Study on the Thermal Degradation of Epoxidized Natural Rubber

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ABSTRACT: The thermal degradation and thermooxidative degradation of epoxidized natural rubber (ENR) were studied by thermogravimetry (TG). In the thermal degradation of ENR, the initial temperature of weight loss $T_0 = 1.20B + 348$, the temperature of maximum weight loss rate $T_p = 1.07B + 392$, and the final temperature of weight loss $T_f = 0.77B + 445$. The C_p, which corresponds to the degradation rate at temperature T_p, increases along with the heating rate B and its mean value is 43%, but C_f, which corresponds to the degradation rate at temperature T_f, is not affected by the heating rate, and its average value is close to 100%. As in the thermooxidative degradation, $T_0 = 1.84B + 246$, $T_p = 0.30B + 378$, and $T_f = 2.27B + 584$. The value of C_p increases along with the heating rate B and its mean value is 36%, but C_f is not affected by the heating rate and the average value approximately equals 100%. The thermal degradation in nitrogen could be a one-step reaction, whereas the thermooxidative degradation has a multiple-step reaction. The reactive environment has a great effect on the thermal degradation of ENR and the difference of the mechanisms of the two reaction systems is obvious. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 67: 2207–2211, 1998

Key words: epoxidized natural rubber; natural rubber; thermal degradation; thermooxidative degradation; reactive environment

INTRODUCTION

ENR is now an established commercial polymer, which is produced by chemical modification of natural rubber (NR) and has some special properties compared with NR. With the epoxidizing group on the polyisoprene backbone, epoxidized natural rubber (ENR) has excellent oil resistance and air-tightness properties. The study of ENR preparation had begun as early as the 1920s,[1] but only in the recent decade has the industrial production and intensive application come into being. The present study focused on the ENR structure and properties. Many reports on the mechanical properties,[2,3] blending,[4,5] as well as anti-scorching properties[6] have already been presented. The improvement of the aging behavior of ENR vulcanizates through selecting the levels of sodium carbonate and sulfur was studied by Amu et al.[7] The research of Gelling and Morrison[8] indicated that the ring-opening reaction of the epoxidizing group which was caused by the catalyzing effect of the

acid leads to poor aging behavior of the sulfur-cured ENR vulcanizates. Hashim and Kohjiya[9] discovered that semi-EV and EV systems are suitable for ENR and the properties of sulfur-cured ENR vulcanizates are similar to those of NR. But only a few reports concerning the degradation of raw ENR were found. In this article, the thermal degradation and thermooxidative degradation of ENR were studied using dynamic thermogravimetry (TG). The effects of the heating rate on the degradation temperature and degradation rate and the effect of the reaction environment changes in the degradation process were considered.

EXPERIMENTAL

Materials

Add the stabilizer and then the solution of formaldehyde into a diluted concentrated NR latex by stirring. Ten minutes later, put an amount of hydrogen peroxide and formic acid into the latex slowly. Stir and heat the reactive mixtures continuously until the temperature reaches 50°C. Keep the reaction temperature for 24 h, so as to prepare the required epoxidized natural rubber latex (ENRL).[10] The ENRL prepared was purified for 24 h through a dialysis process in deionized water. The deionized water used should be changed every 2 h. The pH value of the dialysis water was about 7.0 when dialysis ended. Coat the ENRL onto a clean glass plate and dry in a vacuum chamber at room temperature until the latex film becomes transparent. The ENRL test sample was prepared after the water was removed. The degree of ENRL epoxidation that was determined by infrared (IR) spectroscopy[11] is about 50 mol %.

Thermogravimetry

The thermogravimetry analysis was carried out with a Perkin–Elmer TG S-2 thermogravimetry analyzer. The mass of each sample is 4–7 mg and the reaction environment is air or nitrogen (45 mL min), and the heating rate ranges from 5 to 30°C min. The thermogravimetric analysis (TG) and derivative thermogravimetry (DTG) curves were recorded in the course of heating from room temperature to 700°C.

RESULTS AND DISCUSSION

Thermal Degradation of ENR

The study of the thermal degradation of ENR was carried out in nitrogen. Figure 1 shows the TG and DTG curves of the thermal degradation of ENR at six different heating rates B. The TG curve is a smooth weight loss curve. The DTG curve shows only one weight loss peak. This indicates that the degradation could be a one-step reaction. With the increment of the heating rate, the TG and DTG curves move toward the high-temperature zone. The degradations at six different heating rates are similar to each other.

Figure 2 shows the effect of the heating rate B on the degradation temperature T. T_0 is the initial temperature of weight loss; T_f, the final temperature at weight loss; and T_p, the temperature at the maximum weight loss rate or the top of the DTG curve peak, which are obtained from the TG curve by a bitangent method. The peak width of the DTG curve can be expressed as $T_f - T_0$.

It can be seen from Figure 2 that the degradation temperature increases with the heating rate, indicating that the heating rate is the main factor that affects the degradation temperature. The relations of these factors are as follows:

$$T_0 = 1.20B + 348, \quad T_p = 1.07B + 392,$$
$$T_f = 0.77B + 445$$

The thermal degradation temperature increases with increasing of the heating rate, which is caused by heat hysteresis. In addition, the thermal degradation temperature can be expressed more exactly with an equilibrium degradation temperature T^0 when the heating rate approaches zero as shown below:

$$T_0^0 = 348, \quad T_p^0 = 392, \quad T_f^0 = 445$$

The peak width $T_f - T_0 = 97 - 0.43B$ and decreases with the increment of the heating rate.

Table I shows the relationship between the heating rate and the thermal degradation rate C in the degradation of ENR. C_p and C_f are the thermal degradation rates which correspond to T_p and T_f, respectively. C_p is the thermal degradation rate at $T = T_p$, and $C_p = 100\%$ − weight percent of the residues. C_f is the thermal degradation rate at $T = T_f$ and $C_f = 100\%$ − weight percent of the residues. The value of C_p increases with the
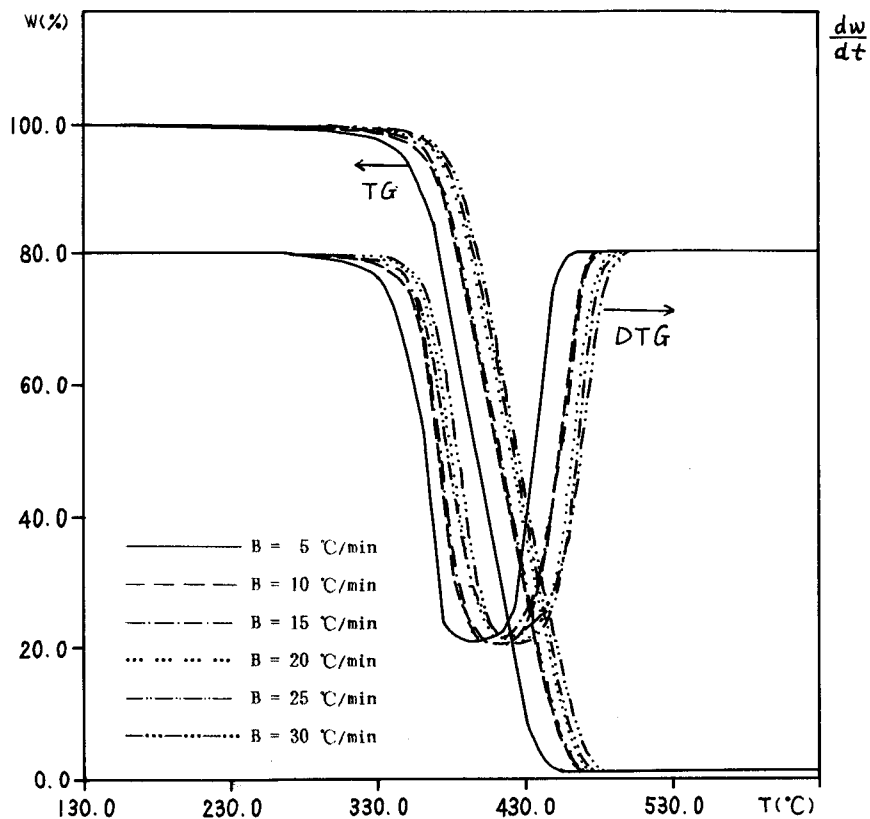
Figure 1 TG and DTG curves of ENR thermal degradation.

heating rate and the average value is 43%. C_f is not affected by the heating rate and its value approximately equals 100%, indicating that the degradation proceeds thoroughly.

Thermooxidative Degradation of ENR

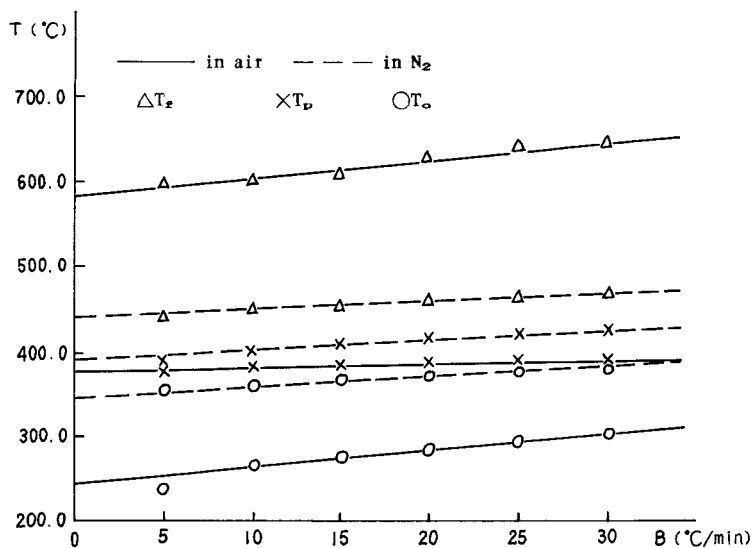The thermooxidative degradation of ENR was carried out in air. Figure 3 shows the TG and DTG

Figure 2 Relation between B and T at ENR degradation.

Table I   Relation Between *B* and *C* at ENR Degradation

| ENR Degradation		B (°C/min)					
		5	10	15	20	25	30
In N$_2$	C_p (%)	30	42	45	41	52	51
	C_f (%)	99.2	99.3	99.2	99.4	99.5	99.4
In air	C_p (%)	34	34	33	36	40	39
	C_f (%)	99.3	99.6	99.0	99.6	99.7	99.7

curves of the thermooxidative degradation of ENR at six different heating rates. There are several apparent turning points on the TG curve, so it is not a smooth curve, indicating that the degradation is not a one-step reaction. Around the main peak of the DTG curve, there are some small peaks or shoulder peaks. These peaks could not be separated completely, but overlap each other, indicating that the degradation consists of several reactions. There is an apparent weight loss peak at about 530°C that shows the oxygen having taken part in the degradation reaction.

Figure 2 illustrates that the thermooxidative degradation temperature increases linearly with the heating rate. The equations are as follows:

$$T_0 = 1.84B + 246, \quad T_p = 0.30B + 378,$$
$$T_f = 2.27B + 584$$

As for the equilibrium thermooxidative degradation temperatures, they are $T_0^0 = 246$, $T_p^0 = 378$, and $T_f^0 = 584$, respectively. The peak width is expressed as $T_f - T_0 = 338 + 0.43B$ and increases
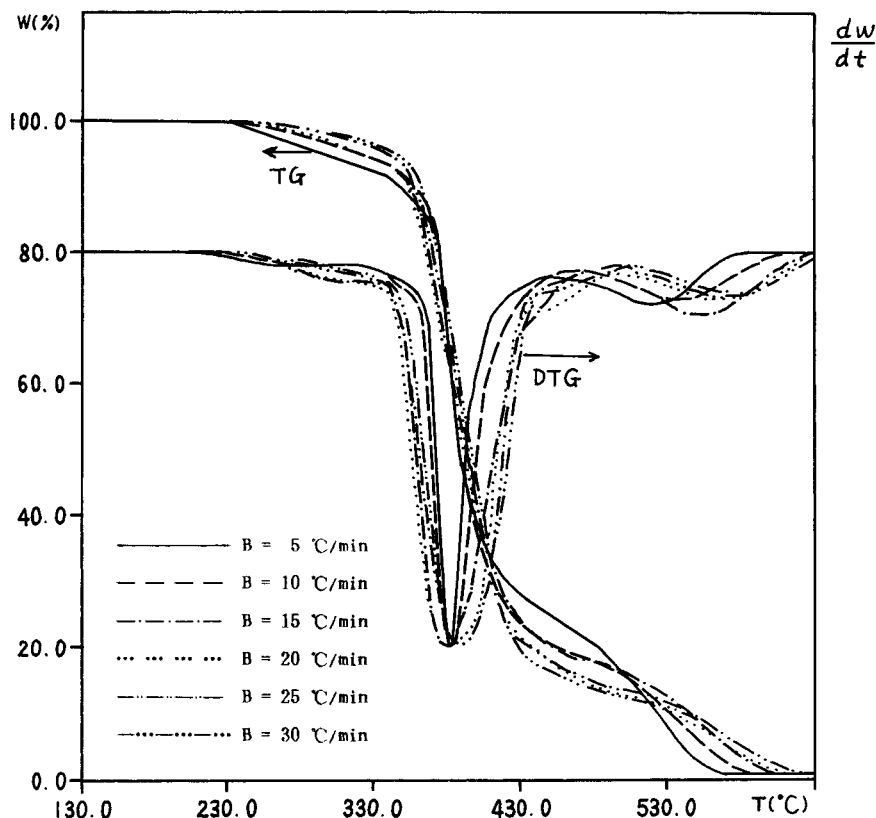
Figure 3   TG and DTG curves of ENR thermooxidative degradation.

with the heating rate. Table I shows that the thermal degradation rate of ENR increases along with the increment of the heating rate and the average value of C_p is 36%. C_f reaches 100% and is not affected by the heating rate.

Effect of Reaction Environments on ENR Degradation

The thermal degradation reaction of ENR in nitrogen could be a simple one-step reaction and proceeds thoroughly. But in air, because oxygen has taken part in the reaction, it is a thermooxidative degradation reaction. Besides a strong degradation peak appearing at 380°C on the DTG curve, there is another peak at 530°C. Around the main peak, there are some small peaks, indicating that the reaction is rather complicated. Compared with the thermal degradation, the oxidative reaction of thermooxidative degradation causes the degradation temperature T_0^0 of ENR to decrease from 348 to 246°C, T_p^0 to decrease from 392 to 378°C, but T_f^0 to increase from 445 to 584°C. When oxygen is taking part in the reaction, the initial temperature of the weight loss of ENR decreases about 100°C and the final temperature of the weight loss of ENR increases to 140°C, showing that the degradation process is prolonged.

The relationships of the width of the main degradation peaks of the DTG curves of the two reactions with the heating rate are linear, the difference being that the thermal degradation is an inverse ratio and the thermooxidative degradation is direct. Thus, the reaction environment has obvious effects on ENR degradation and the mechanism of the two types of degradation are different; more details concerning this will be forthcoming.

CONCLUSIONS

The thermal degradation of ENR could be a one-step reaction. The thermal degradation temperature increases with the heating rate. The peak width of the DTG curve decreases with an increased heating rate. C_p increases along with the heating rate, but C_f is not affected by the heating rate.

The thermooxidative degradation of ENR is a multiple-step reaction. The thermooxidative degradation temperature increases with the heating rate. The peak width of the DTG curve increases with the heating rate. C_p increases with the heating rate, but C_f is not affected by the heating rate.

The thermal degradation of ENR was carried out in nitrogen, whereas the thermooxidative degradation of ENR was conducted in air. Each degradation has a different mechanism.

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