A DSC Study of the Crosslinking of Polychloroprene with ZnO and MgO

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SYNOPSIS

Polychloroprene and compounds of polychloroprene with ZnO and MgO were crosslinked by heating in a DSC at a programmed rate. The reaction was stopped at points along the thermogram and the crosslink density of the compound determined. The amount of chlorine evolved during reaction was measured as $ZnCl_2$ and/or $MgCl_2$. Two crosslinking processes were identified, both involving reaction of the 1,2 units in the polymer chain; the first comprising a rapid crosslinking reaction that occurs prior to the isomerization of 1,2 units and the second, a much slower reaction of isomerized 1,2 units. $ZnCl_2$, which forms during compounding and on crosslinking, catalyzes the first reaction, while ZnO promotes the allylic rearrangment of 1,2 units. MgO increases the scorch time by trapping HCl evolved during compounding, thus limiting the amount of the crosslinling catalyst ($ZnCl_2$) formed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polychloroprene (CR) comprises chains containing four basic structual units.[1,2-4]

Behal et. al.[5] suggested that the thermovulcanization of CR consits of two parallel reactions, one occurring via the intermolecular dehydrochlorination of allylic chlorine and the second via other active sites that they did not specify. Early suggestions that crosslinking, in the presence of ZnO, involves an ether linkage, has been disproved.[6,7] A possible Diels-Alder crosslinking reaction has, likewise, been discounted,[7,8] while the involvement of an allylic carbocation has been suggested.[7] It is generally agreed that, in the presence and absence of ZnO, tertiary allylic rearrangment of 1,2 units preceeds crosslinking,[9,10] the allylic rearrangement being promoted by ZnO. Isomerized 1,2 units may crosslink with 1,4 units in neighboring chains, or lead to cyclization reactions. The loss of HCl, on crosslinking, correlates with the decrease in the number of isomerized 1,2 units.[9] The addition of MgO to a ZnO compound decreases the rate of cure and increases

the scorch time.[11,12] MgO is thought to scavenge chloride ions produced during crosslinking. It has also been suggested that the retarding effect of MgO is brought about by coordination of magnesium (MgO is a Lewis base) to the Lewis acid, thus deactivating the $ZnCl_2$ crosslinking catalyst.

This article reports on the crosslinking of CR in the presence of ZnO and MgO. The reaction was followed by heating samples in a DSC, stopping the reaction at points along the thermogram, and analyzing the samples.

EXPERIMENTAL

Materials: 97% 1,4-polychloroprene (Bayprene 210), rubber grade ZnO (Gentyre), CR grade MgO (Tycon), granular $ZnCl_2$ (Hopkins and Williams).

MIXING PROCEDURE

The samples were mixed in a Barbender Plasticorder using a type W30 mixing head with a 30 mL capacity. The mixing temperature was maintained below 45°C by passing chilled water through the mixing head. The CR chips were first dusted to remove the excess

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Trans-1,4 (85%)   Cis-1,4 (10%)

1,2- (1.5%)   3,4- (1%)
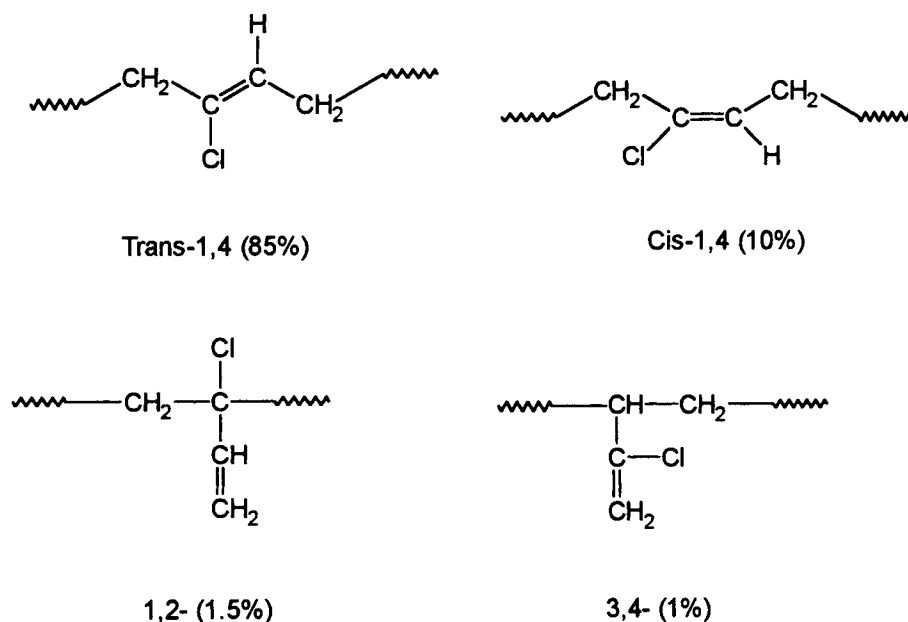
Scheme 1   Main structural units in polychloroprene chain. The extent of each type in a typical commercial polymer is shown in brackets.

talc that is used by the manufacturer as a coating for the chips, and were then milled on an unheated two roll mill to from a single rubber sample. The sample was weighed and cut to the correct mass. Three-quarters of the weighed sample was placed in the Brabender and masticated for 1 min at 30 rpm. The curatives were then added slowly over a 2-min period and the remainder of the rubber was added, after which the sample was mixed for a further 10 min at 30 rpm. The samples were removed from the Brabender and passed through the mill twice. $ZnCl_2$ is very hygroscopic, and where it alone was added to compounds, it was found that weighing it directly on a piece of rubber and then adding it immediately to the Brabender provided the easiest method of addition. In all compounds that contained $ZnCl_2$ as well as another solid component, the $ZnCl_2$ was dissolved in a small amount of ethanol. The other components were added to this solution and the ethanol evaporated, thereby coating them with the precipitated $ZnCl_2$. In all cases, experiments were carried out on the same day as the samples were mixed.

Crosslinking was conducted by heating the samples at a programmed rate in aluminium pans in a Du Pont 910 DSC module connected to a Du Pont 9000 Thermal Analyzer. High purity nitrogen, at a flow rate of 75 mL/min, was used as a purge gas. An empty aluminium pan served as reference sample. Samples of about 20 mg were weighed on the microbalance and encapsulated in an aluminium DSC pan.

Samples were heated in the DSC to the required temperature, rapidly removed, and placed in liquid nitrogen to quench the reaction. Heating rates of 2.5 and 10°C/min were employed. Two samples were heated to the selected temperature, one was analyzed for both extractable Zn and extractable Mg, and a crosslink density measurement was carried out on the second sample.

Quenched samples were placed in 10 mL of a 50/50 (v/v) solution of benzene and ethanol and extracted for 48 h. It was found that a 50/50 (v/v) solution of ethanol and benzene provided the best results. Using control samples containing known amounts of $ZnCl_2$ and $MgCl_2$ it was found for unvulcanized samples an average of 73% ($\pm$ 2%) of the $MgCl_2$ was extracted and an average of 89% ($\pm$ 3%) of the $ZnCl_2$ was extracted. For vulcanized samples, an average of 86% ($\pm$ 0.5%) of the $MgCl_2$ was extracted and 100% ($\pm$ 0.5%) of the $ZnCl_2$ was extracted.

After 48 h, the samples that had not dissolved, i.e., samples that were crosslinked were removed from the solution and the solution allowed to evaporate. H_2O (20 mL) was added to dissolve remaining residue. For samples that had dissolved, i.e., samples that were not crosslinked, the benzene/ethanol solution was evaporated off, leaving a thin layer of

rubber on the walls of the container. H_2O (20 mL) was added to this container and allowed to extract for a further 48 h. The solutions were diluted to the required concentration and the amount of the zinc and magnesium in the solution determined by atomic absorption spectrophotometry.

The Flory-Rehner equation[13] was used to calculate crosslink densities from Vr, the volume fraction of rubber in a swollen vulcanizate. Samples were swollen in benzene for 48 h before determining the mass of the swollen gel and were dried in vaccuum before reweighing. A solvent polymer interaction parameter of 0.4284 was calculated from literature data.[14]

Isothermal studies were carried out in a small mold (4 g CR) at 150°C. At selected times the samples were removed from the mold and dumped into liquid nitrogen to quench the reaction. Crosslink density measurements were done on a sample cut from the center of the vulcanizate.

Thermogravimetric analysis was conducted using a Du Pont 951 thermogravimetric analyzer (TG) module, which was connected to a Du Pont 9000 Thermal Analyzer. High purity nitrogen was used as a purge gas, maintaining a flow rate of 75 mL/min.

A Perkin-Elmer 603 Atomic Absorption Spectrophotometer with a 10 cm Perkin-Elmer Burner

Control was used for the analysis of zinc (213.9 nm) and magnesium (285.2 nm) extracted from the samples. An acetylene–air mixture was used for the flame, with an acetylene pressure of 0.85 kg/cm² and an air pressure of 2.2 kg/cm².

The NMR Spectrometer used was a Varian Gemini 200 model operating on 200 MHz. Samples were dissolved in deuterated chloroform.

A Monsanto Oscillating Disk Rheometer 100S with an arc of 1° operated at a temperature of 150°C was used to obtain the rheometer curves.

RESULTS

CR

The DSC thermogram obtained on heating CR is irregular, with a poorly defined baseline, but shows a large exotherm commencing around 230°C (Fig. 1). It is well known that CR can crosslink in the absence of curatives.[9] The reaction was stopped at points along the thermogram and the samples swelled in benzene. It is seen that the crosslinking starts at about 180°C and increases gradually to a plateau between 180°C and 200°C. From 220°C to 260°C, the increase in the crosslink density is more rapid. From the TG it can be seen that the mass loss coincides with the increase in the crosslink
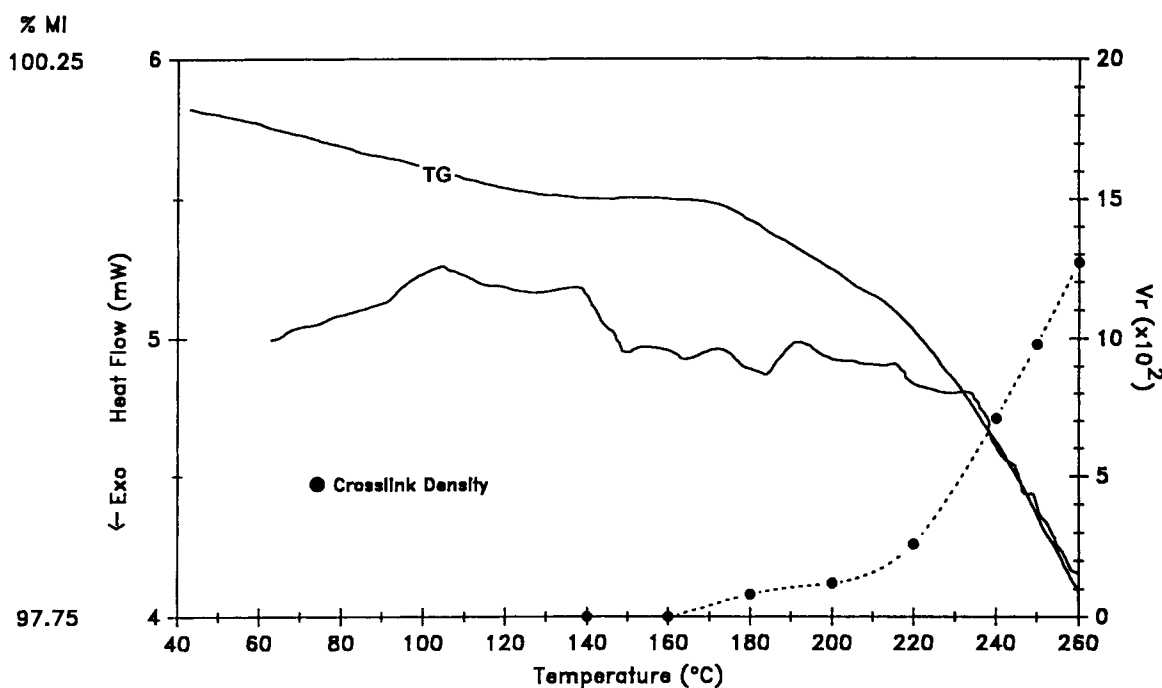
Figure 1   DSC thermogram (M_D = 18.3964 mg), crosslink density and TG (%Ml = % mass loss) for CR; heating rate 10°C/min.

density. At 220°C, where the crosslink density increases more rapidly, there is a more rapid mass loss, which may be ascribed to HCl evolution. In this project, the reaction was not studied above 260°C and the maximum crosslink density obtained at 260°C is 2.43×10^{-5} mol/mL (*Vr* of 0.127). The crosslink density at this point corresponds to 12% of the tertiary allylic chlorine atoms being involved in crosslink formation, assuming crosslinking to involve reaction between a rearranged 1,2 unit and a 1,4 unit in the polymer chain as suggested by Miyata and Atsumi.[9] (Note: crosslink density is plotted in terms of *Vr* values and not $1/2M_c$, as *Vr* values are more sensitive in the lower crosslink density region, and the plateau value in the crosslink density is more easily illustrated. M_D is the mass of the sample used to obtain the DSC thermogram.)

CR/ZnO

Figure 2(a) is a typical thermogram obtained for a CR/ZnO mix. After mixing, the compound contains a small amount of $ZnCl_2$. The amount of $ZnCl_2$ extracted is equivalent to 2% of the ZnO added to the compound and corresponds to 2.4×10^{-5} mol of chlorine atoms/g of CR.

ZnO has been shown to promote the allylic rearrangement of the chlorine atoms of the 1,2 units,[10] a reaction that is said to precede crosslinking. Associated with the large, narrow exotherm at $\pm$ 160°C (Fig. 2), is a rapid increase in the crosslink density and an accompanying increase in the amount of extractable zinc ($ZnCl_2$). There is, however, only a very slight exothermic trend in the DSC curve in the temperature region associated with the second increase in the crosslink density and in the amount of extractable zinc.

On heating the sample, the crosslink density initially increases to 1.45×10^{-5} mol/mL (*Vr* of 0.100), after which it remains constant up to about 220°C, when there is again a gradual increase in the crosslink density [Fig. 2(a)]. The second increase commenced in the temperature region in which the change of the rate of crosslinking was observed in the absence of any promoters (Fig. 1). The increase in the crosslink density is accompanied by an increase in the amount of extractable zinc. Over the whole range, the shape of the curve for the amount of extractable zinc vs. reaction temperature is mimicked by that for the change in crosslink density with temperature. The mass loss is negligible as HCl evolved is trapped by the ZnO to form $ZnCl_2$.

Both the crosslink density and the rate of the crosslinking reaction are unaffected by the ZnO loading. Figure 3 shows the result of an isothermal study at 150°C on two samples, one containing 1 phr and the other containing 5 phr ZnO. As can be seen, similar crosslink densities are reached in both cases, and the rate of the crosslinking is the same. The DSC thermograms for a 1 phr and 5 phr sample are also similar.

On heating the CR/ZnO compound at the slower rate of 2.5°C/min (Fig. 4), the vulcanization exotherm occurs at 130°C, about 30°C earlier than for a heating rate of 10°C/min. The crosslink density reaches a plateau after the exotherm at a value of 2.00×10^{-5} mol/mL (*Vr* of 0.116), which is higher than is obtained at the faster heating rate. There is once again a further increase in the crosslink density starting at about 180°C and the final value reached is 7.45×10^{-5} mol/mL (*Vr* of 0.206) at 260°C.

CR/MgO (4 phr)

The DSC thermogram for the CR/MgO system shows a large exotherm starting at about 210°C (Fig. 5). The exotherm initiates some 20°C earlier than in the absence of MgO and peaks just before 260°C, while at any given temperature the crosslink density is slightly higher. After mixing, 3.1% of the MgO can be extracted as $MgCl_2$. This corresponds to 2.19 $\times 10^{-5}$ mol of chlorine atoms/g of CR. No mass loss is observed as the HCl evolved on crosslinking is trapped by MgO as $MgCl_2$. The increase in the $MgCl_2$ extracted parallels the increase in the crosslink density. Crosslinking, the formation of increased amounts of $MgCl_2$, and the exotherm occur in the same temperature region. The small amount of crosslinking that occurred prior to the rapid crosslinking reaction, observed on heating CR on its own, was not observed in this system.

CR/ZnCl₂ (Zn = 1 phr ZnO)

The DSC thermogram for the $CR/ZnCl_2$ system (Fig. 6) shows a large exotherm commencing at about 170°C and a second large exotherm at temperatures above 230°C. The crosslink density of the samples starts to increase at 110°C and increases gradually until 200°C. The mass loss at the lower temperatures may be attributed to the HCl evolved during crosslinking. Crosslinking commenced much earlier than in any of the other compounds.
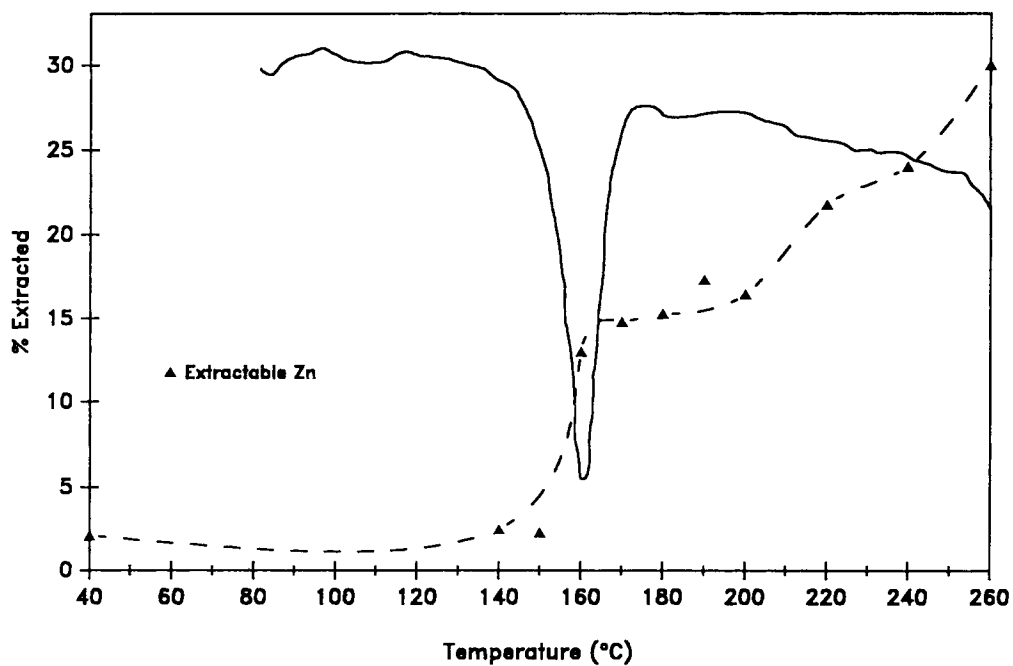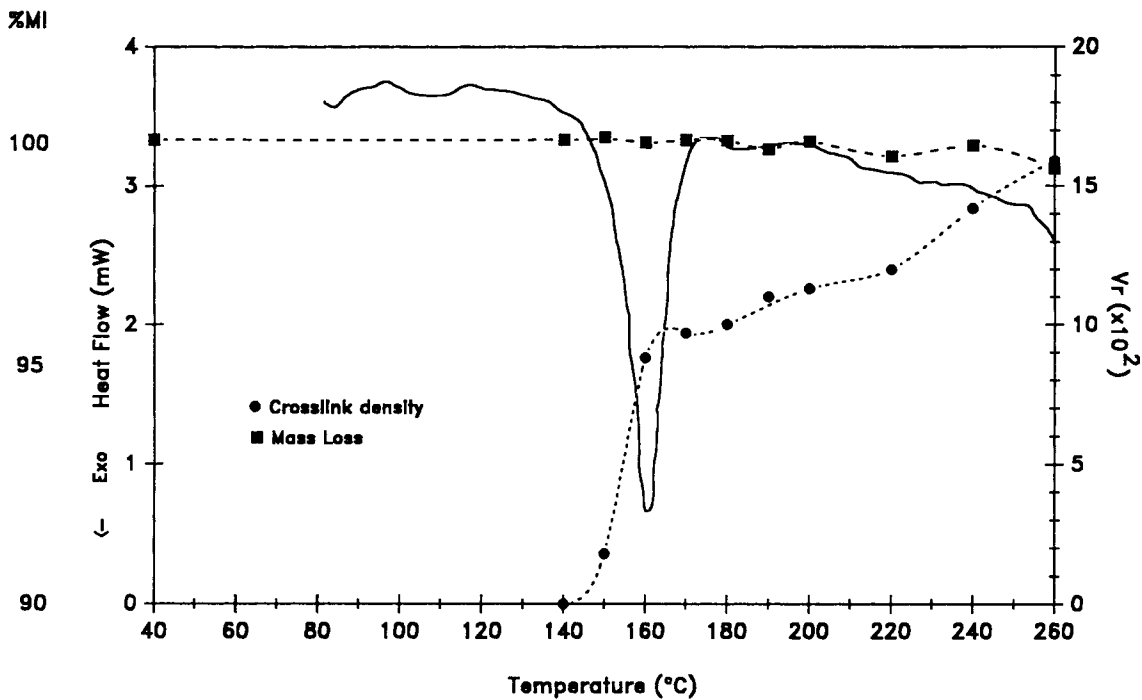
Figure 2   (a) DSC thermogram (M_D = 17.1732 mg), crosslink density and mass loss (%Ml) for CR/ZnO (5 phr); heating rate 10°C/min. (b) DSC thermogram and extractable zinc for CR/ZnO (5 phr ZnO).
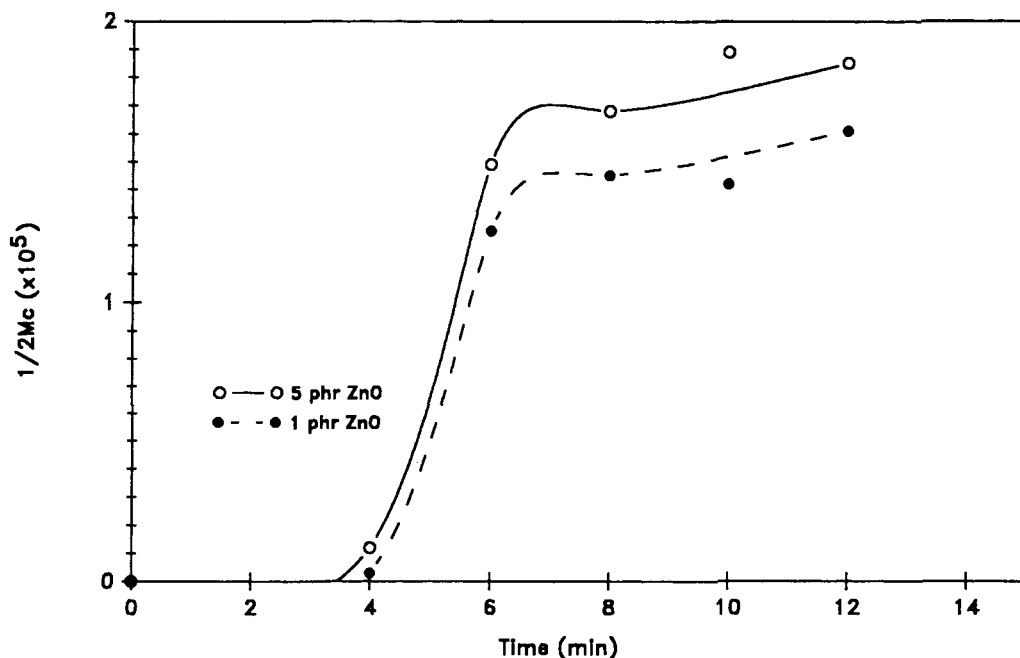
Figure 3 Effect of 1 phr and 5 phr ZnO loading on crosslink density in isothermal study at 150°C.

CR/ZnO/ZnCl₂ (Zn = 1 phr ZnO)

The addition of $ZnCl_2$ to the CR/ZnO compound does not alter the onset temperature of the cross-linking exotherm (cf. Fig. 2 and Fig. 7), nor does it change the crosslink density. On analyzing samples heated to different temperatures in the DSC, a plateau in both the crosslink density and the extractable zinc is observed, the crosslink density plateau value being very similar to that obtained without $ZnCl_2$. At higher temperatures, there is again an increase in both the crosslink density and the amount of extractable zinc. The DSC shows two exotherms, the first a broad shallow peak coinciding with the first crosslinking reaction and the formation of $ZnCl_2$, and the second a more prominent exotherm corresponding with a further increase in crosslink density above 180°C. This compound contains a total amount of zinc that is equivalent to the amount of zinc in a 1 phr ZnO compound, and soon after the onset of the high temperature crosslinking process, a rapid mass loss is observed. At this point, 100% of the zinc in the system is accounted for, as extractable zinc and additional HCl evolved cannot be trapped. The thermogram becomes increasingly exothermic in this region.

CR/MgO/ZnCl₂ (4 phr MgO; Zn = 1 phr ZnO)

There is only a small change in the thermogram for the $CR/MgO/ZnCl_2$ system compared to that seen

in the absence of $ZnCl_2$ (cf. Fig. 5 and Fig. 8). The main difference is that a small amount of crosslink-ing occurs before the rapid reaction at 180°C. The small amount of $ZnCl_2$ present may have initiated crosslinking at 140°C, prior to the onset of high temperature crosslinking. About 5.7% of the MgO originally present can be extracted after compound-ing. As in the CR/MgO system, the formation of $MgCl_2$ accompanies crosslinking.

CR/ZnO (5 phr)/MgO (4 phr)

The addition of MgO to the CR/ZnO system has the effect of delaying the crosslinking reaction (cf. Fig. 2 and Fig. 9). In the case of the CR/ZnO compound, there is a rapid increase in the crosslink density at about 150°C, while in the $CR/ZnO/MgO$ compound, no rapid crosslinking is observed until about 180°C. The increase in the crosslink density is also less rapid. The retarding effect of MgO on the crosslinking reaction is well known.[1,12] The retarding effect of MgO can also be seen when the rheometer curves for the two samples at 150°C are compared (Fig. 10). In the CR/ZnO compound, the induction period prior to the increase in the torque is about 4 min, while for the $CR/ZnO/MgO$ compound the induction period is about 5 min. The rate of increase of the torque value is also smaller in the $CR/ZnO/MgO$ compound than in the CR/ZnO compound. In the CR/ZnO compound, the torque increases rapidly and then begins to level off after
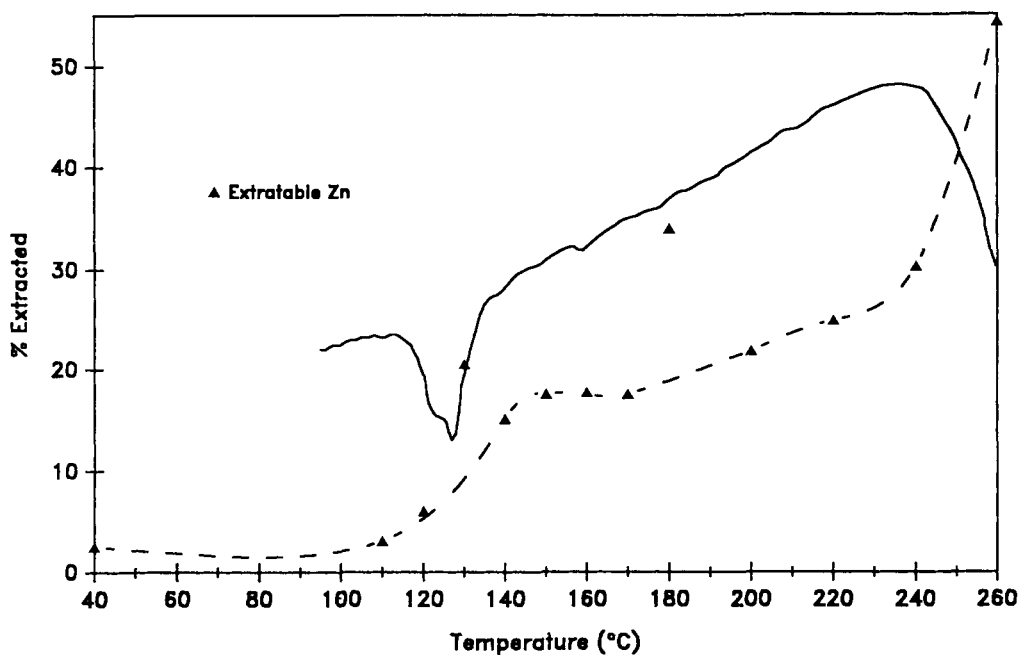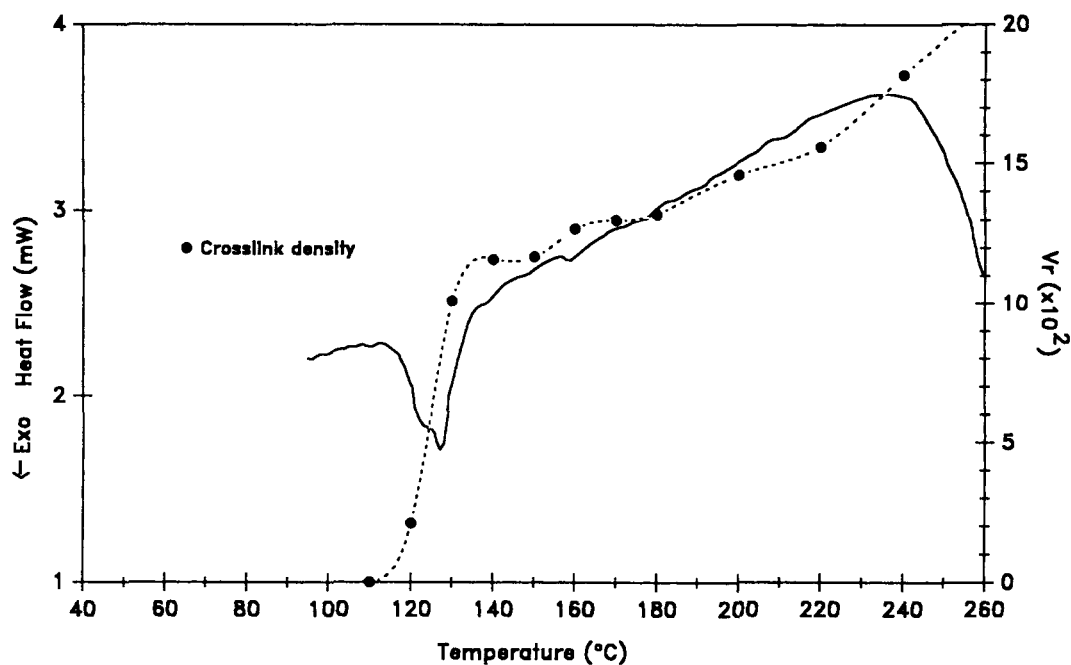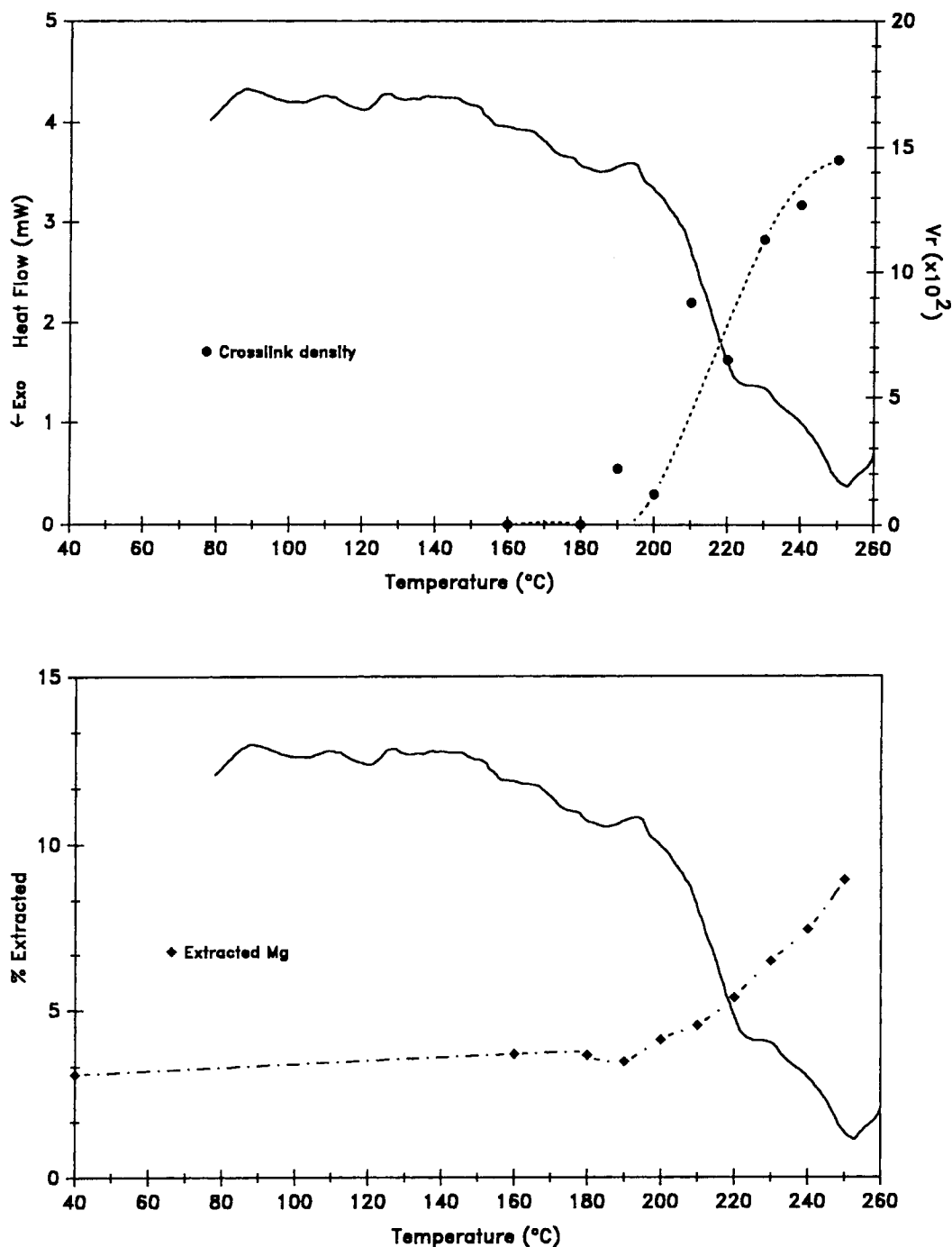
Figure 4 (a) DSC thermogram (M_D = 16.1782 mg) and crosslink density for CR/ZnO (5 phr) compound; heating rate of 2.5°C/min. (b) DSC thermogram and extractable Zn for CR/ZnO (5 phr) compound; heating rate of 2.5°C/min.

about 10 min, while for the CR/ZnO/MgO compound there is only a slow steady increase in the torque.

In the DSC study (Fig. 9) the increase in the crosslink density is accompanied by a rapid increase in the amount of extractable zinc, while the amount of extractable magnesium increases only very slightly over the whole of the temperature range. The plateau value in the crosslink density at 160°C to 180°C, observed with ZnO, is not evident here and the crosslink density increases smoothly to a value of 2.93×10^{-5} mol/mL (V_r of 0.138) at 260°C.
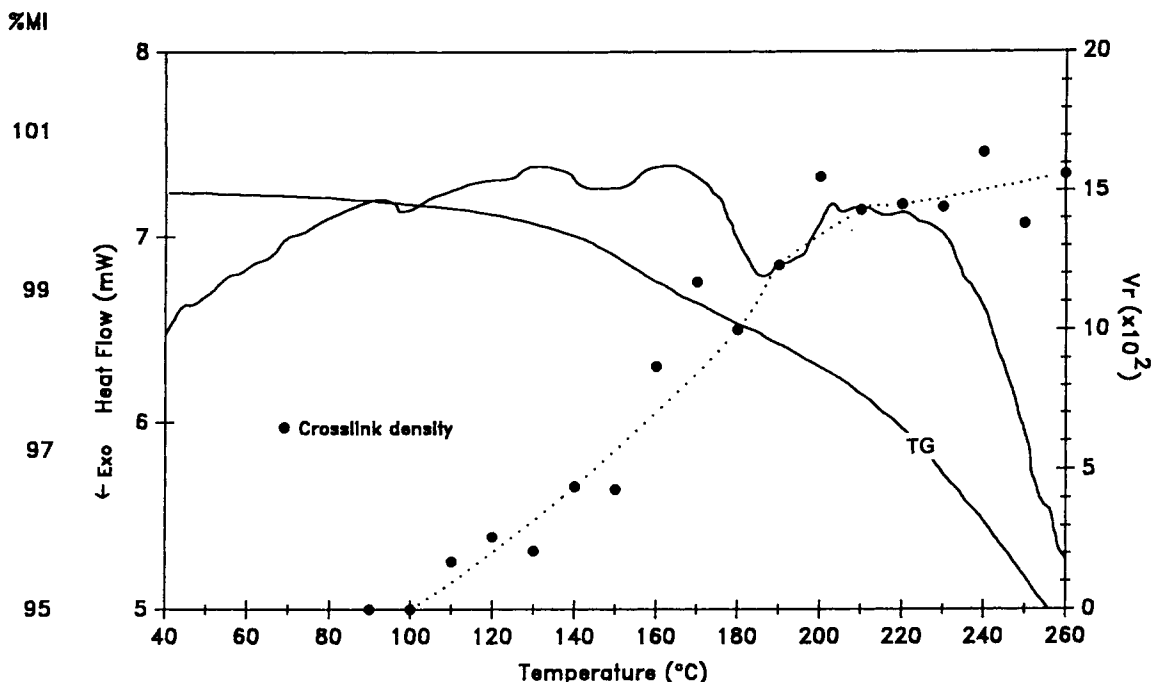
Figure 5 (a) DSC thermogram (M_D = 20.0852 mg) and crosslink density for the CR/ MgO compound (4 phr MgO); heating rate 10°C/min. (b) DSC thermogram and extractable Mg for CR/MgO compound (4 phr MgO); heating rate 10°C/min.

The DSC thermogram shows two peaks, a small peak at 180°C, coincident with the formation of a small amount of $ZnCl_2$, and a much larger exotherm that occurs just prior to the rapid increase in the crosslink density and the amount of extractable zinc. It would appear that the amount of crosslinking accompa-

nying the formation of small amounts of $ZnCl_2$ around 160°C is insufficient to render the samples insoluble. Note that while MgO retards the first crosslinking reaction, it does not significantly affect the onset of the second crosslinking reaction.

Analysis shows that after compounding, 4% of

Figure 6   DSC thermogram (M_D = 21.7950 mg), TG, and crosslink density for CR/ZnCl$_2$
(Zn $\equiv$ 1 phr ZnO); heating rate 10°C/min.

the MgO added can be extracted as soluble MgCl$_2$, while the extractable ZnCl$_2$ has been reduced to 0.5%, compared to 2% of the ZnO loading in the absence of MgO.

CR/ZnO/MgO/ZnCl$_2$ (5 phr ZnO; 4 phr MgO; Zn = 1 phr ZnO, ZnCl$_2$)

The addition of ZnCl$_2$ to the CR/ZnO/MgO system has the effect of shifting the DSC exotherm to 160°C, the same temperature as it occurred at in the CR/ZnO system (cf. Fig. 2 and Fig. 11). Crosslinking starts at about 140°C and increases steadily until 180°C, where a plateau is reached at a crosslink density value of 1.34 × 10^{-5} mol/mL (Vr of 0.096). This plateau crosslink density value is about the same as in the CR/ZnO compound. The rate of crosslinking is slower than that for the CR/ZnO compound, probably due to the presence of MgO. The amount of extractable zinc once again follows the increase in the crosslink density, while the extractable Mg only increases slightly over the temperature range.

After compounding, 5.7% of the total amount of zinc added to the system is extractable, while about 4.7% of the Mg is extractable. When Figure 9 and Figure 11 are compared, it can be seen that the addition of ZnCl$_2$ to the CR/ZnO/MgO system has the effect of shifting both the exotherm and cross-

linking reaction 20°C earlier. The addition of ZnCl$_2$ appears to have eliminated the retarding effect of MgO on the crosslinking reaction. A plateau value in the crosslinking density is observed in the CR/ZnO/MgO/ZnCl$_2$ compound that is not observed in the CR/ZnO/MgO compound and would indicate that, while ZnCl$_2$ shifted the first crosslinking reaction, it had little effect on the second crosslinking reaction. The final crosslink densities in both the systems are similar.

DISCUSSION

Catalysis by ZnCl$_2$

In CR compounds, HCl is evolved during mixing and, depending on the formulation, is trapped as ZnCl$_2$ or MgCl$_2$. The amount of HCl evolved is a function of the mixing time (Table I) and procedure. It is clear that ZnCl$_2$ catalyzes the crosslinking process, crosslinking commencing at lower temperatures in all compounds that contain ZnCl$_2$. It is most likely that chain-end radicals, formed during compounding, initiate a reaction sequence[15] that liberates HCl and with extended mixing times the samples become darker in color.

In compounds with both ZnO and MgO, the bulk of the HCl evolved during mixing is trapped as
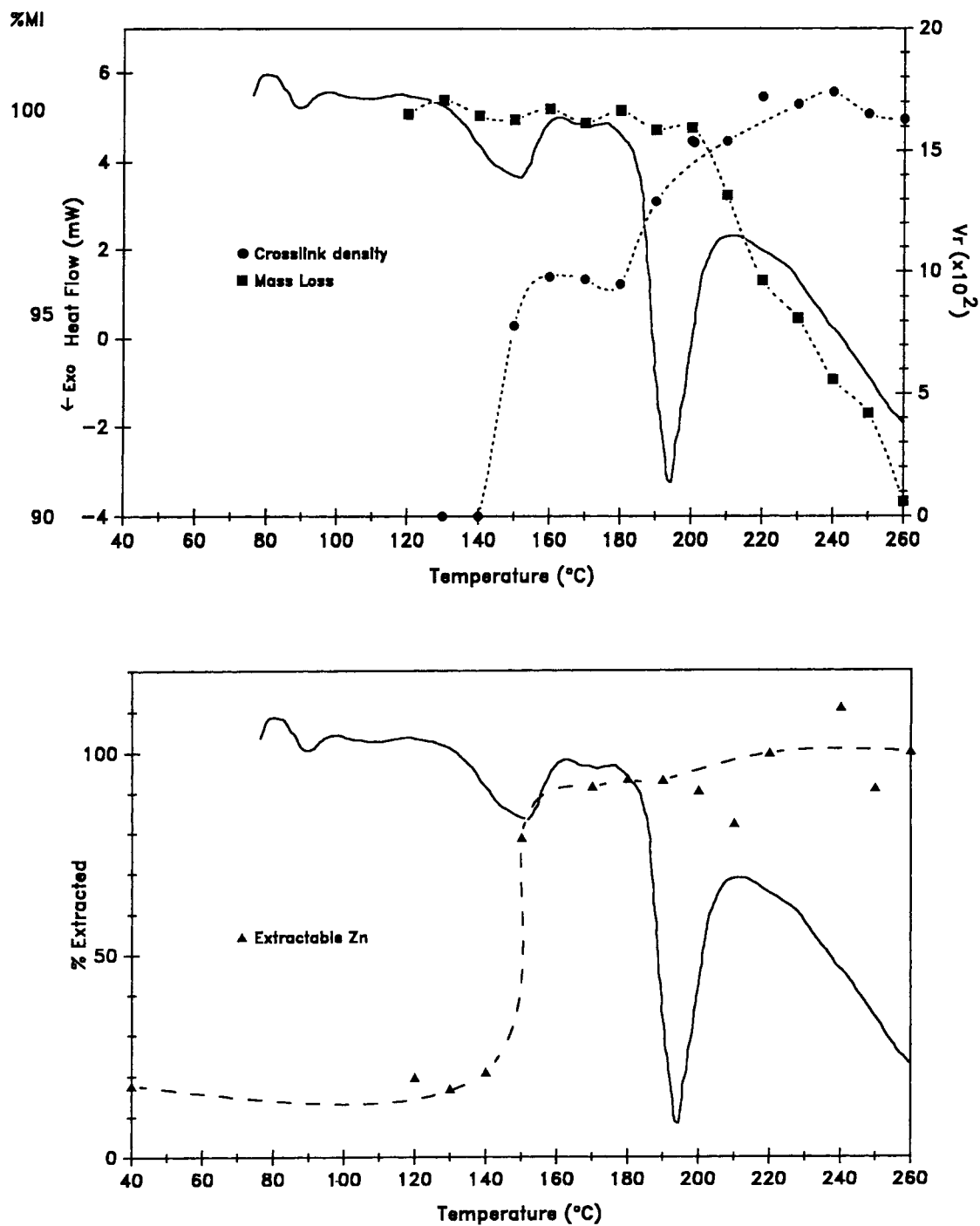
Figure 7 (a) DSC thermogram (M_D = 19.5009 mg), crosslink density, and mass loss (%Ml) for the CR/ZnO/ZnCl$_2$ system (1 phr); heating rate of 10°C/min. (b) DSC thermogram and extractable Zn for CR/ZnO/ZnCl$_2$ system (1 phr); heating rate of 10°C/min.

MgCl$_2$ (after mixing a CR/ZnO/MgO compound, 3.0 × 10^{-5} mol/g of Mg is extracted while only 2.7–10^{-6} mol/g of Zn is extractable). When ZnCl$_2$ and

MgO are mixed into rubber, an exchange reaction occurs, indicating that the MgCl$_2$/ZnO system is more stable than the ZnCl$_2$/MgO system. This oc-
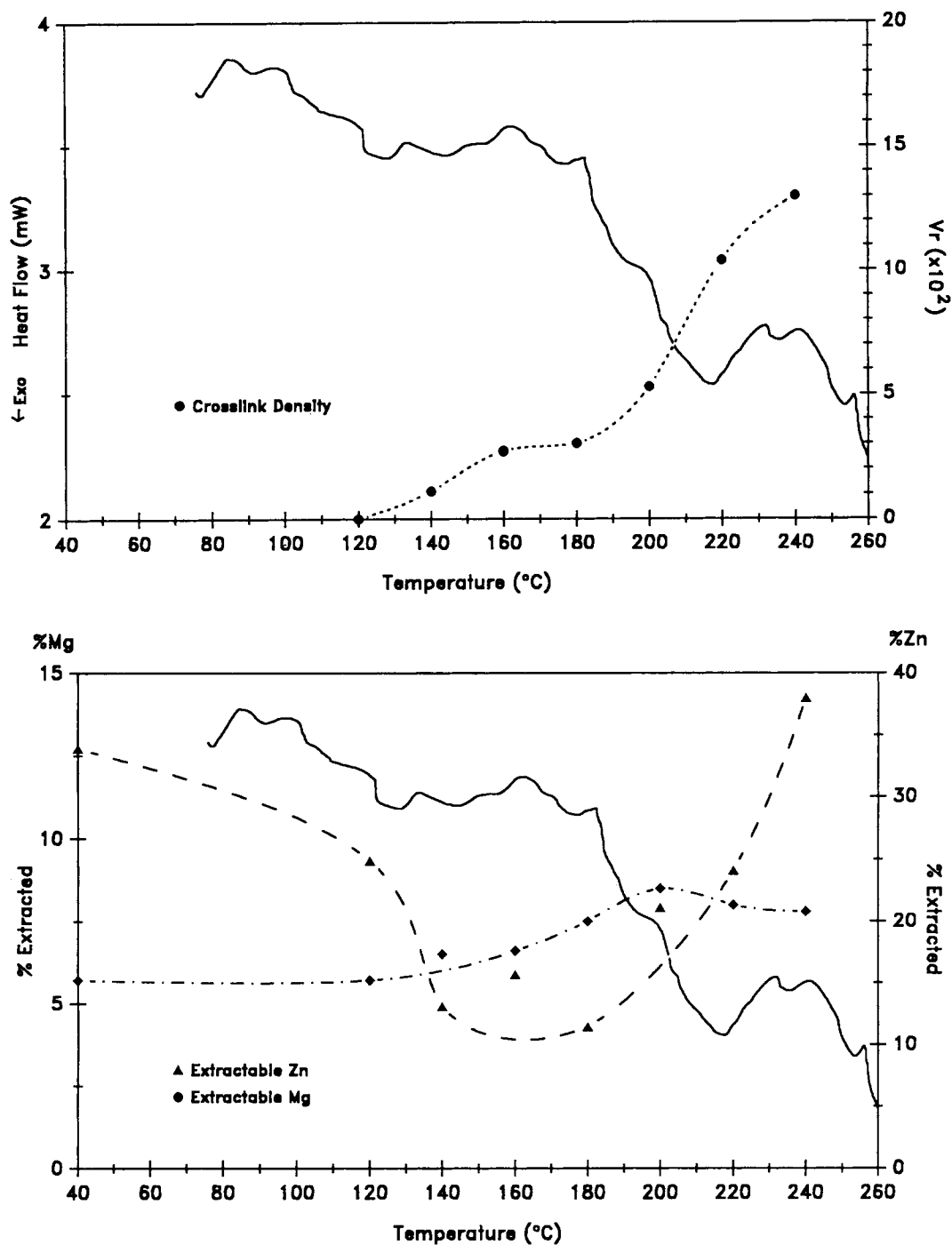
Figure 8   (a) DSC thermogram (M_D = 22.9616 mg) and crosslink density for CR/MgO/ ZnCl$_2$ (4 phr MgO; Zn = 1 phr ZnO) system; heating rate of 10°C/min. (b) DSC thermogram, extractable Zn and Mg for CR/MgO/ZnCl$_2$ (4 phr MgO; Zn = 1 phr ZnO) system; heating rate of 10°C/min.

curred in the CR/MgO/ZnCl$_2$ compound and at higher temperatures in the CR/ZnO/MgO/ZnCl$_2$ compound. As will be discussed below, the HCl

evolved during crosslinking is mainly trapped as ZnCl$_2$, little additional MgCl$_2$ being produced (Fig. 9). This may be attributed to HCl formation being
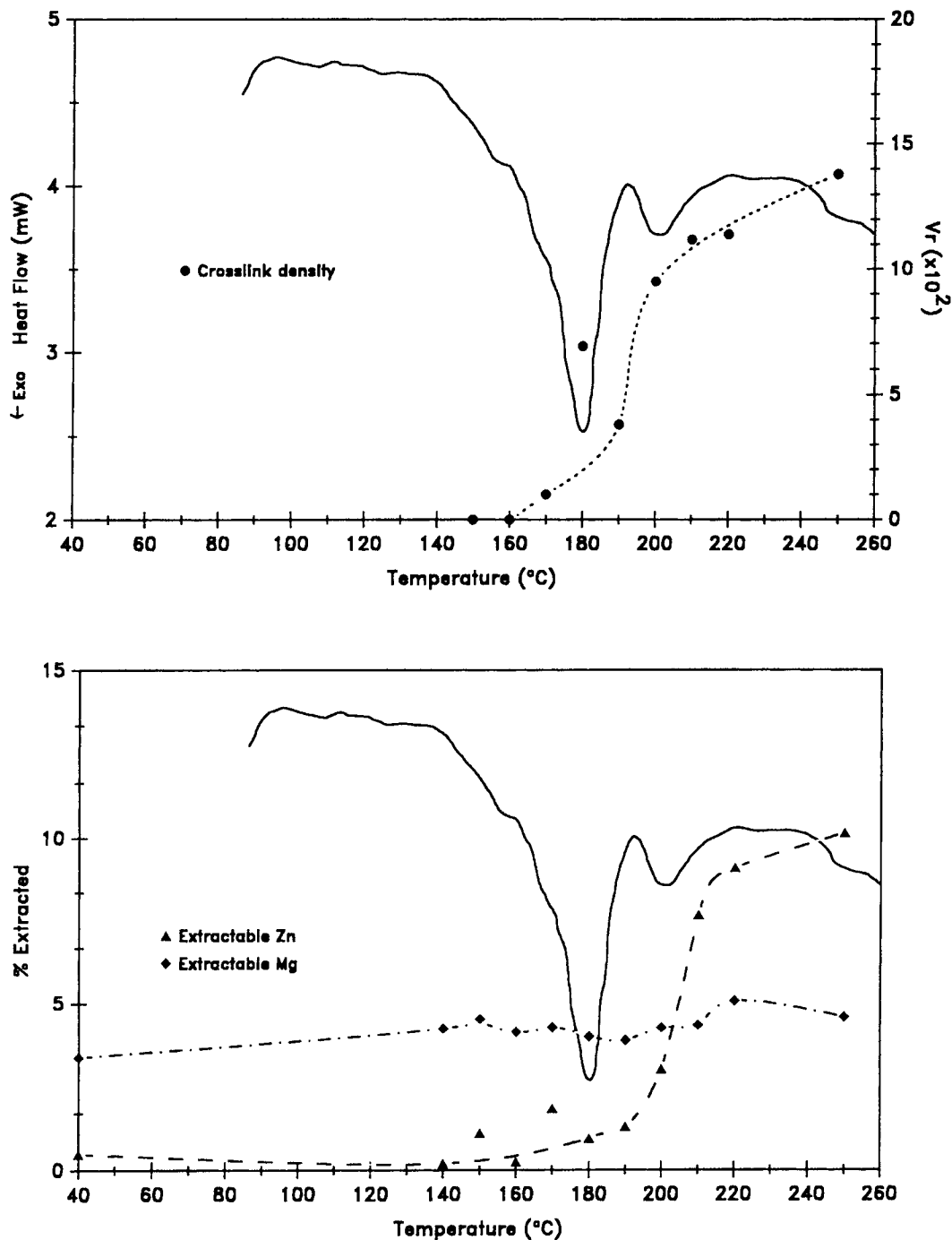
Figure 9 (a) DSC thermogram (M_D = 22.8012 mg) and crosslink density for the CR/ZnO/MgO (5 phr ZnO; 4 phr MgO) compound; heating rate of 10°C/min. (b) DSC thermogram extractable Zn and Mg for the CR/ZnO/MgO (5 phr ZnO; 4 phr MgO) compound; heating rate of 10°C/min.

closely associated with ZnO particles or with ZnCl$_2$ that has formed in proximity to the particles. MgCl$_2$ is formed only during mixing and when MgO acts as a trap for HCl evolved on vulcanization in the absence of ZnO.

Crosslinking Reactions

The rheometer cure curves for the CR/ZnO compound (Fig. 10) show an induction period before the onset of crosslinking, which is followed by a march-
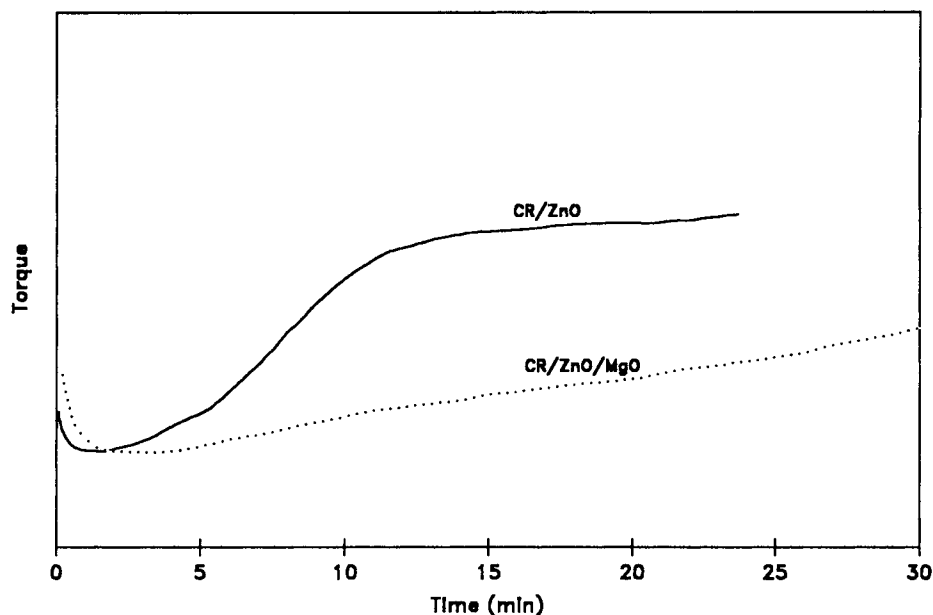
Figure 10 Rheometer curves for CR/ZnO (5 phr) and CR/ZnO/MgO (5 phr ZnO; 4 phr MgO) compounds at 150°C

ing cure. This is well known. Isothermal vulcanization in a press, too, shows the steady increase in the crosslink density as the reaction progresses (Fig. 3). Neither of these results are novel.

What is new, and most important, is that the dynamic DSC program used in this study allowed the crosslinking process to be separated into two reaction sequences, one initiating at temperatures below 160°C, and the second at temperatures above 180°C (at a scanning rate of 10°C/min). This distinction cannot be made using the isothermal studies where the two reactions, both of which lead to crosslink formation, merge.

It is evident from Figures 1–9 and 11 that there are two distinct crosslinking events. As the temperature is raised, a point is reached were the first reaction occurs very readily, the crosslink density rapidly reaching a plateau value at which it remains constant for up to 40°C (Figs. 2 and 4) before the onset of a second, slightly less rapid increase in the crosslink density. The plateau value reached between 160°C and 180°C is variable from compound to compound. For example, the plateau crosslink density is 2.65×10^{-7} mol/mL in CR and 1.65×10^{-5} mol/mL in the CR/ZnO compound. In some cases, the first crosslinking reaction is absent or virtually absent, e.g., in the CR/MgO compound (Fig. 5), while in the CR/ZnCl$_2$ compound the reactions merge and the plateau is difficult to identify (Fig. 6). In the CR/ZnO/MgO compound, the first plateau in the crosslink density is also not evident, but

a plateau in the amount of extractable Zn is observed, and it can be concluded that the crosslinking that occurred at the plateau was insufficient to render the sample insoluble.

The evolution of HCl, detected either as ZnCl$_2$ or MgCl$_2$, also ceases at the plateau, the concentration of the extractable chloride remaining constant until the next crosslinking reaction commences. Low crosslink density plateaus correspond with low extractable chloride values and high crosslink density values with high extractable chloride values. However, there is no simple relation between the crosslink density and the amount of HCl evolved for the different compounds. The number of moles of HCl evolved always exceeds the moles of crosslinks formed (Table II). This applies to both the first and the second crosslinking processes.

The fact that the crosslink density reaches a limiting (plateau) value as the temperature is increased indicates that the species responsible for crosslinking is exhausted, i.e., the species that leads to crosslinking can also be destroyed via a parallel noncrosslinking reaction. The literature suggests that the 1,2 units isomerize and then partake in crosslink formation.[10] However, although the crosslink density value at the plateau is variable, it is in all cases very much lower than would apply if crosslinking involved the reaction and consumption of all the 1,2 units. The efficient crosslinking of all 1,2 units would give a crosslink density of 1.7×10^{-4} mol/mL. Nevertheless, the 1,2 units are the most reactive sites
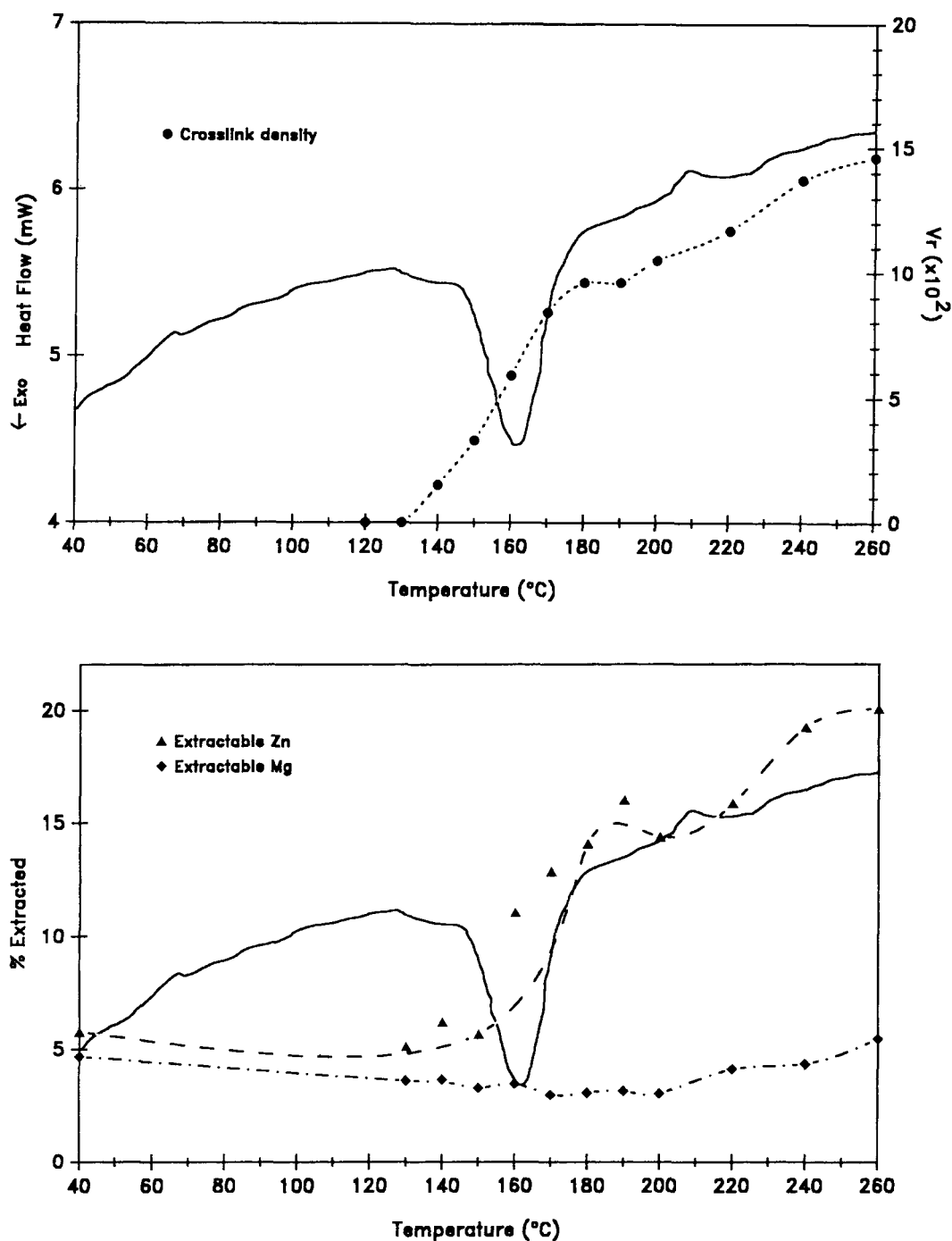
Figure 11 (a) DSC thermogram ($M_D = 14.2890$ mg) and crosslink density, for the CR/ ZnO/MgO/ZnCl₂ (5 phr ZnO; 4 phr MgO; Zn = 1 phr ZnO, ZnCl₂) compound; heating rate of 10°/min. (b) DSC thermogram, extractable Zn and Mg for the CR/ZnO/MgO/ ZnCl₂ (5 phr ZnO; 4 phr MgO; Zn = 1 phr ZnO, ZnCl₂) compound; heating rate of 10°C/ min.

along the polymer chain, and it follows that they must somehow be involved in the first crosslinking process.

Although it is generally believed that crosslinking

involves reaction of the 1,2 units only after rearrangement of the allylic chlorine to the terminal position,[10] the data presented in this article can best be explained by the involvement of the unisomerized

Table I   Amount of Extractable Zn after Mixing and the Position of the Vulcanization Exotherm for CR/ZnO (5 phr) Compounds

Mixing Time (min)	Vulc. Exotherm (°C)	Extractable Zn (% of ZnO Added)
5	163°C	3.7
10	161°C	4.1
30	154°C	6.9
60	151°C	—
90	132°C	10.8

1,2 units in the first crosslinking process. For these units, the alternative to an intermolecular cross-linking reaction is isomerization. In the presence of the crosslinking catalyst, $ZnCl_2$, the slower the isomerization process, the higher will be the plateau value reached in the first crosslinking process. At a heating rate of 10°C/min, the first crosslinking process is essentially absent in CR and in the CR/MgO compound (Figs. 1 and 5). As mentioned above, $ZnCl_2$ catalyzes the crosslinking process, as is indicated by the earlier onset of crosslinking in compounds where $ZnCl_2$ is present. Such $ZnCl_2$ may be added to the compounds as in Figures 6, 7, and 11, or may be formed during the compounding process as occurs in compounds containing ZnO. The catalytic acceleration of the unisomerized crosslinking process leads to a higher plateau crosslink density, and in all these compounds the first crosslinking reaction leads to a crosslink density value of the order of 1.40×10^{-5} mol/mL. The moles of HCl

evolved exceed the moles of crosslinks formed and the brown color that develops in the vulcanizate is indicative of some conjugation introduced along the chain by the loss of HCl.

ZnO is known to promote isomerization,[10] but as mixes with ZnO always generate some $ZnCl_2$ during compounding, this will initiate crosslinking and, in the process, evolve more HCl (i.e., the crosslinking process is autocatalytic). Isomerization is, nevertheless, rapid in the presence of ZnO, as can be seen by the rapidity with which the plateau value is reached (even at 140°C) in ZnO containing compounds, i.e., the unisomerized units that crosslink are rapidly exhausted.

On curing a CR/ZnO compound at a slower rate of 2.5°C/min (Fig. 4), it is noticed that crosslinking occurs earlier and that a higher plateau crosslinking value is achieved. This supports the contention that crosslinking of unisomerized 1,2 units occurs more readily than their isomerization, the slower heating rate allowing time for crosslinking before the temperature is raised to a point were isomerization occurs at a significant rate. At still lower heating rates, an even higher crosslink density should be obtained. Because crosslinking is catalyzed by $ZnCl_2$, a CR/$ZnCl_2$ compound was heated at a rate of 1°C/min and a crosslink density of 5.53×10^{-5} mol/mL achieved at 150°C and a value of 8.48×10^{-5} mol/mL at a temperature of 180°C. These values are well above the value of 1.44×10^{-5} mol/mL, which is the maximum crosslink density reached in the first reaction on heating at 10°C/min.

It follows that the species involved in the second crosslinking reaction, which initiates rapidly only

Table II   Crosslink Density (1/2 Mc) and Extractable Chloride Values at Plateau and Final Values

Compound	First Plateau		Final Values (260°C)		Difference in $1/2M_c$ Between First Plateau and Final Value (mol/mL × 10⁵)
	Xlink dens. mol/mL (×10⁵)	Ext. Cl mol/mL (×10⁴)	Xlink dens. mol/mL (×10⁵)	Ext Cl mol/mL	
CR	0.03	—	2.43	—	2.40
CR/ZnO	1.45	1.52	4.06	3.47	2.61
CR/ZnO[a]	3.26	1.73	6.22[b]	2.58[b]	2.96
CR/ZnO/ZnCl₂	1.39	—	4.29	—	2.90
CR/ZnCl₂	—	—	3.27	—	3.27
CR/MgO	0.00	0.00	3.25	1.10	3.25
CR/ZnO/MgO	0.00	0.04	2.93	1.29	2.93
CR/ZnO/MgO/ZnCl₂	1.34	1.10	3.31	1.84	1.97
CR/MgO/ZnCl₂	0.14	0.32	2.57[b]	0.38	2.43

[a] Heated at 2.5°C/min.
[b] At 220°C.

at higher temperatures (at a heating rate of 10°C/min), involves a less reactive species. The isomerized 1,2 units are less reactive (as indicated by the fact that isomerization occurs spontaneously as the temperature is raised). The second crosslinking reaction occurs rapidly in the region above 180°C, the onset temperature being slightly influenced by $ZnCl_2$, which also appears to catalyze this reaction, but not with the same efficiency as it does the first crosslinking reaction. This can be seen when Figures 1 and 2 are compared.

Although the extent of the crosslinking in the first reaction varies greatly, the fraction of 1,2 units involved in the reaction is small (< 8%), which means that more than 90% of the units were able to isomerize. The concentration of the isomerized 1,2 units responsible for the second reaction is, therefore, essentially the same in all compounds, and it is significant that in all cases the increase in the crosslink density between the plateau value and 260°C (the highest temperature used in this study) is close to 3.0×10^{-5} mol/mL (Table II). This also applies to CR without any ZnO (Fig. 1) and shows that the rate of the second reaction is constant and independent of the composition of the compound. The crosslinking takes place when the carbenium ion formed on the 1,2 units alkylates the olefinic center of the predominant 1,4 units. Miyata and Atsumi[9] have pointed out that for the isomerized polymer in the absence of any curatives, the (evolved HCl)/(crosslink) ratio is 1.4, suggesting some cyclization as opposed to crosslinking by 1,2 units. The amount of extractable chlorine produced during the second crosslinking process varies greatly in the different compounds but always exceeds the mol of crosslinks and may be taken as support for the cyclization process. Miyata and Astumi[9] showed a linear relationship between the loss of isomerized 1,2 units and HCl evolution, the reaction taking 20 h for completion at 150°C. When using a dynamic program the fraction of 1,2 units that have reacted at 260°C is still small, though at these very high temperatures degradation of the polymer becomes important, and a decrease in the overall crosslink density may be experienced, despite the ongoing crosslinking process.

This study suggests that the marching curve obtained in rheometer cured samples (Fig. 10) is due to the crosslinking of the isomerized 1,2 units. At 150°C, the temperature at which samples are normally cured in the rheometer, the rate will be much slower than the reaction observed in the DSC at 190°C and above. Furthermore, the fact that crosslinking of the isomerized units is a slow process, as

indicated by the completion of the reaction at 150°C requiring 60 min[10] in the presence of ZnO, shows that it cannot possibly account for the rapid rise in the rheometer torque at short cure times (Fig. 10). The crosslinking that occurs in the early part of the cure curve, and that which is of practical importance, is due to the reaction of the unisomerized units. This suggestion is a radical departure from the generally accepted theory that the marching cure may be due to reaction of the more stable 1,4 units.

The results of Miyata and Atsumi[10] are not inconsistent with the above. They showed that in benzene solution CR could be isomerized in 30 min at 150°C and in 10 min at 110°C in the presence of ZnO, which promotes isomerization. They suggested complete isomerization without crosslinking. As their compounds had very low molecular masses, the polymer remained soluble even on completion of the reaction. A simple calculation will show that the small degree of crosslinking in the first reaction would have gone unnoticed, particularly as their solution contained ZnO that will accelerate isomerization, but did not contain $ZnCl_2$ to catalyze crosslinking (ZnO was added from solution, preventing $ZnCl_2$ formation). Miyata and Atsumi[10] emphasized that HCl loss from unisomerized units did not occur, as no NMR peaks corresponding to the terminal vinyl groups other than those of the 3,4 units originally in the polymer could be found after crosslinking, nor did conjugation occur. However, even in the compounds studied in this article less than 8% of the 1,2 units crosslinked by 180°C. In their samples, where no $ZnCl_2$ catalyst was present, the extent of this reaction would be negligible. Instead, it is possible that they observed the slow reaction of the isomerized units only.

CONCLUSIONS

The data presented in this article can best be explained in terms of two crosslinking processes that occur in CR and CR compounds containing ZnO. Crosslinking is associated with the simultaneous evolution of HCl. The first, fairly rapid process, involves reaction of the highly reactive tertiary allylic chlorine in the 1,2 units of the polymer chain. Isomerization of these units occurs concurrently with crosslinking, and crosslinking ceases once all the units have been isomerized. The second stage of the reaction is attributed to crosslinking initiated by the isomerized 1,2 units, but the reaction is much slower and is not of practical importance in vulcanization. Reactions during the marching part of the rheometer

cure curve are attributed to this process. $ZnCl_2$ produced during mixing catalyzes the crosslinking reaction which, in turn, produces more $ZnCl_2$. MgO retards the reaction by trapping HCl and delaying the buildup of $ZnCl_2$ during the mixing process. The result is that crosslinking of the unisomerized 1,2 units is prevented and only crosslinking of isomerized 1,2 units occurs.

REFERENCES

1. J. A. Brydson, *Rubber Chemistry,* Applied Science Publishers, Ltd, London, 1979.
2. R. Petiaud and Q. Tho Pham, *J. Polym. Sci.: Polym. Chem. Ed.,* **23,** 1333 (1985).
3. B. Iván, J. P. Kennedy, and S. S. Plathottam, *J. Polym. Sci.: Polym. Chem. Ed.,* **18,** 1685 (1980).
4. R. C. Ferguson, *Anal. Chem.,* **36,** 2204 (1964a).
5. M. Behal, *J. Polym. Sci.,* **35,** 507 (1988).
6. C. A. Hargneaves and D. C. Thompson, in *Encyclopedia of Polymer Science and Technology,* Vol. 3, H. F. Mark, Ed., Interscience Publishers, John Wiley and Sons, Inc., New York, 1965, p. 705.
7. I. Kuntz, R. L. Zapp, and R. J. Pancirov, *Rubber Chem. Technol.,* **57,** 813 (1984).
8. R. Vukov, *Rubber Chem. Technol.,* **57,** 284 (1984).
9. Y. Miyata and M. Atsumi, *J. Polym. Sci.: Part A: Polym. Chem.,* **26,** 2561 (1988).
10. Y. Miyata and M. Atsumi, *Rubber Chem. Technol.,* **62,** 1 (1971).
11. D. B. Forman, in *Rubber Technology,* M. Morton, Ed., Van Nostrand Rienhold Company, New York, 1973.
12. A. C. Stevenson, in *Vulcanization of Elastomers,* G. Alliger and I. J. Sjothun, Eds., Robert E. Krieger Company, New York, 1978.
13. P. J. Flory, *J. Chem. Phys.,* **18,** 108 (1950).
14. J. E. G. Lipson and J. E. Guillet, *J. Polym. Sci., Polym. Phys. Ed.,* **19,** 1199 (1981).
15. D. L. Gardner and I. C. McNeill, *Eur. Polym. J.,* **7,** 603 (1971).