

Study on Thermal Degradation of Sol and Gel of Natural Rubber

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ABSTRACT: The thermal degradation of natural rubber (NR) in air at a constant heating rate was studied by using of the thermogravimetry (TG) and thermogravimetry and differential thermal analysis (TG-DTA) simultaneous techniques. It indicates that the temperature of thermal degradation of gel and sol of NR rises linearly along with the increment of the heating rate, whereas the heating rate has little effect on the degree of thermal degradation. Accompanying other side reactions, the thermal degradation of NR is not a simple random chain scission process, and it is an exothermic reaction. The dynamic variation of molecular structure of NR during the thermal degradation was studied using Fourier transform infrared spectroscopy (FTIR). It shows that the products of the thermal degradation of both sol and gel of NR are hydroperoxide, carbonyl, and hydroxyl compounds. The formation of gel makes the temperature of the thermal degradation of NR decrease and the rate of the thermal degradation increase; thus, the thermal stability of NR is reduced. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1339–1344, 2000

Key words: natural rubber; gel; sol; thermal degradation

INTRODUCTION

In recent decades, both the production of natural rubber (NR) and synthetic rubber still keeps a certain proportion in the market, although the synthetic rubber developed rapidly after the World War I. Now NR still accounts for more than one-third of the total rubber consumption. This is due to the lower development of synthetic rubber limited by the energy crisis, such as the petroleum crisis. On the other hand, at present, some of the important products can only be manufactured by NR due to its excellent common proper-

ties.^{1–3} Because of its importance, further research on NR is really necessary. NR is a natural biosynthesis polymer, and there is 6–8% of non-rubber components existing in its composition. Therefore, during the research and development, more problems may occur in NR than in synthetic rubber. In addition, the molecular structure of NR is even more complex than that of synthetic rubber, so there are still a lot of unsolved problems.

In the early 1960s, scholars from Malaysia revealed that there were some unusual groups existing in NR molecular chain, which caused NR molecules to be crosslinked.⁴ In fact, some gel, which is insoluble in an organic solvent and also a kind of crosslinking molecule, is produced gradually during the storage of NR. The structure of gel is different from that of sol, which has a linear molecular structure.⁵ Besides, the structural

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variation of gel and its effect on raw NR properties are obvious.^{6,7}

Many reports on the effect of heat and oxygen on NR vulcanizate have been published. However, the study on the thermal oxidative behavior of raw NR seems to be scarce. After NR was changed from linear polyisoprene molecules (sol) into a crosslinking structure (gel), its aging behavior and thermal stability have been changed. The effect of heat and oxygen on sol and gel of raw NR is different,⁸ and further study of these problems is necessary. The thermal degradations of gel and sol of NR were studied by using of thermogravimetry (TG), thermogravimetry and differential thermal analysis (TG-DTA) simultaneous techniques, as well as Fourier transform infrared spectroscopy (FTIR) in this article.

EXPERIMENTAL

Materials

Fresh NR latex was obtained from the local field of NR plantation, the latex was coagulated with

5% acetic acid, and the coagulum was pressed to about 2 mm thick with a sheeting mill. The sheet was dried in an oven at 70°C until the rubber sheet became transparent so as to make Sample 1. Put Sample 1, as well as desiccant P₂O₅, was put into a desiccator, and the desiccator was heated in an oven at 70°C for 24 h, making the accelerated storage test to get Sample 2. The screen filtering method was adopted to determine the gel content of the samples, and the aperture of screen was 0.175 mm.⁵⁻⁷ The gel content of Sample 1 is 0, and the sample 2 is 37%.

Instruments

The following instruments were used: a Shimadzu TD-40 thermal analyzer (TG-DTA), a Perkin-Elmer TG S-2 thermogravimetry analyzer, and a Nicolet-5DX Fourier transform infrared spectrometer.

Methods

NR sample, (3-4 mg) was put into the lead crucible, and the temperature was raised from room

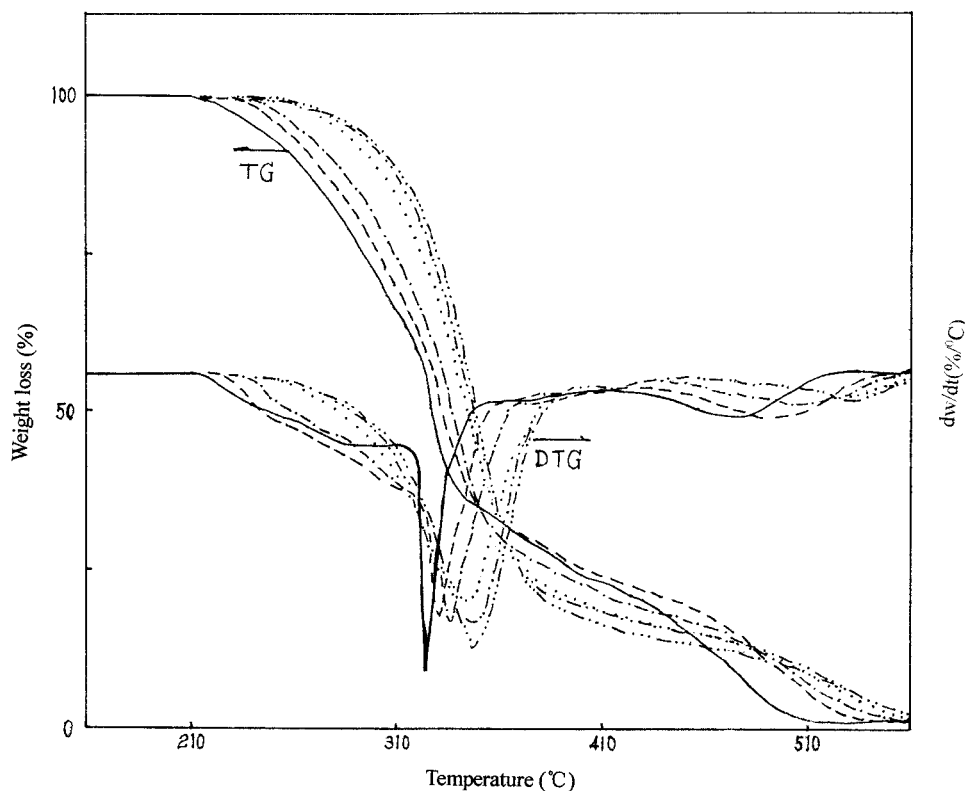


Figure 1 TG and DTG curves of the thermal degradation of Sample 1: (—) $B = 5^{\circ}\text{C min}^{-1}$; (---) $B = 10^{\circ}\text{C min}^{-1}$; (-·-) $B = 15^{\circ}\text{C min}^{-1}$; (···) $B = 20^{\circ}\text{C min}^{-1}$; (-·-·) $B = 25^{\circ}\text{C min}^{-1}$; and (-···-) $B = 30^{\circ}\text{C min}^{-1}$.

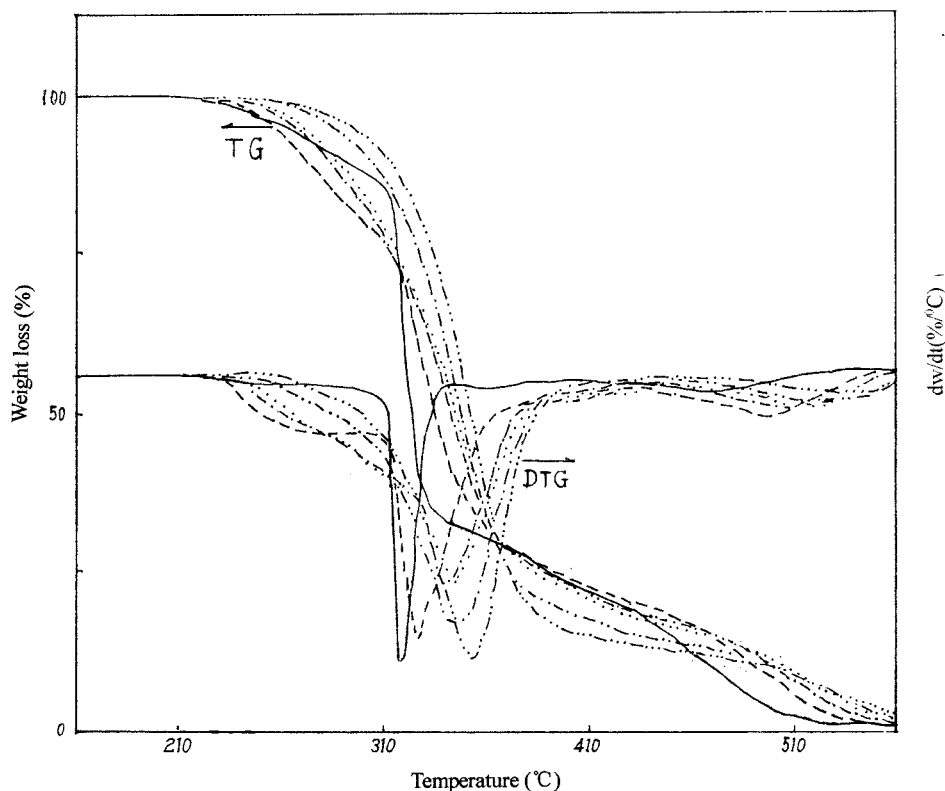


Figure 2 TG and DTG curves of thermal degradation of Sample 2: (—) $B = 5^\circ\text{C min}$; (---) $B = 10^\circ\text{C min}$; (-·-) $B = 15^\circ\text{C min}$; (···) $B = 20^\circ\text{C min}$; (-·-·) $B = 25^\circ\text{C min}$; (-·-·-·) $B = 30^\circ\text{C min}$.

temperature to 600°C at 5°C min , 10°C min , 15°C min , 20°C min , 25°C min , and 30°C min , respectively, in air flow (45 mL min). The thermogravimetry-derivative thermogravimetry (TG-DTG) curves were recorded. FTIR analysis was carried out by use of the film transmission method. The results were shown in the differential absorption spectrum (spectrum degraded for n h minus spectrum degraded for 0 h).⁹

RESULTS AND DISCUSSION

The Effect of Heating Rate (B) on Degradation Process

Figures 1 and 2 show the TG curves and the corresponding DTG curves of the thermal degradation of samples 1 and 2 in air, respectively. It can be seen that there is a big turn and some small turns on the TG curve; and the curve is not smooth, which indicates that the degradation is not a one-step reaction. A sharp degradation peak is found in the DTG curve between 320 and

360°C ; another smoother degradation peak can be seen between 450 and 550°C , and the later becomes smaller and smaller along with the increment of B . The thermal degradation of NR may have many kinds of reactions in air. During the early degradation (before 300°C), oxidation, crosslinkage, and chain scission may occur at the same time, and the main reaction may be oxidation and crosslinkage. In this case, no weight loss occurs, or weight loss is slower. During the late degradation (after 300°C), the main reaction is oxidative degradation, and obvious weight loss occurs.

Effect of Heating Rate (B) on Degradation Temperature (T)

The relations between B and T of NR at the thermal degradation in air are shown in Figure 3. T_0 stands for initial temperature of weight loss, and T_f stands for final temperature of weight loss, which are obtained from TG curve by bitangent method. T_p stands for peak temperature of DTG

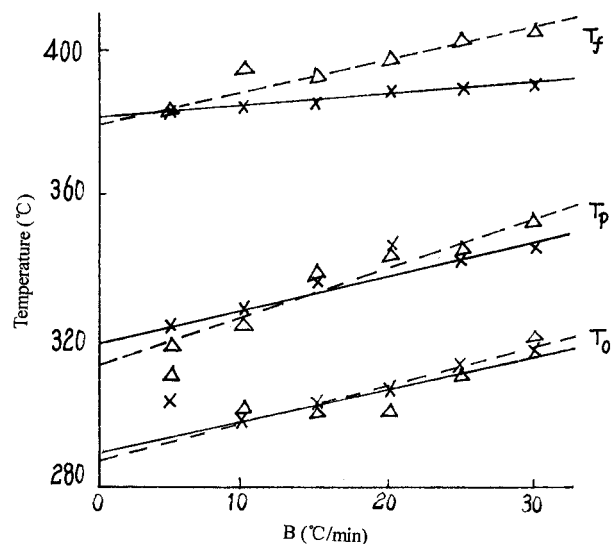


Figure 3 Relations between B and T at thermal degradation of Sample 1 (\times — \times) and Sample 2; (Δ - - - Δ).

curve or temperature at maximum weight loss rate. The peak width of DTG that shows the temperature range of degradation process can be expressed with $T_f - T_0$. It can be seen that the thermal degradation temperatures of NR rise linearly along with the increment of B , and their relationships can be expressed as follows. Sample 1: T_0 ($^{\circ}\text{C}$) = $0.95B + 289$; T_p ($^{\circ}\text{C}$) = $0.94B + 321$; T_f ($^{\circ}\text{C}$) = $0.34B + 382$. Sample 2: T_0 ($^{\circ}\text{C}$) = $0.95B + 287$; T_p ($^{\circ}\text{C}$) = $1.33B + 314$; T_f ($^{\circ}\text{C}$) = $0.90B + 380$.

The reason that the thermal degradation temperature increases along with rising of B is heat hysteresis. So, the thermal degradation temperature is more suitable to be expressed with equilibrium degradation temperature T° ($B = 0$). The equilibrium thermal degradation temperatures of NR are shown, respectively, as follows. Sample 1: $T_0^{\circ} = 289$; $T_p^{\circ} = 321$; $T_f^{\circ} = 382$. Sample 2: $T_0^{\circ} = 287$; $T_p^{\circ} = 314$; $T_f^{\circ} = 380$.

The peak widths are as follows. Sample 1: $T_f - T_0 = 93 - 0.61B$. Sample 2: $T_f - T_0 = 93 - 0.05B$.

Relation Between Degradation Rate (C) and B

Figure 4 shows the thermal degradation rate C_p and C_f corresponding to T_p and T_f , respectively, when the degradation conducts at different values of B . C_p is the thermal degradation rate at $T = T_p$, and $C_p = 100\%$ minus the weight percent of the residues. C_f is the thermal degradation rate

at $T = T_f$, and $C_f = 100\%$ minus the weight percent of the residues. The result indicates that C_f has a linear relationship to B , and the value of C_f increases with rising of B . C_p increases lightly along with the increment of B at $B < 20^{\circ}\text{C min}$, but when $B > 20^{\circ}\text{C min}$, the value of C_p almost has little change.

Heat Effect of Degradation

Figure 5 shows the thermal degradation TG–DTA curves of NR in air at $B = 10^{\circ}\text{C min}$. It can be seen that at 240°C , NR begins to loss weight, and oxidative degradation starts up; the DTA curve deviates from the baseline and moves towards exothermic side. Sample 1 has a strong exothermic peak when it obviously loses weight, and this is an exothermic reaction caused by oxidation. The DTA curve is more smooth at 380 to 450°C ; whereas at 470°C , an exothermic peak occurs on the DTA curve again. Two exothermic peaks of Sample 2 consist of degradation of sol and gel. The former exothermic peak may be caused by the degradation of gel, and the late one may represent the degradation of sol and the degradation temperature of sol is close to the Sample 1. There is a small exothermic peak at 440°C , which may be caused by some other components.

FTIR Analysis of Thermal Degradation

Figures 6 and 7 are the FTIR differential spectra of thermal degradation for 1, 2, and 3 h, respec-

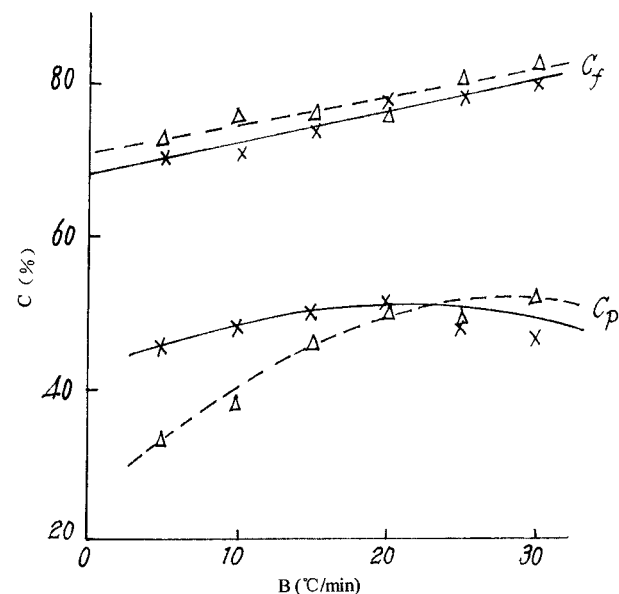


Figure 4 Relations between B and C at thermal degradation of Sample 1 (\times — \times) and Sample 2 (Δ - - - Δ).

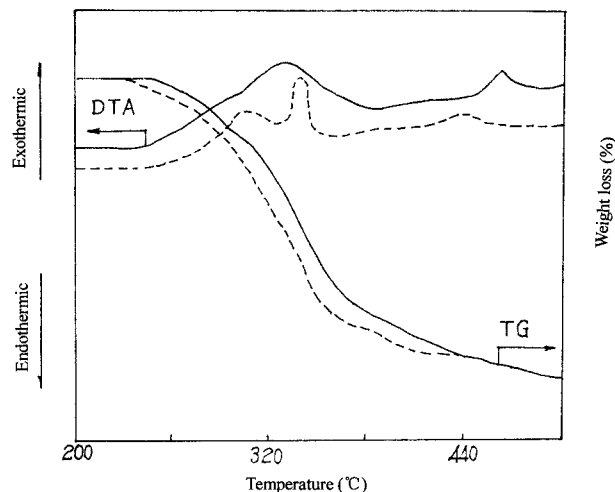


Figure 5 Thermal degradation TG-DTA curves of Sample 1 (—) and Sample 2 (-----) at $B = 10^\circ\text{C min}$.

tively, in air at 145°C . The absorbance of Sample 2 at 835 , 1375 , 1450 , and 1660 cm^{-1} decreases greatly with a prolonging of thermal degradation period, whereas the absorbance at 1715 and 3500 cm^{-1} increases along with the prolonging of ther-

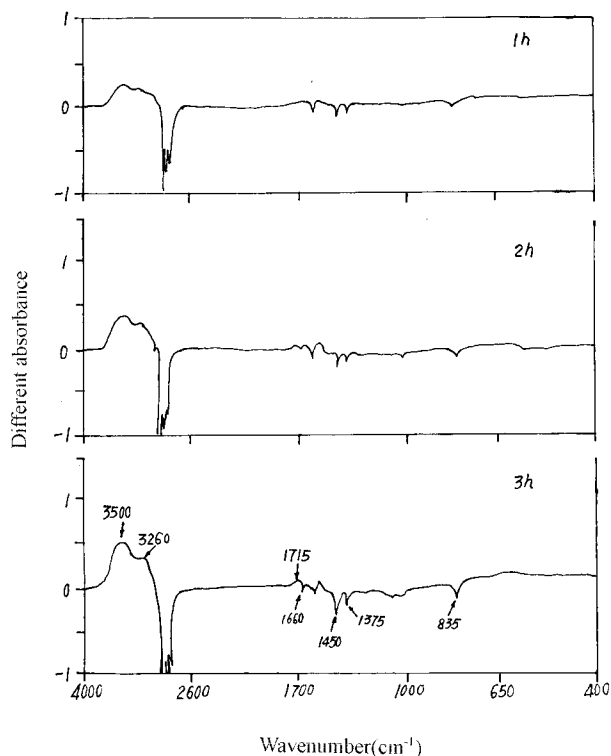


Figure 6 FTIR differential spectrum of the thermal degradation of Sample 1 at 145°C in 1, 2, and 3 h.

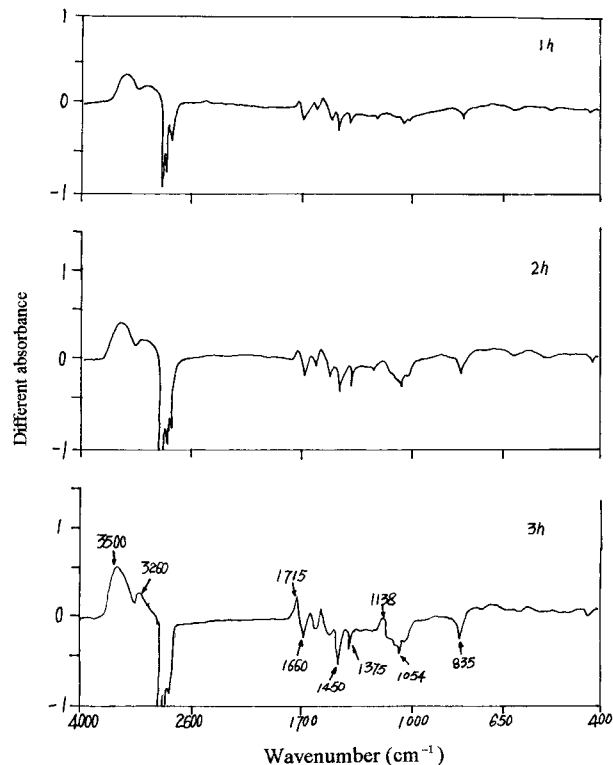


Figure 7 FTIR differential spectrum of thermal degradation of Sample 2 at 145°C in 1, 2, and 3 h.

mal degradation time. With the same reaction temperature and reaction time, the absorbance of Sample 1 at the above-mentioned wave numbers has no obvious changes. Due to the effect of heat and oxygen, NR occurs a thermal degradation. In result, its molecular chain breaks into pieces. Therefore, in the degradation process, the absorbance of carbon-carbon double bond (835 and 1660 cm^{-1}) and the secondary methyl group (1450 cm^{-1}) decrease obviously, whereas those of carboxyl group (1715 cm^{-1}) and hydroxyl group (3500 cm^{-1}) have a marked increment. It indicates there are aldehyde, ketone, carboxylic acid, and ester existing in the products of NR thermal degradation.

Through comparison of Figures 6 and 7, it is found that both samples 1 and 2 have similar products: hydroperoxide, hydroxyl, and carbonyl compounds. The only difference is the strength of characteristic absorbance peak, namely, the reaction degree. Taking the reaction degree into consideration, the result that Sample 2 achieved in 1 h is equal to that of Sample 1 done in 3 h.

Effect of Gel on Thermal Degradation Process

Figure 5 shows that both the degradations of samples with gel (Sample 2) and without gel (Sample 1) are not one-step reactions (refer to the DTG curves of Figures 1 and 2). Sample 2 begins to lose weight earlier, and the equilibrium degradation temperature is $T_0^\circ = 287$, $T_p^\circ = 314$, $T_f^\circ = 380$, respectively. Compared with Sample 2, Sample 1 loses weight later, and the equilibrium degradation temperature is $T_0^\circ = 289$, $T_p^\circ = 321$, and $T_f^\circ = 382$. The reason might be that there is weak bond in the crosslinking structure of gel, and it is easy to break by heating. The heat effects of the degradation of Sample 1 and Sample 2 are different. When Sample 2 loses weight in the first step of degradation, two exothermic peaks will appear continuously, and the degradation process completes quickly. The scission of weak bond of gel probably induced the main molecular chain of NR to degrade; thus, the degradation was carried out more easily. The results of FTIR study (Figs. 6 and 7) also demonstrate that the rate of thermal degradation of Sample 2 is much greater than that of Sample 1. It illustrates the thermal stability of NR will decrease after gel is produced.

CONCLUSIONS

The thermal degradation of NR in air is not a simple random chain scission process, but also has some side reactions that are carried out si-

multaneously. In addition, the process of degradation is an exothermic reaction. The thermal degradation temperature of NR rises linearly along with the increment of heating rate, but thermal degradation rate has little variation. When gel produces from NR, the degradation products of NR basically have no change, but the thermal degradation temperature drops, the thermal degradation rate increases, and the thermal stability is reduced.

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