

Effect of Atmosphere on the Thermal Decomposition of Chlorinated Natural Rubber from Latex

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ABSTRACT: The kinetics of the thermal decompositions of chlorinated natural rubber (CNR) from latex under both air and nitrogen atmospheres were studied with thermogravimetric analysis (TGA). The thermooxidative decomposition of CNR had two weight-loss step changes in the TGA curves, which occurred at the two distinct temperature ranges of about 160–390 and 390–850°C, respectively. The gaseous products of the first step change were mainly HCl with a little CO₂, and the apparent reaction order (n) was 1.1. The reaction activation energy (E) increased linearly with the increment of heating rate (B), and the apparent activation energy (E_0), calculated by extrapolation back to zero B , was 101.7 kJ/mol. B s ranging from 5 to 30°C/min were used. The initial temperature of weight loss (T_0) was $1.31B + 252^\circ\text{C}$, where B is in degrees Celsius per minute. The final temperature of weight loss (T_f) was $0.93B + 310^\circ\text{C}$, and the temperature of maximum weight-loss rate (T_p) was $1.03B + 287^\circ\text{C}$. The decomposition weight-loss percentage at T_p (C_p) and that at T_f (C_f) were not affected by B , and the average values were 38 and 60%, respectively. The second weight-loss step change was an oxidative decomposition of the molecular main chain. The value of n was 1.1. E increased linearly with the increment of B , and E_0 was 125.0 kJ/mol. C_f after the second step approached 100%, which indicated complete decomposition. The thermal decomposition of CNR in a N₂ atmosphere had only one weight-loss step change with an n of 1.1. E increased linearly with the increment of B , and E_0 was 98.6 kJ/mol. T_0 was $1.25B + 251^\circ\text{C}$, T_f was $0.91B + 315^\circ\text{C}$, and T_p was $1.09B + 286^\circ\text{C}$. C_p and C_f were not affected by B , and the average values were 37 and 68%, respectively. The weight percentage of more stable, nonthermal decomposed residue was about 30%. The thermal decompositions of CNR in both atmospheres were similar, mainly by dehydrochlorination, at the low temperature range (160–390°C) but were different at the high temperature range (390–850°C). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2590–2598, 2001

Key words: chlorinated natural rubber; natural rubber latex; thermal decomposition; thermooxidative decomposition; thermogravimetric analysis; elastomers; thermal properties

INTRODUCTION

Chlorinated natural rubber (CNR), which is traditionally prepared by the chlorination of natural

rubber in CCl₄ solution, has excellent film formation, penetrance, and inflammation resistance; corrosion resistance properties; and thermal stability.¹ It has been broadly applied as a raw material for paints, inks, adhesives, and acid-proof and alkali-proof products. The traditional CCl₄-solution process has been prohibited in many countries because it has many disadvantages, including high equipment investment costs and hazards to the environment and health of the

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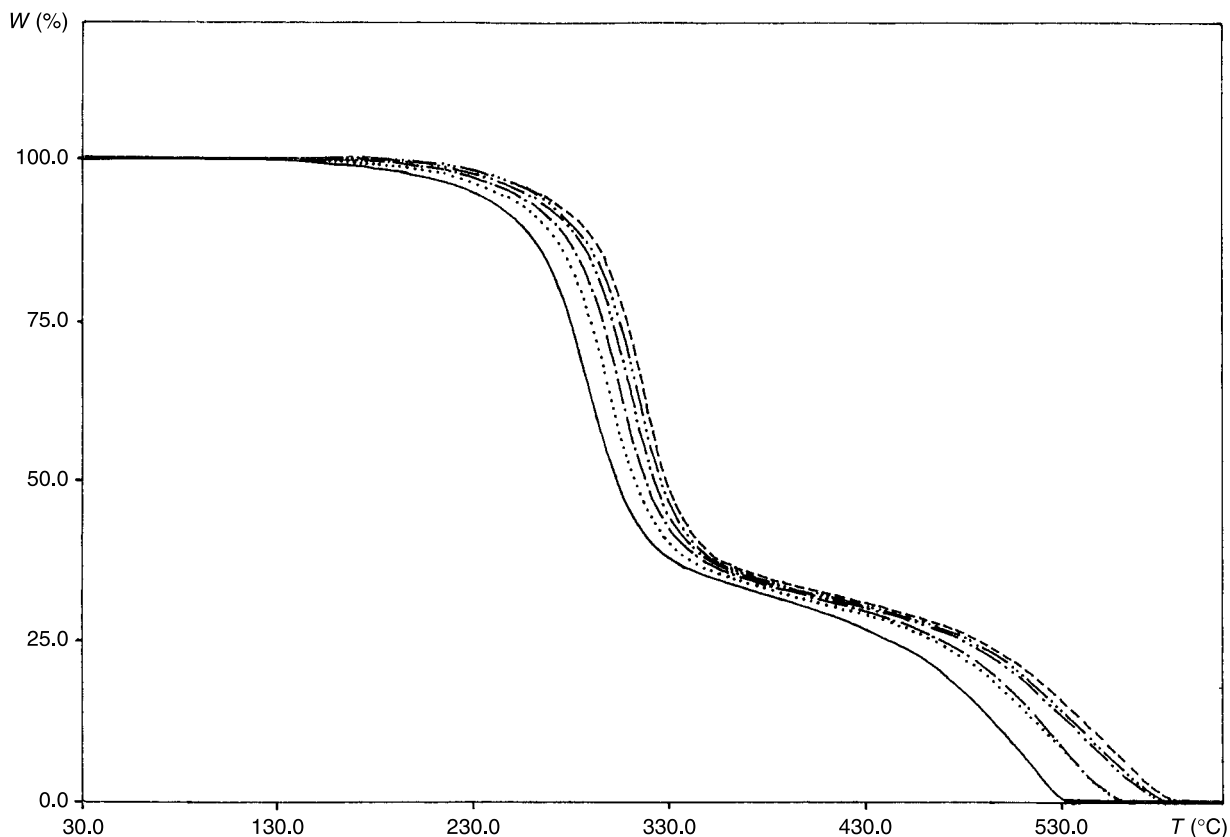


Figure 1 TGA curves of the thermooxidative decomposition of CNR. Weight (W) is expressed on the vertical axis as a percentage of the initial weight. Temperature (T) is expressed on the horizontal axis in degrees Celsius. (—) $B = 5^\circ\text{C}/\text{min}$, (\cdots) $B = 10^\circ\text{C}/\text{min}$, ($\cdot\text{---}\cdot$) $B = 15^\circ\text{C}/\text{min}$, ($-\cdots-$) $B = 20^\circ\text{C}/\text{min}$, ($-\cdot\cdot\cdot-$) $B = 25^\circ\text{C}/\text{min}$, and ($-\text{---}-$) $B = 30^\circ\text{C}/\text{min}$.

workers. This makes the production of CNR from latex an attractive alternative process. Zhong and others²⁻⁶ studied the preparation of CNR in aqueous media. There have also been studies of the molecular structure of CNR by IR spectroscopy and NMR.⁷⁻¹² The chlorination mechanism of CNR has been studied in detail.¹³⁻¹⁶ However, until now, there have been few reports on the thermal and thermooxidative decompositions of CNR from latex. In this article, we report on a study of the thermal and thermooxidative decomposition processes of CNR from latex with thermogravimetric analysis (TGA). The apparent reaction order (n), the activation energy (E), and the frequency factor (A) were calculated. The relations between heating rate (B) and the various decomposition temperatures [initial (T_0), maximum (T_p), and final (T_f)] and between the decomposition weight-loss percentages at T_p and T_f (C_p and C_f , respectively), and the effect of atmospheres on thermal decomposition are discussed.

EXPERIMENTAL

Materials

Distilled water was added to a three-necked, round-bottomed flask. The temperature was kept constant with a water bath. Chlorine gas was passed into the water until saturation was reached. The natural rubber (NR) latex, which was stabilized with Vulcanstab LW, was added while the mixture was stirred. At the same time, the chlorine gas was passed into the flask continuously. CNR with a preliminary chlorination was produced. The chlorine gas continued to pass into the flask for the predetermined reaction time, and then, the reaction was stopped. The product was neutralized with dilute sodium hydroxide solution. The product was filtered, washed with distilled water, and then dried in a vacuum at $50 \pm 1^\circ\text{C}$ to get a CNR powder sample with a chlorine content of 65% (by the method of Volhard¹⁷).

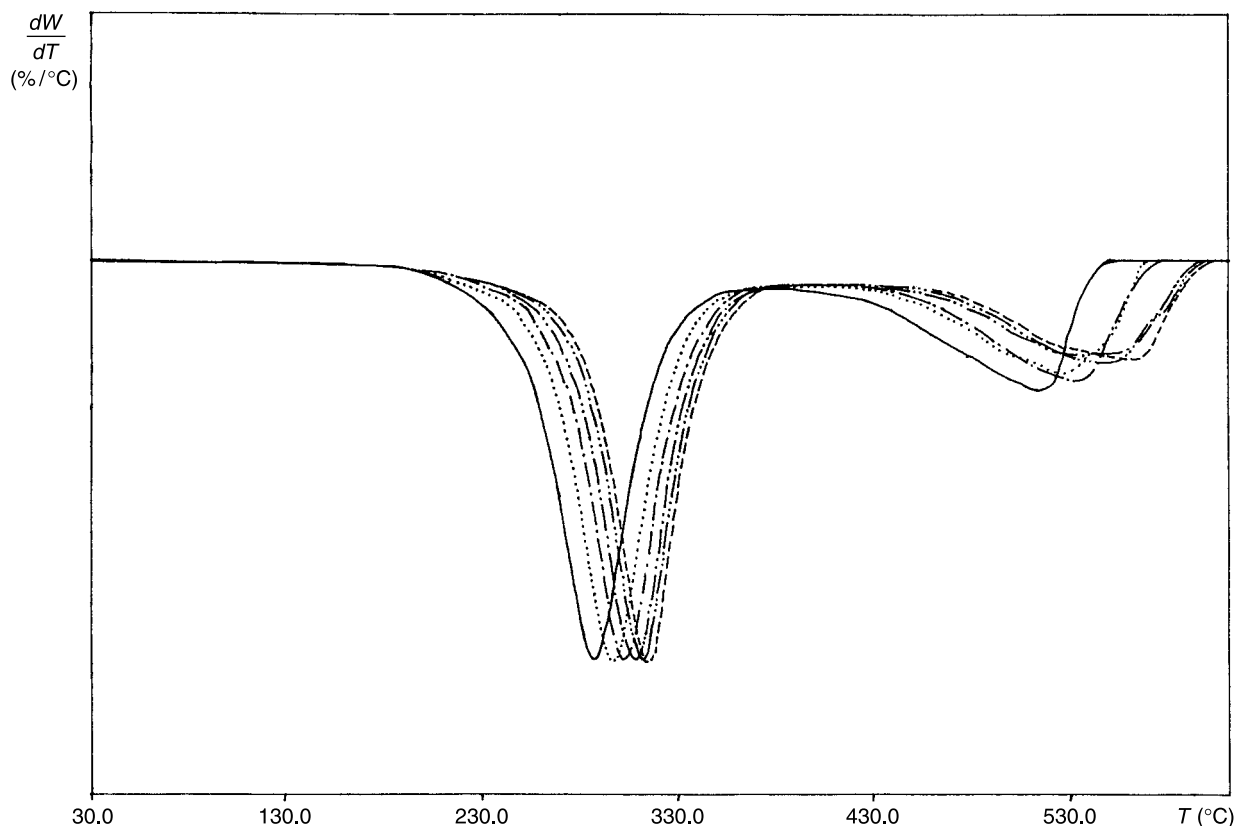


Figure 2 DTG curves of the thermooxidative decomposition of CNR. The rate of change in weight (dW/dt), or weight-loss rate, is shown on the vertical axis. Temperature (T) is expressed on the horizontal axis in degrees Celsius. (—) $B = 5^\circ\text{C}/\text{min}$, (\cdots) $B = 10^\circ\text{C}/\text{min}$, ($\cdot - \cdot$) $B = 15^\circ\text{C}/\text{min}$, ($- \cdots$) $B = 20^\circ\text{C}/\text{min}$, ($- \cdots$) $B = 25^\circ\text{C}/\text{min}$, and ($- - -$) $B = 30^\circ\text{C}/\text{min}$.

TGA

TGA was carried out with a PerkinElmer thermal gravimetric analyzer. The mass of the sample was about 8.00 mg. The carrier gas was either air or nitrogen with a flow rate of 50 mL/min. The temperature rose from 30 to 850°C at B s of 5, 10, 15, 20, 25, and 30°C/min, respectively.

Data Processing

Reaction kinetic factors were obtained by the processing of TGA data through the Coats–Redfern¹⁸ method. With the integration of the reaction kinetic equation

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

and use of the Arrhenius equation

$$k = Ae^{-E/RT} \quad (2)$$

the following equations were obtained:

$$\begin{aligned} \ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\} \\ = \ln[(1 - 2RT/E)AR/BE] - E/RT \quad (n \neq 1) \quad (3) \end{aligned}$$

and

$$\begin{aligned} \ln[-\ln(1 - \alpha)/T^2] = \ln[(1 - 2RT/E)AR/BE] \\ - E/RT \quad (n = 1) \quad (4) \end{aligned}$$

where α is the reaction degree, T is the absolute temperature, and R is the gas constant. Where $n \neq 1$, a line can be obtained from the plot of $\ln\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\}$ versus $1/T$, where the slope is $-E/R$ and the intercept is $\ln[(1 - 2RT/E)AR/BE]$. Where $n = 1$, a line can be obtained from the plot of $\ln[-\ln(1 - \alpha)/T^2]$ versus $1/T$, where the slope is $-E/R$, and the intercept is $\ln[(1 - 2RT/E)AR/BE]$. When the least squares fitting

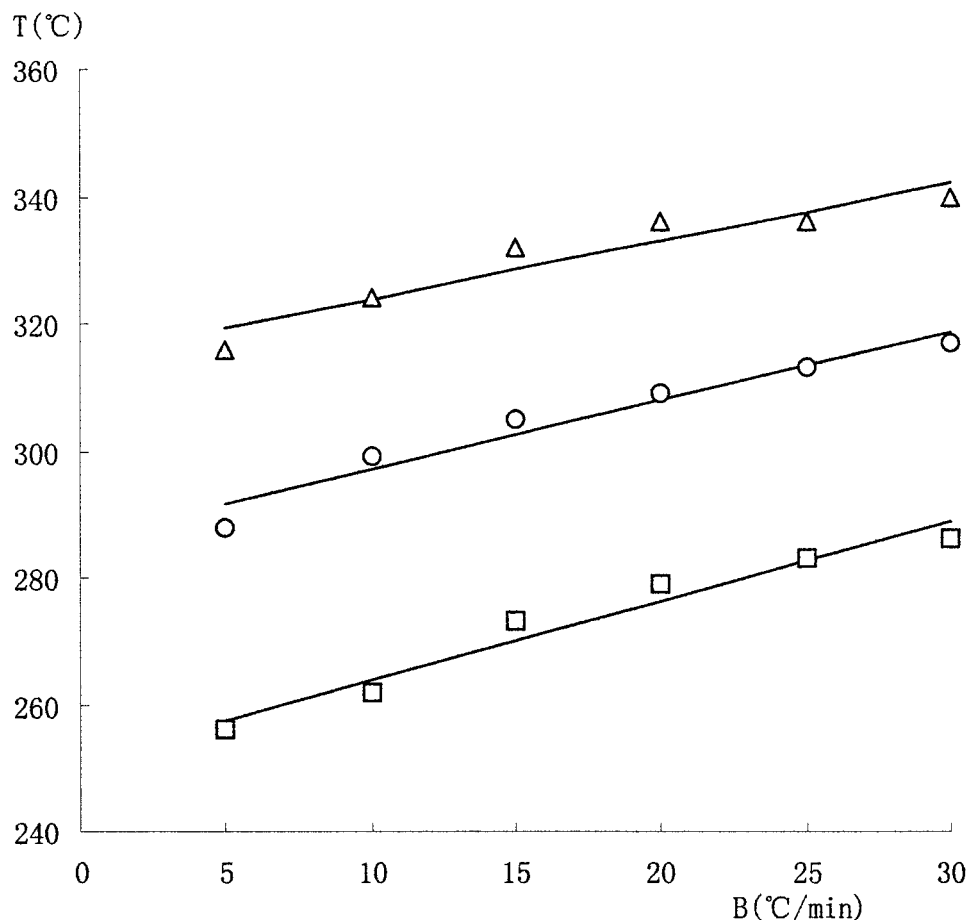


Figure 3 Relation between B and the decomposition temperature in the first step of the thermooxidative decomposition of CNR. (\square) T_0 , (\circ) T_p , and (\triangle) T_f .

method is adopted with different ns , the n with the maximum correlation coefficient (r) is the apparent reaction order.

RESULTS AND DISCUSSION

Effect of B on the Process of Thermooxidative Decomposition

The thermooxidative decomposition of CNR was carried out in air. Figures 1 and 2 show the TGA and the derivative thermogravimetry (DTG) curves of thermooxidative decompositions of CNR at six different B s. There are two obvious step changes on the TGA curves and two corresponding peaks on the DTG curves, indicating that the thermooxidative decomposition of CNR might be carried out in two steps. The first weight-loss step at 160–390°C was mainly caused by the dehydrochlorination of CNR, along with the possible crosslinking of the molecular chains of CNR so

that the gaseous products were mainly HCl and a little CO_2 .¹⁹ The second weight-loss step at 390–600°C was caused by the oxidative decomposition of CNR, of which the gaseous product was mainly CO_2 .¹⁹ The TGA and DTG curves shift toward the high temperature with the increment of B . The features seen in the TGA and DTG curves at six different B s are similar.

Table I Relation Between B and C_p and C_f in the First Step of the Thermooxidative Decomposition of CNR

| | B (°C/min) | | | | | | M |
|-------|--------------|----|----|----|----|----|-----|
| | 5 | 10 | 15 | 20 | 25 | 30 | |
| C_p | 39 | 39 | 37 | 38 | 38 | 39 | 38 |
| C_f | 61 | 60 | 60 | 60 | 60 | 60 | 60 |

Table II Relation Between B and C_f in the Second Step of the Thermooxidative Decomposition of CNR

| | B ($^{\circ}\text{C}/\text{min}$) | | | | | | M |
|-------|---------------------------------------|-----|-----|-----|-----|-----|-----|
| | 5 | 10 | 15 | 20 | 25 | 30 | |
| C_f | 99 | 100 | 100 | 100 | 100 | 100 | 100 |

Relation Between B and the Thermooxidative Decomposition Temperature

Figure 3 shows the relations between B and the decomposition temperature in the first step of the thermooxidative decomposition of CNR. T_0 and T_f were obtained from the TGA curves by a bitangent method, and the T_p is the temperature at maximum weight-loss rate. The peak width of the DTG curve can be expressed as $T_f - T_0$. Figure 3 shows that the decomposition temperatures increased with the increment of B . The relations between B in degrees Celsius per minute and temperature were as follows:

$$T_0 = 1.31B + 252 \quad T_p = 1.03B + 287$$

$$T_f = 0.93B + 310$$

The thermooxidative decomposition temperatures increased linearly with the increment of B because of heat hysteresis, and so the decomposition temperatures should be expressed more exactly as equilibrium temperatures (T^0 s; which are the decomposition temperatures when B approaches zero). The thermooxidative decomposition T^0 s of CNR were as follows:

$$T_0^0 = 252 \quad T_p^0 = 287 \quad T_f^0 = 310$$

The peak width $T_f - T_0$ was $-0.38B + 58^{\circ}\text{C}$, and it decreased with the increment of B .

Effect of B on Thermooxidative Decomposition Loss

Table I shows the relations between B and C_p and C_f in the first weight-loss step. The C_p and C_f are the percentage of thermooxidative decomposition losses at T_p and T_f , respectively:

$$C_p = 100\% - \text{wt } \% \text{ of residues}$$

$$C_f = 100\% - \text{wt } \% \text{ of residues}$$

The results indicate that the C_p and C_f were not affected by B ; their mean values were 38 and 60%, respectively.

Table II shows the relationship between B and C_f in the second-step reaction. C_f was not affected by B and approached 100%, indicating that the second thermooxidative decomposition of CNR proceeded to completion.

Kinetics of Thermooxidative Decomposition

Table III shows the kinetic parameters in the first weight-loss step. The mean of all n values of the first step at different B s was 1.1. The value of E increased linearly with the increment of B . As calculated by the linear regression least squares method, the apparent activation energy (E_0) at a B of $0^{\circ}\text{C}/\text{min}$ was 101.7 kJ/mol. The values of r were over 0.995.

Table IV shows the kinetic parameters in the second-step reaction. The mean value of n was 1.1. E_0 was 125.0 kJ/mol. The values of r were over 0.995.

Effect of B on the Process of Thermal Decomposition in a N_2 Atmosphere

The thermal decomposition of CNR was carried out in nitrogen. Figures 4 and 5 depict the TGA

Table III Kinetic Parameters of the First Step of the Thermooxidative Decomposition of CNR

| | B ($^{\circ}\text{C}/\text{min}$) | | | | | |
|---------------------|---------------------------------------|-------|-------|-------|-------|-------|
| | 5 | 10 | 15 | 20 | 25 | 30 |
| n | 1.1 | 1.1 | 1.0 | 1.1 | 1.1 | 1.2 |
| E (kJ/mol) | 105.3 | 109.9 | 115.0 | 120.0 | 124.1 | 125.8 |
| $A \times 10^{-10}$ | 0.10 | 0.38 | 1.39 | 3.89 | 10.72 | 16.21 |
| r | 0.997 | 0.996 | 0.995 | 0.995 | 0.995 | 0.995 |

Table IV Kinetic Parameters of the Second Step of the Thermooxidative Decomposition of CNR

| | B ($^{\circ}\text{C}/\text{min}$) | | | | | |
|---------------------|---------------------------------------|-------|-------|-------|-------|-------|
| | 5 | 10 | 15 | 20 | 25 | 30 |
| n | 1.1 | 1.1 | 1.0 | 1.1 | 1.1 | 1.2 |
| E (kJ/mol) | 144.6 | 163.9 | 172.2 | 180.1 | 203.6 | 205.7 |
| $A \times 10^{-11}$ | 0.01 | 0.22 | 1.23 | 3.06 | 135.7 | 183.1 |
| r | 0.995 | 0.997 | 0.997 | 0.996 | 0.995 | 0.995 |

and DTG curves of the thermal decompositions of CNR at six different B s. Only one step change appears on the TGA curves, and one corresponding peak appears on the DTG curves, indicating that thermal decomposition of CNR in N_2 was dominated by a single reaction process, which was ascribed to the dehydrochlorination of CNR.¹⁹ The TGA and DTG curves shift toward a higher temperature with the increment of B . The

shape of TGA and DTG curves at the six different B s are similar.

Relation Between B and Thermal Decomposition Temperature

Figure 6 shows the relations between B and the various decomposition temperatures (T_0 , T_p , and T_f). Figure 6 shows that the thermal decomposi-

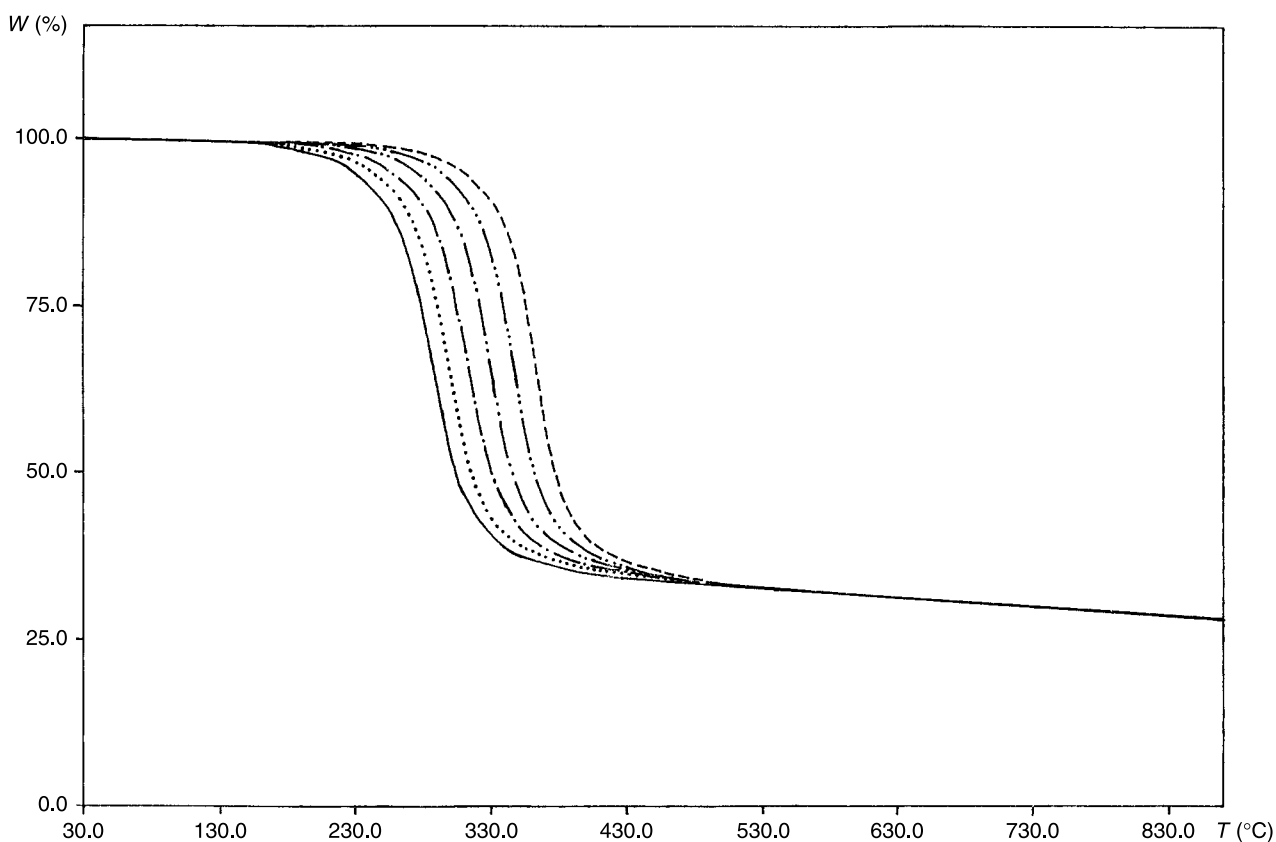


Figure 4 TGA curves of the thermal decomposition of CNR. Weight (W) is expressed on the vertical axis as a percentage of the initial weight. Temperature (T) is expressed on the horizontal axis in degrees Celsius. (—) $B = 5^{\circ}\text{C}/\text{min}$, (\cdots) $B = 10^{\circ}\text{C}/\text{min}$, ($- \cdot - \cdot$) $B = 15^{\circ}\text{C}/\text{min}$, ($- \cdot \cdot -$) $B = 20^{\circ}\text{C}/\text{min}$, ($- \cdot \cdot \cdot$) $B = 25^{\circ}\text{C}/\text{min}$, and ($- - -$) $B = 30^{\circ}\text{C}/\text{min}$.

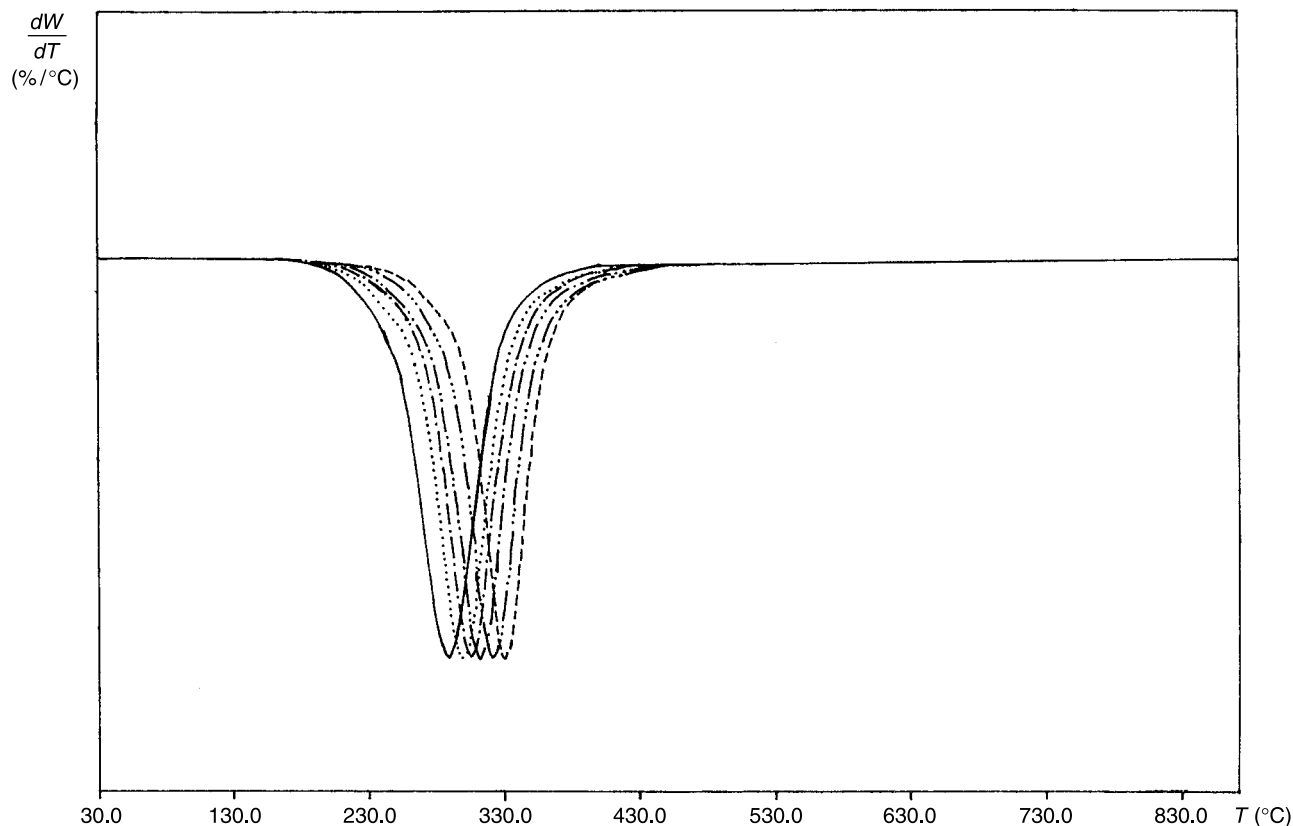


Figure 5 DTG curves of the thermal decomposition of CNR. The rate of change in weight (dW/dt), or weight-loss rate, is shown on the vertical axis. Temperature (T) is expressed on the horizontal axis. (—) $B = 5^\circ\text{C}/\text{min}$, (\cdots) $B = 10^\circ\text{C}/\text{min}$, ($-\cdot-\cdot$) $B = 15^\circ\text{C}/\text{min}$, ($-\cdot\cdot-$) $B = 20^\circ\text{C}/\text{min}$, ($-\cdot\cdot\cdot$) $B = 25^\circ\text{C}/\text{min}$, and ($-\cdot-\cdot-$) $B = 30^\circ\text{C}/\text{min}$.

tion temperatures increased with the increment of B , indicating that the B had a significant effect on T_0 , T_p , and T_f . The relations were as follows:

$$T_0 = 1.25B + 251 \quad T_p = 1.09B + 286 \\ T_f = 0.91B + 315$$

The thermal decomposition T_0 's of CNR were as follows:

$$T_0^0 = 251 \quad T_p^0 = 286 \quad T_f^0 = 315$$

The peak width is expressed as $T_f - T_0 = -0.34B + 64^\circ\text{C}$, and it decreased with the increment of B .

Effect of B on Thermal Decomposition Loss in a N_2 Atmosphere

Table V shows the relationship between B and the thermal decomposition losses C_p and C_f . The results indicate that the values of C_p and C_f were not affected by B ; their mean values were 37 and

68%, respectively. The undecomposed residue was about 30% and was stable in the temperature range of the experiment.

Kinetics of the Thermal Decomposition of CNR in a N_2 Atmosphere

Table VI shows the kinetic parameters of the thermal decomposition of CNR. The value of n for the dehydrochlorination of CNR in a N_2 atmosphere was 1.1. E_0 was 98.6 kJ/mol. The values of r were over 0.993.

Effect of Atmosphere on the Thermal Decomposition Processes of CNR

The thermooxidative decomposition of CNR in air was carried out in two steps. After the dehydrochlorination reaction, the molecular main chain of CNR began to be oxidized into carbon dioxide. The thermal decomposition of CNR in nitrogen was mainly caused by dehydrochlorination. At

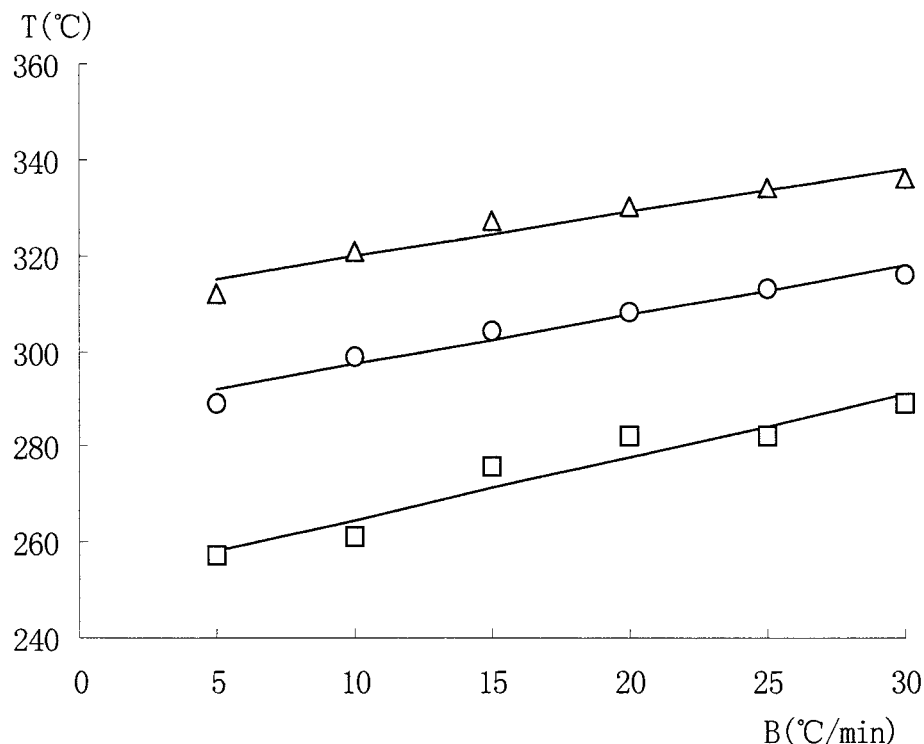


Figure 6 Relation between B and the thermal decomposition temperature of CNR. (\square) T_0 , (\circ) T_p , and (\triangle) T_f .

the temperature range of 160–390°C (see Figs. 1, 2, 4, and 5), the dehydrochlorination of CNR occurred in both atmospheres. All the decomposition temperatures increased along with B . The values of T_0^0 , T_p^0 , and T_f^0 in both atmospheres were very close. The value of n of decomposition in both atmospheres was 1.1. The E_0 's were 101.7 and 98.6 kJ/mol, respectively, which is close to the effective E of the dehydrochlorination reaction of poly(vinylchloride) (94–126 kJ/mol).²⁰ As indicated by the results, the reaction was mainly dehydrochlorination, which occurred in both atmospheres in the low temperature range. The n of 1.1 was very close to the theoretical first-order value, which indicates that the decomposition of

CNR was mainly a first-order reaction. However, there were other possible reactions, such as crosslinking, that were not accounted for, and so we report the experimentally determined n of 1.1 as it was. At the high temperature range (390–850°C), because of the existence of O_2 in air, the oxidative decomposition of main chain of CNR occurred after the elimination of HCl from CNR to produce carbon dioxide with a decomposition loss of almost 100%. When the decomposition of CNR was carried out in nitrogen, about 30 wt %, consisting of the more stable undecomposed residue, still remained at up to 850°C.

CONCLUSIONS

The thermooxidative decomposition of CNR in air shows two weight-loss step changes in the TGA curve. At the first step, the equilibrium decomposition temperatures T_0^0 , T_p^0 , and T_f^0 were 252, 287, and 310°C, respectively. The mean C_p and C_f for the first step were 38 and 60%, respectively. The mean C_f after the second step was 100%, indicating that thermooxidative decomposition of CNR proceeded to completion. The n s of the two steps

Table V Relation Between B and C_p and C_f in the Thermal Decomposition of CNR in a N_2 Atmosphere

| | B (°C/min) | | | | | | M |
|-------|--------------|----|----|----|----|----|-----|
| | 5 | 10 | 15 | 20 | 25 | 30 | |
| C_p | 37 | 37 | 37 | 36 | 38 | 38 | 37 |
| C_f | 68 | 68 | 68 | 68 | 68 | 68 | 68 |

Table VI Kinetic Parameters of the Thermal Decomposition of CNR in a N₂ Atmosphere

| | <i>B</i> (°C/min) | | | | | |
|------------------------------|-------------------|-------|-------|-------|-------|-------|
| | 5 | 10 | 15 | 20 | 25 | 30 |
| <i>n</i> | 1.1 | 1.1 | 1.0 | 1.2 | 1.1 | 1.2 |
| <i>E</i> (kJ/mol) | 100.7 | 108.3 | 111.2 | 115.0 | 119.1 | 121.6 |
| <i>A</i> × 10 ⁻¹⁰ | 0.36 | 2.59 | 5.14 | 12.49 | 33.61 | 59.29 |
| <i>r</i> | 0.997 | 0.995 | 0.996 | 0.995 | 0.995 | 0.993 |

were both 1.1. The E_0 's of the two steps were 101.7 and 125.0 kJ/mol, respectively.

The thermal decomposition of CNR in nitrogen shows only one weight-loss step change in the TGA curve with an n of 1.1. T_0^0 , T_p^0 , and T_f^0 were 251, 286, and 315°C, respectively. C_p and C_f were 37 and 68%, respectively. E_0 was 98.6 kJ/mol. The thermal decompositions of CNR in both atmospheres were similar, with decomposition mainly occurring by dehydrochlorination, at the low temperature range (160–390°C) but were different at the high temperature range (390–850°C).

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