ZnO}$  and  $\text{ZnCl}_2$ , and identifies the roles of  $\text{ZnO}$ ,  $\text{ZnCl}_2$ , and conjugated diene butyl in the vulcanization process.

## EXPERIMENTAL

### Materials

The materials used in this article were: Polysar 1255 CIIR; ethylene propylene diene terpolymer (EPDM) (Polysar, Canada); polybutadiene (BR) (Karbochem, South Africa); polyisoprene (IR) (Karbochem, South Africa);  $\text{ZnO}$  (Zinc Process, South Africa);  $\text{ZnCl}_2$  (Saarchem, South Africa); and calcium stearate (Chemserve, South Africa).

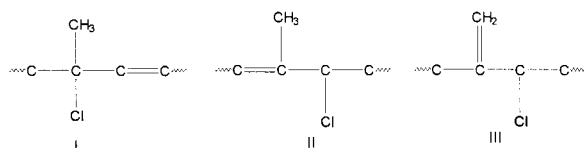
CIIR samples used for characterization were dissolved in deuterated chloroform, and <sup>1</sup>H-NMR spectra were taken at 313 K on a Bruker DMX-600 spectrometer.

Compounds were mixed in a Brabender Plastimeter as described earlier,<sup>5,6</sup> and vulcanized at a programmed heating rate in sealed aluminium pans in a standard Du Pont DSC cell connected to a Du Pont 9000 Thermal Analyzer and isothermally in a press at 150°C.<sup>5,6</sup> Formulations are quoted in brackets in the text in parts per hundred rubber (phr). Thermogravimetric (TG) analysis was performed on a Du Pont Thermal Analyzer. The reaction was stopped at various temperatures (DSC) or times (press), and soluble zinc ( $\text{ZnCl}_2$ ) extracted with a 40/60 (v/v) solution of ethanol and benzene following procedures previously described for the extraction of soluble compounds from crosslinked and uncrosslinked rubbers samples.<sup>7</sup> Zinc was analyzed for by atomic absorption (AA) spectroscopy. Crosslink densities were determined by swelling in benzene.<sup>6</sup> A polymer-solvent interaction parameter of 0.521 was used in the Flory-Rehner equation.<sup>8</sup> The percentage extractable chlorine quoted in the figures and in the text refers to the mass percentage of the total chlorine originally present in CIIR.

## RESULTS

### Structure of the Chloroisoprene Unit in CIIR

Various authors have reported on the structure of CIIR. Based on decomposition studies, Baldwin et al.<sup>2</sup> suggested that CIIR comprised three isomers (Fig. 1) with different reactivities, while more recent reports using NMR<sup>9</sup> mainly showed the exomethylene isomer. To check and reconfirm the structure of the chloroisoprene unit in CIIR, high-field NMR experiments were performed. Such measurements allow determination not only of the structure of the chloroisoprene unit in CIIR,

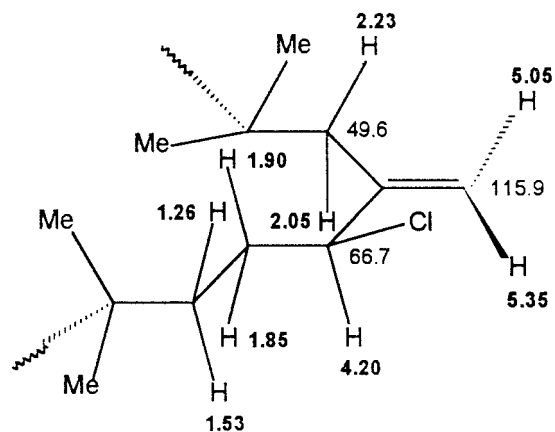


**Figure 1** Isomeric structures present in CIIR according to Baldwin et al.<sup>2</sup>

but also how it is incorporated in the isobutylene polymer. First, a conventional  $^1\text{H-NMR}$  spectrum was taken, showing the CIIR used in this study to exhibit nine relevant signals (Table I), six of which are AB patterns. Two singlets at 5.00 and 5.35 ppm are suggestive of two olefinic protons, the large difference in chemical shift being explained by the presence of an allylic chlorine. The triplet at 4.20 ppm indicates the presence of an allylic, chlorinated methylene signal, whereas the intense AB pattern appearing at 2.05 and 2.23 ppm may be attributed to the other two allylic hydrogen atoms. C—H and H—H correlation spectroscopy confirms these assignments. Because no additional couplings are observed for the 2.05/2.23 AB pattern, it may be concluded that this allylic  $\text{CH}_2$  unit must be attached to a quaternary carbon atom, i.e., the dimethyl part of an isobutylene unit. The hydrogen atom appearing at 4.20 ppm couples with the second AB pattern that is observed at 1.85 and 1.90 ppm. From the C—H correlation spectrum and the Attached Proton Test (APT) spectrum it may be concluded that this is the  $\text{CH}_2$  positioned adjacent to the chlorinated position. Both hydrogens further exhibit crosspeaks with signals at 1.53 and 1.26 ppm, the third AB pattern in this spectrum, and assignable to a  $\text{CH}_2$  unit. Because no additional couplings were observed, these signals must derive from an isobutylene  $\text{CH}_2$ , which is immediately attached to a quaternary atom ( $>\text{CMe}_2$ ). Evaluating, the

**Table I** Chemical Shift (ppm) and Assignment of  $^1\text{H-NMR}$  Spectra of CIIR

ppm	Number of Hydrogen Atoms, Multiplicity
1.26, 1.53	2H, AB pattern
1.85, 1.90	2H, AB pattern
2.05, 2.23	2H, AB pattern
4.20	1H, triplet
5.05	1H, triplet
5.35	1H, triplet



**Figure 2** Structure and incorporation of the chloroisoprene unit in CIIR ( $^1\text{H-NMR}$  chemical shifts in bold, selected  $^{13}\text{C-NMR}$  chemical shifts in italics).

chloroisoprene unit in CIIR consists of a chlorinated exomethylene isoprene unit, as also reported by Chu et al.,<sup>9</sup> which is incorporated in the isobutylene polymer as shown in Figure 2. Besides the NMR signals that can be attributed to the chloroisoprene unit, minor additional peaks may be observed. These cannot, however, be assigned to the other two isomers that may be produced upon chlorination of IIR. These signals must be caused by other, unidentified structures or impurities. Therefore, it may be concluded that the content of the chlorinated exomethylene isoprene isomer in CIIR, the reactive component in vulcanization, approximates 100%.

### CIIR

The DSC curve obtained upon heating CIIR at  $5^\circ\text{C}/\text{min}$  shows two thermal events, an endotherm peaking at  $121^\circ\text{C}$  associated with the melting of calcium stearate (present in the rubber as a stabilizer), and a broad exotherm, the onset at approximately  $250^\circ\text{C}$ .

The reaction was stopped at points along the DSC curve and samples swelled in benzene. At the programmed heating rate of  $5^\circ\text{C}/\text{min}$ , crosslinking only initiated well above  $200^\circ\text{C}$  (Table II), with a maximum crosslink density of  $0.43 \times 10^{-5}$  mol/mL and associated mass loss of 1.86% recorded at  $250^\circ\text{C}$ . Samples heated to higher temperatures became discolored and tacky, with reversion reactions dominating at these high temperatures. At  $300^\circ\text{C}$ , once all crosslinks had been destroyed, a mass loss of 7.36% was recorded. TG analysis showed that when CIIR was heated at

**Table II Crosslink Density of CIIR Heated (A) at 5°C/min to Various Temperatures and (B) Isothermally at 150°C for Various Periods of Time**

A		B	
Temperature (°C)	Crosslink Density ( $\times 10^6$ mol/mL)	Time (min)	Crosslink Density ( $\times 10^6$ mol/mL)
220	0	60	0
230	0.5	90	0
240	0.9	120	gel
250	4.3	140	1.7
260	2.1	160	2.5
300	0	180	3.1

5°C/min, rapid degradation of the polymer occurred at 244°C, the same temperature region in which the exotherm occurred. Degradation is exothermic, and it must be concluded that the exotherm is associated with further reactions of degradation products.

Under milder conditions (150°C) crosslinking will occur, but only on extended heating periods. Table II shows that after 120 min a gel was detected, and after 180 min a maximum crosslink density of  $3.1 \times 10^{-6}$  mol/mL was recorded, accompanied by a 1.30% mass loss.

### CIIR/ZnO

A typical DSC cure curve obtained on heating CIIR(100)/ZnO(5) at 5°C/min is shown in Figure 3. The curve heralds two thermal events, a small endotherm at 123°C, due to the melting of calcium stearate, and an exotherm with two closely situated peaks. The onset of the exothermic event is at 163°C, and the peaks are at 171 and 180°C.

Crosslinking of halo-butylys by unconventional curing formulations requires the removal of halogen from the polymer chain, the HCl evolved being trapped by ZnO.<sup>2,3</sup> This is substantiated by the negligible mass loss of 0.32%, which was recorded after heating a CIIR(100)/ZnO(5) sample to 250°C, compared to a loss of 2.10% in the absence of ZnO.

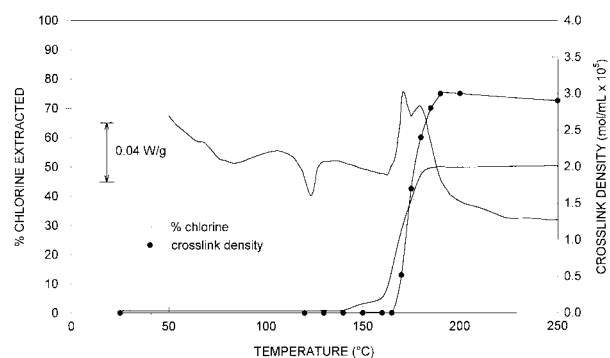
The zinc content of the extract from a vulcanized sample was analyzed by means of AA, and the chloride was quantified by potentiometric titration with AgNO<sub>3</sub>. The ratio of Zn : Cl was found to be 1 : 2.06, thus confirming that the zinc extracted was indeed ZnCl<sub>2</sub>. Determination of

chlorine evolved in the vulcanization of CIIR could, therefore, be followed by analysing for zinc as ZnCl<sub>2</sub>, using AA.

CIIR/ZnO compounds were heated to various temperatures along the DSC curve, and characterized by crosslink density measurements. Extraction and analysis of soluble zinc gives an indication of the quantity of HCl involved in the vulcanization reaction (Fig. 3). Extractable chlorine was present from the onset of heating, the unheated sample, or control, showing approximately 1 mass % of chlorine in the form of ZnCl<sub>2</sub>. This represents HCl evolved during compounding and trapped by ZnO. Upon heating, the chlorine extracted remained fairly constant until 150°C, at which temperature the amount of extracted chlorine increased rapidly. By 165°C, 15% of the chlorine present in CIIR was extractable, yet no crosslinking had taken place. The onset of the DSC exotherm coincided with the rapid formation of ZnCl<sub>2</sub> and can, therefore, be associated with the trapping of HCl by ZnO.

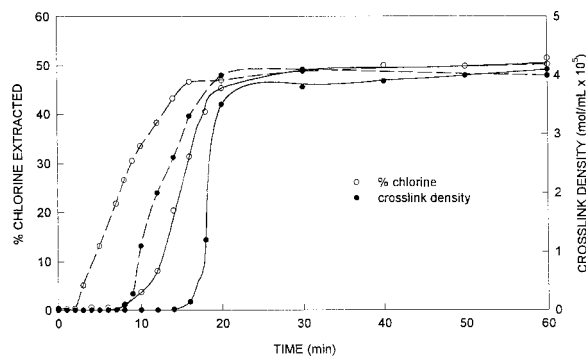
At the onset of crosslinking (170°C), 28% of the chlorine was extractable. Crosslinking was very rapid, the crosslink density of  $0.52 \times 10^{-5}$  mol/mL at 170°C increasing to  $1.7 \times 10^{-5}$  mol/mL at 175°C. After 180°C, an equilibrium maximum amount of 50% of the chlorine was extractable. As with the formation of ZnCl<sub>2</sub>, crosslinking too reached an equilibrium value ( $3.0 \times 10^{-5}$  mol/mL).

The same trends were obtained upon heating CIIR(100)/ZnO(5) isothermally at 150°C (Fig. 4). From the onset of the reaction a small amount of ZnCl<sub>2</sub> was extractable, the concentration of which remained constant until 8 min. After 12 min, 8% of the chlorine was extractable, yet no crosslinking had occurred and only after 14 min, when the



**Figure 3** DSC curve, crosslink density, and extractable chlorine analysis of CIIR(100)/ZnO(5) heated at 5°C/min.



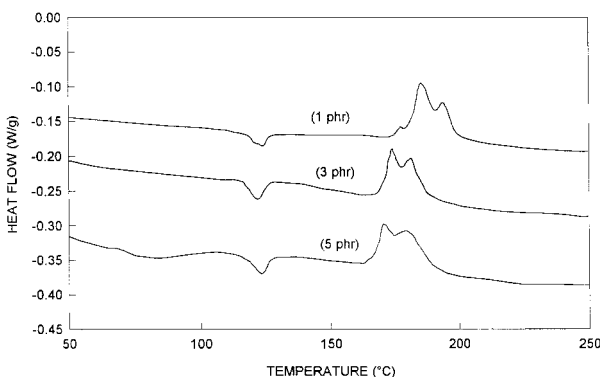


**Figure 4** Crosslink density and extractable chlorine analysis of CIIR(100)/ZnO(5) (—) and CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) (–) heated isothermally at 150°C.

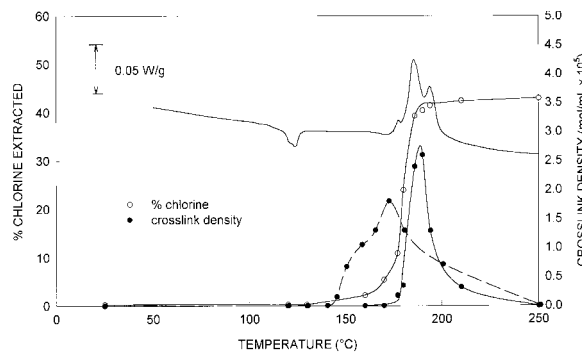
amount of chlorine extractable had increased to approximately 20%, did crosslinking commence. After 30 min, approximately 50% of the chlorine was extractable, at which point a crosslink density of  $4.0 \times 10^{-5}$  mol/mL was recorded. Further heating did not result in the formation of additional ZnCl<sub>2</sub> or crosslinking.

#### Effect of ZnO Loading

The DSC cure curves of CIIR, mixed with 1, 3, and 5 phr ZnO, are presented in Figure 5. Formulations containing lower phr ZnO showed the exotherms associated with the formation of ZnCl<sub>2</sub> to occur at higher temperatures. A decrease in the ZnO level thus caused a delay in dehydrohalogenation. All formulations showed the melting of calcium stearate at approximately 121°C, followed by an exotherm with two, and in the compound with 1 phr ZnO, three peaks in the higher temperature regions.



**Figure 5** DSC curves of CIIR(100)/ZnO(1, 3, and 5 phr) heated at 5°C/min.



**Figure 6** DSC curve, crosslink density, and extractable chlorine analysis of CIIR(100)/ZnO(1) (—) and crosslink density of CIIR(100)/ZnO(1)/ZnCl<sub>2</sub>(5) (–) heated at 5°C/min.

At 170°C, immediately prior to crosslinking, 5% of the chlorine was extractable in the CIIR(100)/ZnO(1) system (Fig. 6). This is also the point at which the exotherm commenced. Further heating caused more rapid formation of ZnCl<sub>2</sub> and the onset of crosslinking (177°C; 11% chlorine extracted,  $1/2M_c = 0.18 \times 10^{-5}$  mol/mL). The increase in ZnCl<sub>2</sub> formation between 180 and 186°C was followed by a more rapid increase in crosslink density. The maximum crosslink density of  $2.6 \times 10^{-5}$  mol/mL was recorded at 190°C.

A noticeable difference in this system, compared to the system containing 5 phr ZnO (Fig. 3), involves the destruction of crosslinks. If half of the chlorine present in the rubber were liberated as HCl during the heating process, the amount of ZnO present in this system (1 phr) is sufficient to trap it as ZnCl<sub>2</sub>, but not if all the chlorine were evolved. The reduction in crosslink density at 194°C ( $1.3 \times 10^{-5}$  mol/mL) was accompanied by a color change in the samples—the creamy white rubber at 190°C changed to a light orange color at 194°C. By 250°C, at which stage the sample was dark red and tacky, complete reversion had occurred. Thermogravimetric analysis revealed the onset of a mass loss at 190°C, and by 194°C a mass loss of 2% was recorded.

Isothermal experiments were performed on three CIIR/ZnO systems, containing different amounts of ZnO (3, 1, and 0.3 phr; Table III). All three systems showed the formation of ZnCl<sub>2</sub> before crosslinking commenced, the formation of ZnCl<sub>2</sub> in the formulations containing lower ZnO levels being delayed more. Crosslinking occurred after 16 min with 3 phr ZnO and after 18 and 20 min with 1 and 0.3 phr ZnO, respectively. In the CIIR(100)/ZnO(0.3) system, which contained the

**Table III** Analysis of CIIR(100)/ZnO (0.3, 1, and 3 phr) Heated at 150°C for Various Times

Time (min)	CIIR(100)/ZnO(0.3)		CIIR(100)/ZnO(1)		CIIR(100)/ZnO(3)	
	% Cl	<sup>a</sup> 1/2Mc	% Cl	<sup>a</sup> 1/2Mc	% Cl	<sup>a</sup> 1/2Mc
0	0.1	0	0.3	0	0.3	0
10	0.2	0	0.4	0	1	0
12	0.4	0	2	0	5	0
14	0.3	0	4	0	17	0
16	1	0	10	0	24	0.6
18	6	0	19	0.4	31	1.3
20	9	0.55	29	1.2	37	2.5
30	11	0.67	49	3.9	50	4
60	11	0.16	52	2.1	50	4.1

<sup>a</sup> Crosslink density as  $1/2Mc \times 10^5$  mol/mL.

smallest amount of ZnO, approximately 11% of the chlorine was extractable, and the compound reached a maximum crosslink density of  $0.67 \times 10^{-5}$  mol/mL before reversion. In the two systems containing larger amounts of ZnO, the crosslink density attained higher maxima ( $4.0 \times 10^{-5}$  mol/mL), at which point about 50% of the chlorine was extractable as  $ZnCl_2$ .

Neither CIIR(100)/ZnO(1) nor CIIR(100)/ZnO(0.3) contained sufficient ZnO to trap all the chlorine in the compound and the compounds exhibited reversion. This suggests that the 50% chlorine not extracted as  $ZnCl_2$  may be present as a zinc salt other than  $ZnCl_2$ . This will be discussed in the next article in this series. After 60 min a reduction of 45% in the crosslink density of the CIIR(100)/ZnO(1) compound was recorded, while a larger decrease of 71% was associated with CIIR(100)/ZnO(0.3). The behavior of the CIIR(100)/ZnO(3) system closely resembled that of the CIIR(100)/ZnO(5) system in that about 50% of the chlorine was extractable as  $ZnCl_2$ , and a maximum equilibrium crosslink density of approximately  $4.0 \times 10^{-5}$  mol/mL was achieved. Both systems contain sufficient ZnO to trap the HCl evolved and no reversion was evident.

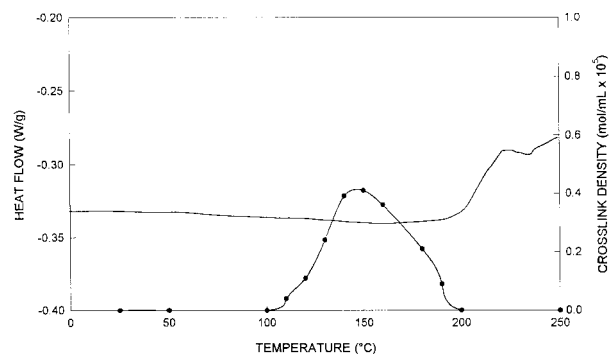
#### CIIR(100)/ $ZnCl_2$ (5)

$ZnCl_2$  is highly deliquescent, and consequently, was dried for 7 days at 75°C before use in compounds. The DSC cure curve of CIIR, compounded with dried  $ZnCl_2$ , and the crosslink densities recorded at various temperatures along the curve, are presented in Figure 7. Unlike in CIIR/ZnO systems, the endothermic melting of calcium

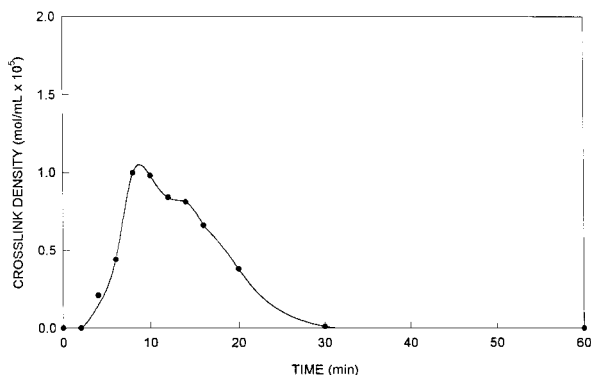
stearate was not observed, suggesting that  $ZnCl_2$  reacted with the calcium stearate, present as a stabilizer. When calcium stearate and  $ZnCl_2$ , in a 1 : 1 mol ratio, were ground together in a mortar and pestle, AA analysis revealed that only 69% of the  $ZnCl_2$  could be recovered. When heating the sample for 30 min at 150°C, 73% of the  $ZnCl_2$  reacted.

Upon heating in the DSC, the formation of a lightly crosslinked network initiated at 100°C. By 150°C, a maximum crosslink density of  $0.41 \times 10^{-5}$  mol/mL was measured, followed by reversion. By 180°C, a mass loss of 2% was recorded. It is apparent from Figure 7 that, unlike in the case of CIIR/ZnO, there was no exothermic event that could be associated with vulcanization. Thus, it is clear that the exotherm in ZnO containing formulations must be attributed to  $ZnCl_2$  formation, and not to the crosslinking reaction.

The isothermal reaction at 150°C, also, showed crosslinking to commence earlier in the presence



**Figure 7** DSC curve and crosslink density of CIIR(100)/ $ZnCl_2$ (5) heated at 5°C/min.



**Figure 8** Crosslink density of CIIR(100)/ZnCl<sub>2</sub>(5) heated isothermally at 150°C.

of dried ZnCl<sub>2</sub> than with ZnO (compare Fig. 8 with Fig. 4). After an induction period of 4 min, the crosslink density increased to a maximum of  $1.0 \times 10^{-5}$  mol/mL at 8 min (Fig. 8), followed by reversion after 12 min. After 60 min, a crosslink density of only  $0.01 \times 10^{-5}$  mol/mL was recorded. As in formulations containing low ZnO loadings, reversion was accompanied by an intense colour change. At the point of maximum crosslink density (8 min) the sample was a light orange, and further heating caused the sample to become tacky and more intensely colored, both changes indicating degradation of the polymer chain. After 60 min, the sample exhibited a dark red color and TG analysis revealed a mass loss of approximately 2%.

CIIR, mixed with undried ZnCl<sub>2</sub>, showed no crosslinking on heating for up to 60 min at 150°C, implying that ZnCl<sub>2</sub> participates in the vulcanization reaction as an associated ionic species, ZnCl<sub>2</sub>, and not as hydrated Zn<sup>2+</sup> and Cl<sup>-</sup> ions. Thus, it is imperative that as much moisture as possible be removed from the highly hygroscopic ZnCl<sub>2</sub>, before its inclusion in the rubber.

Dehydrohalogenation precedes crosslink formation, and failure of moist ZnCl<sub>2</sub> to crosslink CIIR does not mean that it cannot catalyze dehydrohalogenation. To determine whether moist Zn<sup>2+</sup>Cl<sub>2</sub><sup>-</sup> can promote dehydrohalogenation, the following approach was used. Two compounds were mixed, viz. CIIR(100)/ZnCl<sub>2</sub>(5 undried) and EPDM(100)/ZnO(5). A thin section of EPDM/ZnO was placed on top of a CIIR/ZnCl<sub>2</sub> pad and the laminate heated between platens of a small laboratory press for 10 min at 150°C. AA analysis showed that ZnCl<sub>2</sub> was present in the EPDM/ZnO layer after heating. In a control experiment, a laminate comprising layers of CIIR/ZnCl<sub>2</sub> and

EPDM without ZnO was made. No ZnCl<sub>2</sub> was found in the EPDM layer after heating, which proved that ZnCl<sub>2</sub> present in the CIIR/ZnCl<sub>2</sub> layer in the first experiment had not simply diffused into the top layer, but had resulted from HCl evolution. Thus, it can be concluded that undried ZnCl<sub>2</sub> promotes dehydrohalogenation but not the crosslinking process.

#### CIIR(100)/ZnO(x)/ZnCl<sub>2</sub>(y)

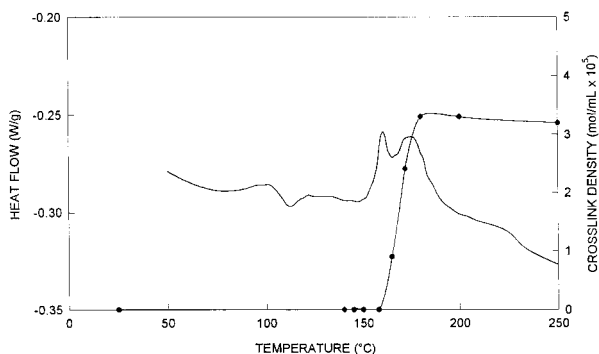
Systems containing both ZnO and ZnCl<sub>2</sub> in varying amounts [CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) and CIIR(100)/ZnO(1)/ZnCl<sub>2</sub>(5)] were heated and analyzed. Because ZnCl<sub>2</sub> is highly deliquescent, the amount of ZnCl<sub>2</sub> added to compounds was determined by AA analysis of samples after mixing. The percentage of chlorine shown in the figures and text is only for ZnCl<sub>2</sub> formed in the reaction, the ZnCl<sub>2</sub> added having been subtracted from the total ZnCl<sub>2</sub> extracted.

The introduction of 1 phr ZnCl<sub>2</sub> into a CIIR(100)/ZnO(5) formulation caused the thermal events associated with ZnCl<sub>2</sub> formation to occur earlier (compare Fig. 9 and Fig. 3). The small endotherm associated with the melting of calcium stearate did not completely disappear and, as in the CIIR/ZnO(5) system, an exotherm at 152°C, with peaks at 161 and 176°C, was observed. Crosslinking commenced at 165°C, and attained an equilibrium value of  $3.3 \times 10^{-5}$  mol/mL at 180°C.

In the isothermal study, rapid formation of ZnCl<sub>2</sub> occurred after 3 min (Fig. 4), and after 7 min, the point at which a gel was detected, 22% of the chlorine was extractable. As in the CIIR(100)/ZnO(5) system, the percentage extractable chlorine and crosslink density reached equilibrium values of 50% and  $4.0 \times 10^{-5}$  mol/mL, respectively. In contrast to the CIIR(100)/ZnCl<sub>2</sub>(5) system, reversion did not occur.

When a CIIR(100)/ZnO(1)/ZnCl<sub>2</sub>(5) sample was heated in a DSC, the higher ZnCl<sub>2</sub> concentration eliminated the calcium stearate melting endotherm and the exotherm associated with ZnCl<sub>2</sub> formation occurred earlier, as reported in Figure 9. The onset of the broad exotherm occurred at 142°C, and peaked at 165°C. Crosslinking began at 145°C (Fig. 6) and passed through a maximum at 172°C ( $1.8 \times 10^{-5}$  mol/mL). After 180 min, reversion occurred, complete breakdown of all crosslinks having occurred at 250°C.

Similarly to the previous system, the isothermal study showed ZnCl<sub>2</sub> formation before



**Figure 9** DSC curve, crosslink density, and extractable chlorine analysis of CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) heated at 5°C/min.

crosslinking commenced (Fig. 10). After 2 min, by which time 25% chlorine was extractable, crosslinking began. The extractable chlorine increased to an equilibrium value of approximately 50% after 7 min, coinciding with the maximum crosslink density ( $4.0 \times 10^{-5}$  mol/mL). Subsequent heating caused limited reversion and by 60 min, the crosslink density had decreased to  $3.2 \times 10^{-5}$  mol/mL.

## DISCUSSION

### Vulcanization Exotherms

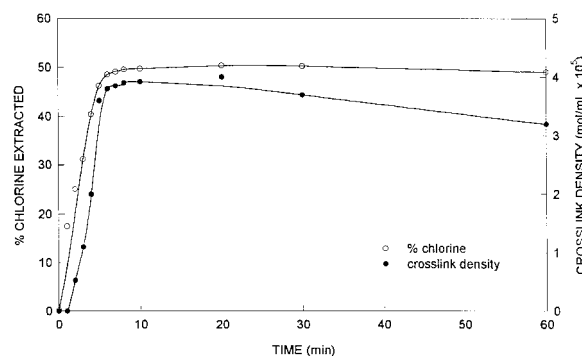
DSC curves obtained on heating CIIR/ZnO samples show an exotherm with a double peak, or two closely associated exotherms (Figs. 3 and 5). The latter would indicate the occurrence of two distinct reactions. Comparing the DSC curve and the graphs of extractable chlorine and crosslink densities show the onset of the first exotherm to coincide with the detection of ZnCl<sub>2</sub>, and the minimum between peaks to coincide with the formation of crosslinks. The formation of ZnCl<sub>2</sub> and of crosslinks may reasonably be associated with two exotherms respectively. However, in the CIIR(100)/ZnCl<sub>2</sub>(5) system, crosslink formation readily occurred without the evolution of sufficient heat to give rise to an exotherm on the DSC curve (Fig. 7), and clearly, the second peak cannot be ascribed to crosslinking.

Water, formed *in situ* by the reaction of HCl with ZnO will readily evaporate from the system at vulcanization temperatures (150°C), resulting in an endotherm. As will be shown in a later article, heating of CIIR and zinc dimethyldithiocarbamate (Zn<sub>2</sub>(dmtc)<sub>4</sub>) also results in the forma-

tion of volatiles. It is suggested that the double-peaked exotherm detected on the DSC traces when CIIR is heated with ZnO, ZnCl<sub>2</sub>, and Zn<sub>2</sub>(dmtc)<sub>4</sub> is due to the superimposition of the exotherm, associated with ZnCl<sub>2</sub> formation, and the endotherm ascribed to the evaporation of volatiles (H<sub>2</sub>O with ZnO and dimethyldithiocarbamic acid and H<sub>2</sub>S with Zn<sub>2</sub>(dmtc)<sub>4</sub>).

### The Role of ZnCl<sub>2</sub> vs. ZnO

It is apparent that in CIIR(100)/ZnO(5) compounds (Figs. 3 and 4) the rate of dehydrohalogenation increased on formation of ZnCl<sub>2</sub>, showing that ZnCl<sub>2</sub>, rather than ZnO, promotes dehydrohalogenation. Upon heating CIIR and ZnO for 8 min, during which time the concentration of ZnO was high, very little dehydrohalogenation occurred; only once ZnCl<sub>2</sub> had formed did the reaction proceed rapidly. Small amounts of ZnCl<sub>2</sub> formed on chain scission and dehydrohalogenation during the mixing process and, coupled with some thermal dehydrohalogenation in the early stages of heating, led to the build-up of ZnCl<sub>2</sub> that gave rise to an autocatalytic dehydrohalogenation process. When the mixing time was increased to 20 min, 2.46% chlorine was extractable after compounding, compared to less than 1%, when the shorter mixing times were employed. Heating this compound at a programmed rate showed crosslinking to occur at a lower temperature (165 compared to 170°C) and in an isothermal study after shorter times (12 compared to 14 min). Promotion of dehydrohalogenation by ZnCl<sub>2</sub> is further emphasized by the earlier formation of ZnCl<sub>2</sub> in the CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) system (3 min) compared with CIIR(100)/ZnO(5) (10 min) (Fig. 4). The short induction period prior to the detec-



**Figure 10** Crosslink density and extractable chlorine analysis of CIIR(100)/ZnO(1)/ZnCl<sub>2</sub>(5) heated isothermally at 150°C.

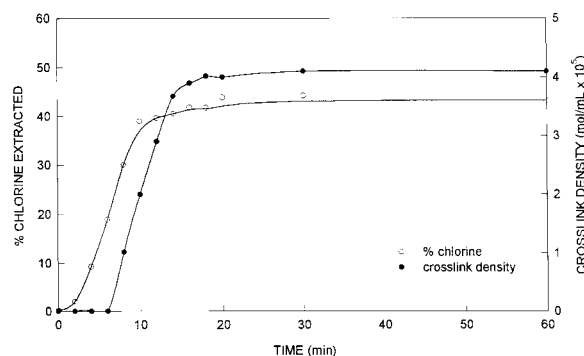


tion of additional  $\text{ZnCl}_2$  in the CIIR(100)/ZnO(5)/ $\text{ZnCl}_2$ (1) system (Fig. 4) can be ascribed to calcium stearate in the compound trapping the initially evolved HCl. Once calcium stearate is exhausted, ZnO will act as a trap, and  $\text{ZnCl}_2$  will be recorded. With higher  $\text{ZnCl}_2$  loadings (5 phr) (Fig. 10) dehydrohalogenation occurred immediately upon heating, without the intervention of an induction period, still evident in Figure 4. DSC cure curves showed the presence of residual calcium stearate in compounds with 1 phr  $\text{ZnCl}_2$  (Fig. 9), while in compounds with 5 phr  $\text{ZnCl}_2$  (Fig. 7), the melting of calcium stearate was no longer discernable, suggesting its complete removal by reaction with  $\text{ZnCl}_2$ , as discussed earlier.

### The Role of Dienes vs. $\text{ZnCl}_2$

Differentiation of the roles played by  $\text{ZnCl}_2$  and by the conjugated diene butyl is difficult, as both are products of dehydrohalogenation, and are not mutually exclusive. A CIIR(100)/ZnO(5) sample was heated for 13 min at  $150^\circ\text{C}$  in a press; the duration allowed for the formation of  $\text{ZnCl}_2$  (and conjugated diene butyl) but not crosslinking. The sample was cooled and divided in two (A and B). Samples of (A), which contained  $\text{ZnCl}_2$  and conjugated diene butyl, were reheated at  $150^\circ\text{C}$  for various times. Crosslinking occurred immediately and a maximum crosslink density of  $4.1 \times 10^{-5}$  mol/mL was measured after a sample had been heated for 17 min (total heat treatment of 30 min).

Fraction (B) was dissolved and reprecipitated as a thin film on the sides and bottom of a pill vial.  $\text{ZnCl}_2$  formed during heating was extracted from the film with a benzene/ethanol solution over a period of 48 h, giving a film that consisted of CIIR, conjugated diene butyl, and insoluble zinc. Samples of the extracted material were reheated at  $150^\circ\text{C}$  for various times (Fig. 11, the times given exclude the original 13-min heat treatment). In contrast to the unextracted samples (A), crosslinking was delayed. Only after heating for an additional 6 min, when 19% chlorine was extractable as  $\text{ZnCl}_2$ , did crosslinking commence, thus indicating that crosslinking only occurred once  $\text{ZnCl}_2$  had reformed. Crosslinking did not initiate immediately, despite conjugated diene butyl already being present in the sample. Reformation of  $\text{ZnCl}_2$  was necessary. Once crosslinking was initiated, the rate increased, and crosslinks attained a maximum value of  $4.0 \times 10^{-5}$  mol/mL. Thus, it

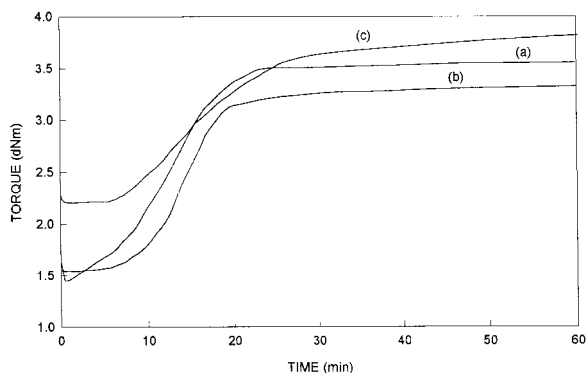


**Figure 11** Crosslink density and extractable chlorine analysis on reheating, at  $150^\circ\text{C}$ , of a CIIR(100)/ZnO(5) sample (B), previously heated at  $150^\circ\text{C}$  for 13 min, followed by extraction of  $\text{ZnCl}_2$  formed.

may appear that the contention that conjugated diene butyl is not a precursor to crosslinking is correct.<sup>2,3</sup> However, as shown earlier, the addition of  $\text{ZnCl}_2$  to a CIIR(100)/ZnO(5) sample reduced but did not eliminate the induction period prior to crosslinking. When a CIIR(100)/ZnO(5) sample was heated isothermally at  $150^\circ\text{C}$ , crosslinking occurred after 14 min, while the addition of 1 phr and 5 phr  $\text{ZnCl}_2$  reduced the induction period to 8 min and 2 min, respectively.

It is clear that the formation of conjugated diene butyl, or alternately an equivalent more reactive unit, is essential for the vulcanization of CIIR by  $\text{ZnCl}_2$ . Kuntz et al.<sup>3</sup> showed that upon heating a blend of CIIR and a synthesized conjugated diene butyl with ZnO, vulcanization was delayed to a greater extent than occurred in CIIR/ZnO. It is not known how the compound was prepared, although it is recognized that the formation of a single-phase polymer blend on a mill or internal mixer is essentially impossible, unless the polymers are highly compatible. For the vulcanization of a blend system containing CIIR and conjugated diene butyl to occur more readily than vulcanization of CIIR, an intimate single phase mix is required.

Polybutadiene (BR), which has an accessible double bond without a deactivating chlorine atom on the carbon  $\alpha$  to the double bond, as in CIIR, was used as a diene to which CIIR would be crosslinked. To prevent phase separation, that would result on mixing the two polymers in an internal mixer or a rubber mill, a CIIR/BR (1 : 1 mass ratio) solution in benzene, containing ZnO and  $\text{ZnCl}_2$  in suspension, was precipitated by the rapid addition of methanol. A blend formed in this manner would possess a much greater degree of



**Figure 12** Rheometer cure curves of (a) CIIR(50)/BR(50)/ZnO(5)/ZnCl<sub>2</sub>(1), (b) CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1), and (c) CIIR(50)/EPDM(50)/ZnO(5)/ZnCl<sub>2</sub>(1) at 150°C.

molecular uniformity and contact between the two polymers than a physical mix.

Rheometer cure curves at 150°C for CIIR(50)/BR(50)/ZnO(5)/ZnCl<sub>2</sub>(1) and CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) are presented in Figure 12. It is evident that the presence of BR caused an immediate increase in torque, while a 7-min induction period applied in the single rubber compound. On curing in a press the CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) compound showed crosslinking to commence after an induction period of 8 min at 150°C (Fig. 4), approximating to the time before the increase in torque of the rheometer cure curve. The CIIR(50)/BR(50)/ZnO(5)/ZnCl<sub>2</sub>(1) compound, vulcanized in a press at 150°C, showed the presence of a gel after only 2 min, followed by rapid crosslinking (Table IV). The absence of the induction period indicates that the formation of crosslinking precursors in this system was not required, BR providing a structure to which CIIR could immediately crosslink. The rheometer cure curve obtained on heating a blend without ZnCl<sub>2</sub>, i.e., CIIR(50)/BR(50)/ZnO(5), revealed a 4-min induction period, prior to the increase in torque. Although reactive units, in the form of double bonds in BR to which crosslinking could occur were present in this system, an induction period was necessary for the formation of ZnCl<sub>2</sub>. Once small amounts of ZnCl<sub>2</sub> were present, crosslinking occurred.

The extent of covulcanization upon heating a CIIR/BR network can be monitored by measuring the mass loss due to solubilization of the uncrosslinked fraction. As all blends comprised of a 1 : 1 mass ratio of the two polymers, extraction of less than 50 mass % of a crosslinked polymer blend confirmed covulcanization. The soluble

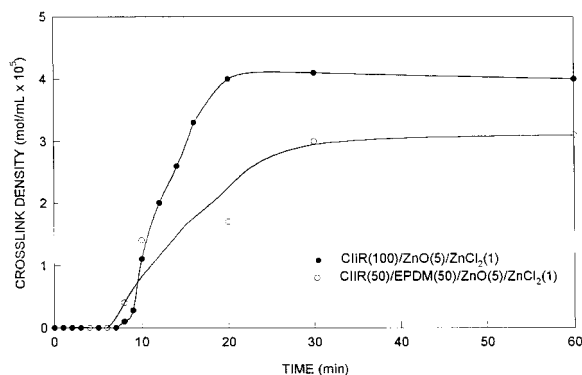
fraction was analyzed by NMR to determine its composition. Although extraction of less than 50 mass % was only recorded in samples heated for longer than 6 min at 150°C (Table IV), NMR data revealed covulcanization of CIIR and BR to have occurred immediately on heating. After heating for 2 min, analysis of the soluble fraction revealed it to comprise of 67 mass % BR and 33 mass % CIIR. (The exact value obtained in an experiment of this nature is, of course, dependent on the relative molecular weights of the polymers). Thus, the crosslinked fraction comprised of 33 mass % and 67 mass %, BR and CIIR, respectively. Further heating caused more BR to be incorporated into the crosslinked network. After 60 min, the two polymers were incorporated in approximately the same quantities (i.e., 48 mass % BR and 52 mass % CIIR).

The higher crosslink densities recorded ( $5.7 \times 10^{-5}$  mol/mL) compared to  $4 \times 10^{-5}$  mol/mL in the absence of BR, further substantiates the necessity of conjugated diene butyl as an intermediate for crosslinking of CIIR. In the blend, ZnCl<sub>2</sub> and reactive sites (in the form of double bonds in BR) were present, and dehydrohalogenation of CIIR was not necessary for vulcanization. Indeed, after heating a sample for 60 min, only 16% of the total chlorine of CIIR was extractable as ZnCl<sub>2</sub>, yet a crosslink density of  $5.7 \times 10^{-5}$  mol/mL had been attained, and most of the polymer had crosslinked (Table IV).

Polyisoprene (IR) also can be crosslinked to CIIR. When CIIR and IR were solution mixed together with ZnO and ZnCl<sub>2</sub>, precipitated with methanol, dried, and heated at 150°C for up to 60

**Table IV** Analysis of the CIIR(50)/BR(50)/ZnO(5)/ZnCl<sub>2</sub>(1) System Heated at 150°C for Various Times

Time (min)	1/2Mc × 10 <sup>5</sup> mol/mL	Mass % Extractable	Soluble Fraction	
			Mass % BR	Mass % CIIR
0	0	100	0	0
2	gel	73.1	67	33
4	0.19	66.8	60	40
6	1.1	49.3	58	42
8	1.8	28.8	55	45
10	2.5	18.1	53	47
20	5	14.8	54	46
30	5.5	11.6	52	48
60	5.7	8.9	52	48

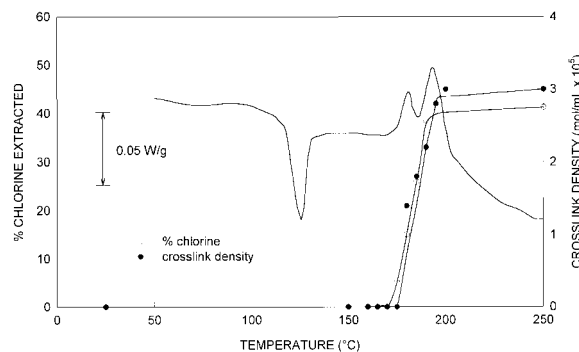


**Figure 13** Crosslink density of CIIR(100)/ZnO(5)/ZnCl<sub>2</sub>(1) and CIIR(50)/EPDM(50)/ZnO(5)/ZnCl<sub>2</sub>(1) heated isothermally at 150°C.

min, it was found that relatively little of the IR could be extracted by leaching with benzene. On the other hand, ethylene propylene diene terpolymers (EPDM), comprising of only 3–8 mass % diene units, would provide a lower reactivity towards CIIR than BR or IR, the probability of a diene unit in EPDM being adjacent to a chlorinated isoprene unit in CIIR being greatly reduced. The rheometer cure curves at 150°C for solution blend obtained with CIIR(50)/EPDM(50)/ZnO(5)/ZnCl<sub>2</sub>(1) showed an induction period (Fig. 12). Thus, despite ZnCl<sub>2</sub> being present, dehydrohalogenation was required for the formation of conjugated diene structures in CIIR and only later was crosslink formation possible. Crosslinking was slower in the blend due to the diluting effect of EPDM (Fig. 13). However, the extraction of less than 50% of the rubber at longer heating periods shows that covulcanization to isolated double bonds in EPDM did occur (Table V).

**Table V** Analysis of the CIIR(50)/EPDM(50)/ZnO(5)/ZnCl<sub>2</sub>(1) System Heated at 150°C for Various Times

Time (min)	1/2M <sub>c</sub> × 10 <sup>5</sup> mol/mL	Mass % Soluble Fraction
0	0	100
2	0	100
4	0	100
6	gel	77.2
8	0.4	66.8
10	1.4	52.5
20	1.7	43
30	3	17.3
60	3.1	16.6



**Figure 14** DSC curve, crosslink density, and extractable chlorine analysis of CIIR(100)/ZnO(5)/calcium stearate(2) heated at 5°C/min.

### Effect of Calcium Stearate

Calcium stearate is added as a stabilizer following the synthesis of CIIR, and its presence alters the rate of vulcanization. Complete removal of calcium stearate proved to be difficult. Inductively Coupled Plasma (ICP) analysis of samples after extraction with various solvents showed approximately 90% of the calcium originally present in the polymer to be unextractable. To monitor its effect it was, therefore, decided to incorporate additional calcium stearate into the polymer and record the changes induced on heating.

The DSC curve for CIIR(100)/ZnO(5) with 2 phr calcium stearate heralds three thermal events (Fig. 14)—the endotherm due to the melting of calcium stearate at 123°C, and the double peaked exotherm ascribed to ZnCl<sub>2</sub> formation. Comparison of the DSC curve with that obtained upon heating CIIR(100)/ZnO(5) (Figs. 14 and 3) shows that, in the presence of additional calcium stearate, the onset of the ZnCl<sub>2</sub> formation exotherm occurred 8°C later. Analysis of extractable zinc substantiated that the delay was caused by calcium stearate (Fig. 14). At 175°C, only 5% of the chlorine was extractable compared to 36% when 2 phr calcium stearate was not added. Further formation of ZnCl<sub>2</sub> was rapid, but a maximum of only 41% of the chlorine was extractable in the form of ZnCl<sub>2</sub>, not 50% chlorine as occurred when less calcium stearate was present to trap HCl. Crosslinking occurred immediately after formation of ZnCl<sub>2</sub>, and was very rapid. This may, in part, be attributed to the higher onset temperature compared to the CIIR(100)/ZnO(5) system and, in part, to the formation of larger amounts of conjugated diene butyl by dehydrohalogenation before ZnCl<sub>2</sub> formed, the initial HCl being trapped by calcium stearate.

Similar trends were obtained when samples were heated isothermally at 150°C, crosslinking initiated after 20 min compared to 15 min at lower calcium stearate loadings. The formation of ZnCl<sub>2</sub> and crosslinking occurred only after samples were heated for 20 and 23 min, respectively, compared to 10 and 14 min in the absence of added calcium stearate.

It is apparent that the inclusion of calcium stearate delays vulcanization. These results are not novel. Baldwin et al.<sup>2</sup> also showed the incorporation of small amounts of calcium stearate to delay vulcanization. They proposed that the delay in vulcanization of CIIR was due to calcium stearate effectively depleting the supply of most reactive allylic halogen, via carboxylic group replacement in a mechanism similar to that suggested by Frye and Horst<sup>10</sup> for the stabilization of PVC by reaction of a metal soap with the allylic chloride. Thus, the formation of ZnCl<sub>2</sub> was precluded. However, NMR analysis in this and other articles<sup>9</sup> has shown chlorine to occur predominantly in one reactive isomeric form, unlike the three isomeric structures of CIIR, as suggested by Baldwin et al.<sup>2</sup> Thus, there is no particular isomer of higher reactivity with which carboxylic group replacement will preferential occur.

It is suggested that HCl, initially formed during the mixing process and via thermal dehydrohalogenation, is trapped as CaCl<sub>2</sub>, preventing the formation of ZnCl<sub>2</sub>. To determine whether CaCl<sub>2</sub> can promote dehydrohalogenation, a thin sheet of a CIIR/CaCl<sub>2</sub>(5) compound was placed below an EPDM/ZnO(5) sheet and the laminate heated for 30 min at 150°C. AA analysis showed that only 5% of the original chlorine was extractable as ZnCl<sub>2</sub> from the EPDM/ZnO layer. Clearly, CaCl<sub>2</sub> does not promote dehydrohalogenation, the small amount of ZnCl<sub>2</sub> detected being ascribed to reaction of HCl, formed via thermal dehydrohalogenation, with ZnO.

As shown earlier, ZnCl<sub>2</sub> can also react with calcium stearate, removing it as a retarder. In accord, DSC curves show the presence of residual calcium stearate in compounds with 1 phr ZnCl<sub>2</sub> (Fig. 9) while in compounds with 5 phr ZnCl<sub>2</sub> (Fig. 6) the melting of calcium stearate is no longer discernable.

## CONCLUSIONS

CIIR crosslinks slowly at 150°C, and upon heating to 260°C, degradation sets in. CIIR, com-

pounded with ZnO, crosslinks more rapidly, although ZnO itself does not promote dehydrohalogenation or crosslinking; it merely acts as a trap for HCl, the ZnCl<sub>2</sub> formed catalyzing the reaction. Crosslinking is preceded by the formation of ZnCl<sub>2</sub> and conjugated diene butyl both of which are necessary precursors for crosslink formation. Dry ZnCl<sub>2</sub> catalyzes dehydrohalogenation and crosslinking, while moist ZnCl<sub>2</sub> promotes dehydrohalogenation and the formation of conjugated diene butyl, but not crosslinking. The addition of dry ZnCl<sub>2</sub> to formulations shortens but does not eliminate the induction period prior to crosslinking. Blends of CIIR/BR and CIIR/IR with ZnCl<sub>2</sub>, precipitated from solution, crosslink without an induction period, the dehydrogenation ZnCl<sub>2</sub> catalyst and a diene, to which crosslinking can occur, being present in the blends.

Calcium stearate, added to CIIR as a stabilizer, traps the initially evolved HCl, preventing the formation of ZnCl<sub>2</sub>, and only once the calcium stearate is exhausted will ZnCl<sub>2</sub> form and the reaction accelerate.

A modification of the cationic crosslinking mechanism, proposed by Baldwin et al.<sup>2</sup> will be proposed in the next article in this series to account for the involvement of both ZnCl<sub>2</sub> and conjugated diene butyl in the crosslinking process.

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