# Study on Hot Air Aging and Thermooxidative Degradation of Peroxide Prevulcanized Natural Rubber Latex Film

**Bei-Long Zhang,[1,2] Mei Chen,[1,2] Ning-Jian Ao,[1,2] Wei-Yong Deng,[1,2] Hui-Lun Liu[1,2]**

[1]*Key Laboratory of Natural Rubber Processing, Ministry of Agriculture, China*
[2]*South China Tropical Agricultural Product Processing Research Institute, P.O. Box 318, Xiashan, Zhanjiang, 524001, Guangdong, China*

**ABSTRACT:** The air-aging process at 120°C and the thermooxidative degradation of peroxide prevulcanized natural rubber latex (PPVL) film were studied with FTIR and thermal gravity (TG) and differential thermal gravity (DTG) analysis, respectively. The result of FTIR shows that the —OH and —COOH absorption of the rubber molecules at IR spectrum 3600–3200 $cm^{-1}$, the —C=O absorption at 1708 $cm^{-1}$, and the —C—OH absorption of alcohol at 1105 and 1060 $cm^{-1}$ increased continuously with extension of the aging time, but the —$CH_3$ absorption of saturated hydrocarbon at 2966 and 2868 $cm^{-1}$, the —$CH_3$ absorption at 1447 and 1378 $cm^{-1}$, and the C=C absorption at 835 $cm^{-1}$ decreased gradually. The result of TG-DTG shows that the thermal degradation reaction of PPVL film in air atmosphere is a two-stage reaction. The reaction order ($n$) of the first stage of thermooxidation reaction is 1.5; the activation energy of reaction ($E$) increases linearly with the increment of the heating rate, and the apparent activation energy ($E_0$) is 191.6 kJ $mol^{-1}$. The temperature at 5% weight loss ($T_{0.05}$), the temperature at maximum rate of weight loss ($T_p$), and the temperature at final weight loss ($T_f$) in the first stage of degradation reaction move toward the high temperature side as the heating rate quickened. The weight loss rate increases significantly with increment of heating rate; the correlation between the weight loss rate ($\alpha_p$) of DTG peak and the heating rate is not obvious. The weight loss rate in the first stage ($\alpha_{f1}$) rises as the heating rate increases. The final weight loss rate in second stage ($\alpha_{f2}$) has no reference to heating rate; the weight loss rate of the rubber film is 99.9% at that time. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3196–3200, 2004

**Key words:** prevulcanized latex; peroxide prevulcanized natural rubber latex; latex rubber film; air aging; infrared difference spectrum analysis; thermooxidative degradation; kinetics

## INTRODUCTION

Sulfur vulcanization is still adopted in the curing of products used in food industry and in medical enterprises. The accelerators used in this system may contain nitrosamines or materials that can form nitrosamines. This constitutes a potential danger to human safety and health. Therefore, searching a new method to substitute the sulfur vulcanization for rubber latex was carried out. A method of peroxide prevulcanization of natural rubber latex was extensively studied to substitute the traditional sulfur vulcanization.[1–4] Because the accelerators need not be used in the peroxide prevulcanization system, the nitrosamines problem can be avoided. The C—C crosslink was formed in the crosslinking structure of the peroxide vulcanized rubber, which is greatly different with the crosslinking structure of the sulfur vulcanization.[5] The heat resistance of the peroxide prevulcanized natural rubber latex (PPVL) film directly affects the prospect of its application; therefore, the study of the hot air aging and the thermooxidative degradation of the PPVL film is a worthwhile work and no report on this respect has been published until now. This article describes the investigation of the air-aging process of PPVL film at 120°C with FTIR and thermooxidative degradation of PPVL film by use of the TG analysis method described by Zhong.[6]

## EXPERIMENTAL

### Materials

The natural latex concentrate was supplied by the affiliated factory of our institute; the tertiary butyl peroxide (PC chemical reagent) was supplied by the Shanghai Chemical Reagent Co., Shanghai, China. The fructose (medical grade) was supplied by Zhangjiang Fructose Factory.

### Preparation of test sample

Ingredients

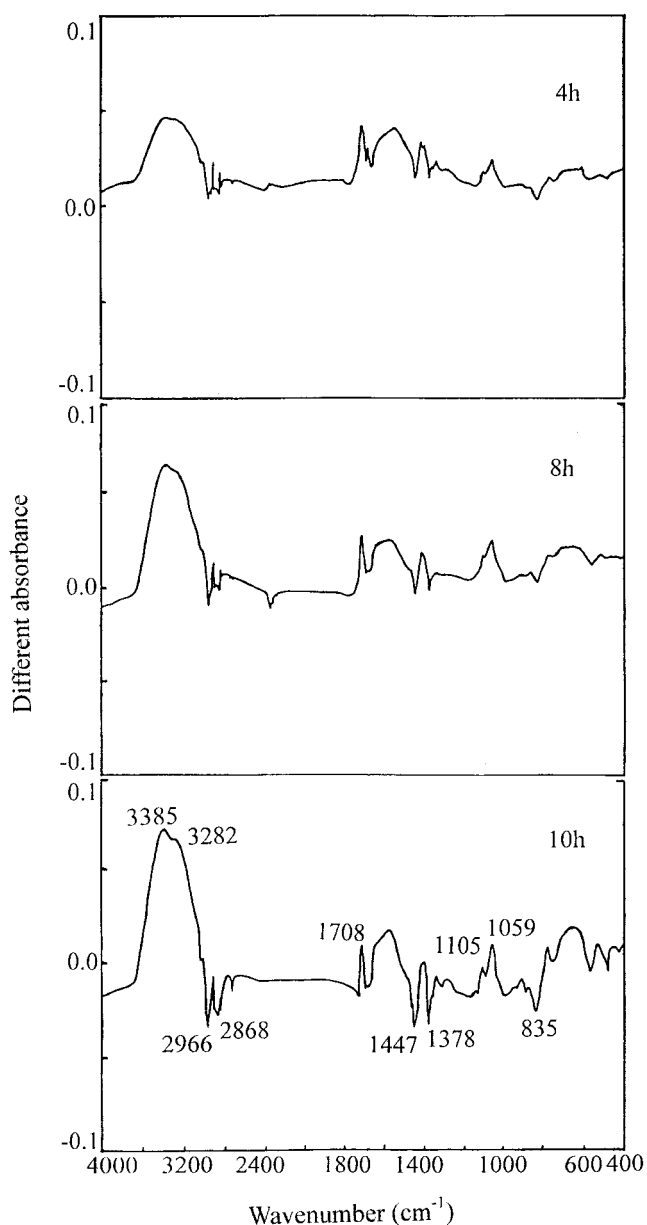| | |
|---|---|
| Natural latex concentrate (based on dry rubber) | 100 |
| Tertiary butyl peroxide | 0.8 |
| Fructose | 1.0 |
| $Fe^{3+}$ | $4 \times 10^{-4}$ |

**Figure 1** IR difference spectrum of PPV the film during hot air aging.

Method of preparation

The tertiary butyl peroxide, fructose (20%), and $Fe^{3+}$ (0.1%) were added to the latex at same time at 70°C. The vulcanization reaction time was 3.5 h; samples were taken and put into Petri dishes for cooling, and the rubber films were prepared in an air-blast thermostatically controlled oven at 50°C. The water-soluble materials were removed from rubber films by leaching them with distilled water for 6 h. Then, the rubber films were dried again in the air-blast thermostatically controlled oven at 50°C. The swelling index $Q$ (i.e., the ratio between the weight of the solvent and the weight of the rubber existing in the swelled vulcanizate) of

the PPVL film was determined according to the method described in ref. 1. The experimental result shows that tensile strength of the PPVL film reaches its peak value when the $Q$ is about 6.[2] The swelling index of the PPVL film used in this experiment is $Q = 5.9$.

**Apparatus and test method**

FTIR analysis

We took a certain quantity of PPVL, smeared it evenly on a glass plate, and dried it at room temperature; a dry rubber film with thickness of about 0.02 mm was then prepared. The dry rubber film was aged in a hot air aging oven at 120°C; the aging times were 4, 8 and 10 h, respectively (see Fig. 1). After aging, the dry rubber film was tested with a Perkin–Elmer Spectrum GX FTIR spectrograph; the spectral resolution was 4 $cm^{-1}$, scanned six times. The result was expressed by difference spectrum. The difference spectrum was calculated as the difference of the absorption spectrum multiplied by the compensating coefficient of thickness of the test sample before and after aging. The same test sample was used in this experiment; thus, the compensating coefficient of thickness is 1. In the difference spectrum, if no change occurred in the test sample, then the spectrogram was a even baseline and the absorbance was 0. If the test sample was changed, then the spectrogram was no longer an even baseline. When the absorbance was more than 0, new radicals were produced or the number of radical increased; when the absorbance was less than 0, some radicals were diminished or the number of radical decreased.[7]

TG analysis

TGA was carried out in air atmosphere on a Perkin–Elmer TGA-7 thermoanalyzer. The temperature rising rates applied were 5, 10, 15, 20, and 25°C/min. The flow rate of air was 50 ml/min.

**RESULTS AND DISCUSSION**

**Hto air aging of PPVL film**

Generally, the main symptoms of IR absorption peak of the natural rubber are the characteristic extended vibration of the $C=CH_2$ at 885 $cm^{-1}$; the absorption band of the terminal olefinic group at 3054, 1631, 966, 910, and 837 $cm^{-1}$ as well as the concentration of double bond at 1663 and 837 $cm^{-1}$ and the absorption band of $CH_3$ at 1449 and 1376 $cm^{-1}$.[8] It is said that the following changes also took place during oxidation of the natural rubber (i.e., the increase of the $C=O$ and —OH radicals and the decrease of double bond). It also verified that diolefinic polymer can lead to chain scission and crosslinking at the same time when the heat and oxygen exist.[9] From Figure 1, it can be seen
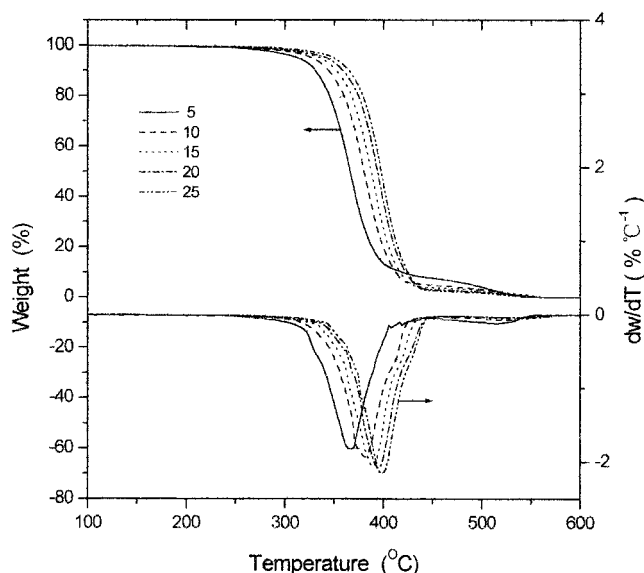
**Figure 2** TG and DTG curve of thermooxidative reaction of PPVL film in air atmosphere.

that the wide absorption band strengthens continuously at 3600–3200 cm$^{-1}$ during hot air aging of the PPVL film, which was caused by the formation of —OH and —COOH during aging process.[7] The absorption peak at 2965 cm$^{-1}$ is the antisymmetrical vibration absorption of the saturated hydrocarbon —CH$_3$ and the absorption peak at 2868 cm$^{-1}$ is the symmetrical vibration absorption of the saturated hydrocarbon —CH$_3$,[10] which indicates that the peroxide vulcanization makes the natural rubber molecules chain to form C—C crosslinkage and makes a part of the natural rubber molecules chain to form saturated hydrocarbon, which is in conformity with ref. 6. Besides, the absorption peak at 1446 and 1378 cm$^{-1}$ is the —CH$_3$ absorption.[8] These absorption peaks weaken gradually with extension of aging time. This is because the methyl group forms free radicals under the action of heat, and on the other hand, the oxidative degradation of rubber molecule also causes the decrease of methyl group. The absorption at 1707 cm$^{-1}$ is the absorption peak of carbonyl group[11]; its strength increases continuously with extension of aging time. The absorption at 1105 and 1060 cm$^{-1}$ is the absorption peak of the alcohol —C—OH[10]; its strength increases gradually with extension of aging time. The

absorption peak at 835 cm$^{-1}$ is the C=C absorption,[8,9] which weakens gradually with the extension of aging time. In comparison, the formation of hydroxyl, carboxyl, and carbonyl groups is quicker than oxidative degradation of methyl and C=C groups.

## Thermooxidative degradation of PPVL film

### Effect of heating rate on thermooxidative degradation process

The thermooxidative degradation of PPVL film was carried out in air atmosphere. Figure 2 shows the curves of thermooxidative degradation of PPVL film at five different heating rates. From Figure 2, it can be seen that TG curve has a large plateau and a small plateau and the DTG curve has a main degradation peak and a secondary degradation peak, which indicates that the thermooxidative degradation reaction of PPVL film in air atmosphere is a two-stage reaction. The first weight loss peak appears at 250–450°C, which may be the degradation reaction of the main chain of the rubber; the second weight loss peak appears at 450–565°C, which may be the oxidative reaction of the residual carbon that could be oxidized into carbon dioxide. During the degradation process, the TG curve and the DTG curve move toward the high temperature side because of heat hysteresis; the degradation rate increases significantly with the increment of heating rate. Table I shows relation of heating rate to DTG peak temperature and maximum weight loss rate.

### Relation between degradation temperature and heating rate

Figure 3 shows the relation between degradation temperature of PPVL film in air atmosphere at first-stage reaction and the heating rate, $\beta$. The effect of different heating rate, $\beta$, on initial degradation temperature of PPVL film was investigated, using the temperature at 5% degradation ($T_{0.05}$) as initial degradation temperature; the initial degradation temperature ($T_{0.05}$), the final degradation temperature ($T_f$), and the temperature at maximum weight loss rate ($T_p$) are obtained from the TG and DTG curves. It can be seen from Figure 3 that the degradation temperature rises linearly with the increment of the heating rate, which

**TABLE I**
**Relation of Heating Rate to DTG Peak Temperature and Maximum Weight Loss Rate**

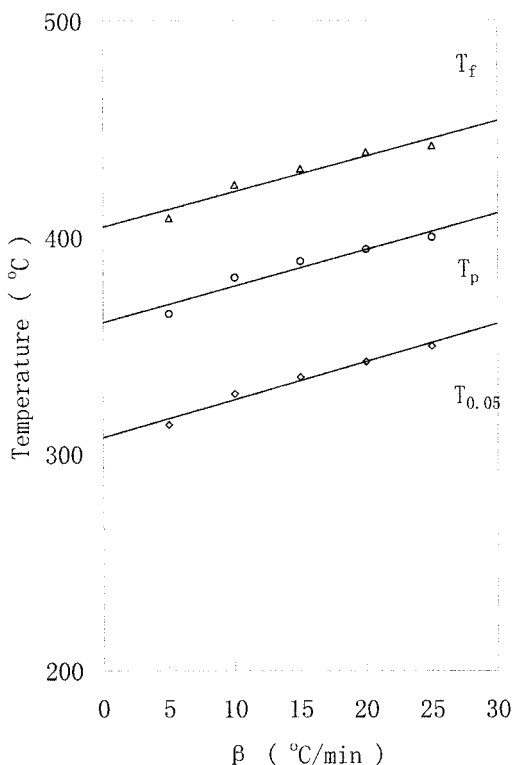|  | $\beta$ (°C min$^{-1}$) | | | | |
|---|---|---|---|---|---|
|  | 5 | 10 | 15 | 20 | 25 |
| DTG peak temperature (°C) | 364.6 | 381.4 | 388.9 | 394.4 | 400.1 |
| Maximum weight loss rate (% °C$^{-1}$) | −1.84 | −1.94 | −2.05 | −2.08 | −2.16 |

**Figure 3** Relation between degradation temperature of PPVL film in air atmosphere at first-stage reaction and heating rate $\beta$.

indicates that the heating rate is the main factor affecting the degradation temperature. Their correlation equation are as follows:

$$T_{0.05} = 1.75\beta + 307.5°C$$

$$T_p = 1.68\beta + 360.7°C$$

$$T_f = 1.63\beta + 404.8°C$$

**Effect of heating rate on degradation rate**

Table II shows the relation between heating rate, $\beta$, and degradation rate, $\alpha$, of PPVL film in air atmosphere; $\alpha_p$ and $\alpha_f$ are the degradation rates corresponding to $T_p$ and $T_f$:

$$\alpha_p = 100\%$$

$$- \text{wt \% (percentage of remained weight at } T_p)$$

$$\alpha_f = 100\%$$

$$- \text{wt \% (percentage of remained weight at } T_f)$$

The test results in Table II indicate that there is no significant correlation between $\alpha_p$ and heating rate; the degradation rate ($\alpha_{f1}$) increases with increment of

heating rate at the end of first-stage reaction. The degradation rate ($\alpha_{f2}$) at the end of second-stage reaction has no reference to heating rate. The PPVL film almost degraded completely, which indicates that the degradation reaction of PPVL film in air atmosphere goes on thoroughly.

**Kinetics of thermooxidative degradation reaction of PPVL film**

The kinetics factor of reaction can be obtained from TG and DTG data during the degradation process. According to the Freeman–Carroll kinetic equation[12]:

$$\frac{\Delta \log(-dw/dT)}{\Delta \log w} = -\frac{(E/R)1/T}{2.303\Delta \log w} + n \qquad (1)$$

a diagram was drawn by using $[\Delta \log(-dw/dT)]/\Delta \log w$ and $1/T/\Delta \log w$ as coordinates and a straight line was obtained. The slope of this line and the activation energy $E$ of this reaction can be obtained. The intercept of this straight line is the reaction order $n$. The frequency factor can be found out from the Rogers–Smith equation[13]:

$$A = \frac{\beta E e^{E/RT_p}}{RT_p^2} \qquad (2)$$

The apparent activation energy $E_0$ can be obtained from the correlation between heating rate and degradation temperature.

Table III shows the kinetic parameters in the first-stage degradation reaction. It can be seen that the main reaction order of different $\beta$ is 1.5, indicating that the degradation reaction of PPVL film should be a reaction with the order of 1.5. The $E$ increases linearly with the increment of heating rate. The apparent activation energy $E_0$ was calculated at a heating rate of 0°C min from linear regression by use of the least-squares method; the calculated $E_0$ equals 191.6 kJ min$^{-1}$. Frequency factor $A$ increases by geometric progression with the increment of heating rate. The value of correlation coefficient is 0.950 and above.

## CONCLUSION

(1) During the hot air aging of PPVL film at 120°C, the number of hydroxyl, carboxyl, and carbonyl

**TABLE II**
**Relation Between Heating Rate $\beta$ and Degradation Rate**

| | $\beta$ (°C min$^{-1}$) | | | | | |
| | 5 | 10 | 15 | 20 | 25 | Average |
|---|---|---|---|---|---|---|
| $\alpha_p$ (%) | 50.8 | 56.1 | 55.6 | 53.7 | 58.5 | 54.9 |
| $\alpha_{f1}$ (%) | 88.7 | 93.9 | 94.8 | 96.0 | 96.7 | 94.0 |
| $\alpha_{f2}$ (%) | 99.8 | 99.8 | 99.8 | 99.9 | 100 | 99.9 |

**TABLE III**
**Reaction Order and Activation Energy of Reaction in First-Stage Reaction**

| | $\beta$ (°C min$^{-1}$) | | | | |
|---|---|---|---|---|---|
| | 5 | 10 | 15 | 20 | 25 |
| $n$ | 1.4 | 1.5 | 1.5 | 1.5 | 1.6 |
| $E$ (kJ mol$^{-1}$) | 198.0 | 226.9 | 228.4 | 239.2 | 255.1 |
| $A$ | $4.84 \times 10^{15}$ | $8.15 \times 10^{17}$ | $9.84 \times 10^{17}$ | $6.72 \times 10^{18}$ | $1.05 \times 10^{20}$ |
| $r$ | 0.996 | 0.962 | 0.950 | 0.961 | 0.965 |

groups on rubber molecular chain increases continuously with the extension of aging time, and the correspondent IR spectrum absorption increases gradually, whereas the oxidative degradation of methyl and C=C increases slowly.

(2) Thermooxidative degradation reaction of PPVL film in air atmosphere is a two-stage reaction. The reaction order ($n$) of the thermooxidative degradation reaction at first stage is 1.5; the activation energy of the reaction ($E$) increases linearly with increment of heating rate. The apparent activation energy ($E_0$) is 191.6 kJ min$^{-1}$; the temperature at 5% weight loss at first stage of degradation reaction ($T_{0.05}$), the temperature at maximum rate of weight loss ($T_p$), and the temperature at final weight loss ($T_{f1}$) move toward the high temperature side with increment of heating rate. The maximum rate of weight loss increases significantly with the increment of heating rate; the correlation between weight loss rate ($\alpha_p$) of DTG peak and heating rate is not obvious. The weight loss rate at the first stage of reaction ($\alpha_{f1}$) increases with the increment of heating rate. The final weight loss rate at second stage of reaction ($\alpha_{f2}$) has no reference to heating rate. The weight loss of the rubber film is 99.9% at that time, and the rubber film almost degraded completely.

## References

1. Said, M. M. D.; Pendle, T. D.; Blackley, D. C. J Natl Rubber Res 1990, 5, 27.
2. Said, M. M. D.; Pendle, T. D.; Blackley, D. C. J Natl Rubber Res 1991, 6, 158.
3. Davies, R. T.; Gazeley, K. F. J Natl Rubber Res 1993, 8, 176.
4. Zhang, B.-L.; Liu, H.-L. Chin J Trop Crops 2001, 22, 1.
5. Loan, L. D. Rubber Chem Technol 1967, 40, 149.
6. Zhong, J.-P.; Li, S.-D., Yu, H.-P.; Wei, Y.-C.; Peng, Z.; Qu, J.-L.; Guo, C.-K. J Appl Polym Sci 2001, 81, 1305.
7. Li, S.-D.; Yu, H.-P.; Peng, Z.; Chen, Y.; Li, P.-S. Chin J Appl Chem 1999, 16, 111.
8. Jia, H.-B.; Liu, S.-P.; Zhang, S.-G. China Synthet Rubber Ind 1997, 20, 1010.
9. Pecsok, R. L.; Painter, P. C. Rubber Chem Technol 1976, 49, 1010.
10. Dong, Q. IR Spectrographic Methods [M]; Chemical Industry Press: Beijing, 1974; pp. 104–128.
11. Morand, J. L. Rubber Chem Technol 1974, 47, 1094.
12. Freeman, E. S.; Carroll, B. J Phys Chem 1958, 62, 394.
13. Rogers, R. N.; Smith, L. C. Anal Chem 1967, 39, 1024.