

Study on Effective Storage Time of Raw Natural Rubber

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ABSTRACT: The effective storage time (i.e., storage life) of raw natural rubber (NR) was investigated with heat-accelerated storage aging combined with thermogravimetry (TG) and differential thermal analysis (DTA) method, as well as the heat aging life equation. The test results show that the effective storage time of raw NR can be estimated more conveniently in relatively shorter time by this method. It is found that the effective storage time of raw NR is associated with rubber processing technology and with ambient temperature during storage, but it has little relation with P_0 and PRI. At ambient temperature, the effective storage time of the natural-coagulated and biological-coagulated

NR is obviously higher than the acetic acid-coagulated NR; the lower the ambient temperature, the longer the effective storage time. The effective storage time of the acetic acid-coagulated NR is 12.2–13.4 years at ambient temperature of 30°C, 23.8–25 years at 25°C, and 47.4–47.9 years at 20°C. The effective storage time of the natural- and biological-coagulated NR is 13.7–15.2 years at 30°C, 29.6–30.4 years at 25°C, and about 62.5–65.8 years at 20°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4114–4119, 2006

Key words: rubber; aging; thermogravimetric analysis; degradation; activation energy

INTRODUCTION

During storage of natural rubber (NR) at room temperature, owing to the effect of the environmental factors (mainly light, heat, and oxygen), the NR molecules degrade, causing the NR to depolymerize and turn to a nonelastic state, then lose its performance characteristics at last.¹ How long can NR stored at room temperature maintains its usability is yet a question to be answered. At 1975, a report was submitted to the International Rubber Conference in Kuala Lumpur, describing that the smoke sheet stored 50 years under Japanese climate conditions still possessed satisfactory performance characteristics.² Study on effective storage time of rubber restricts only to vulcanized rubber and rubber products at present.^{1,3–5} Because of the great difference between the molecular structure of raw NR and vulcanizate, the change of molecular chain of raw NR during storage is also different significantly with that of the vulcanized rubber; therefore, the method used for the evaluation of the effective storage time of the vulcanized rubber cannot be

used for estimation of that of the raw NR. No report is available about the study on effective storage time of raw NR. During storage, the oxidative depolymerization reaction takes place in the molecular chain of raw NR by the action of light, heat, and oxygen, which makes the plasticity value of the NR decrease; on the other hand, the rubber molecules form crystals at lower ambient temperature, which decreases the movement of rubber molecules and increases the stability of the NR. The lower the storage temperature, the more obvious the crystallization of NR molecules, which can prolong greatly the effective storage time.^{2,6} The crystallization of NR molecules is a variation of molecular conformation; the effect of temperature on molecular conformation is relative to activation energy. The authors of this article had predicted the effective storage time of raw NR by use of hot-air aging combined with DTA method and obtained satisfactory results.

EXPERIMENTAL

Apparatus and equipment

Electric heated air-blast oven, plastometer, TG/DTA-320 thermoanalyzer.

Preparation of test samples

Test samples A-1-1, A-1-2, and A-2 are prepared with the fresh latex provided by State Farm A in accordance

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with the following procedure: test samples A-1-1 and A-2 are prepared with fresh latex of different batches preserved with 0.03% ammonia; the latex is coagulated with acetic acid (to coagulate 100 g of fresh latex containing 20% dry rubber and 0.03% ammonia, 4.6 g of acetic acid with concentration of 5% will be needed). Test sample A-1-2 is prepared with the same batch of fresh latex as A-1-1, but treated with natural coagulation (i.e., the fresh latex collected from rubber trees is coagulated under room conditions without any coagulating agent added) of 7 days. All coagulum are processed on the production line in rubber processing factory of the State Farm A through creping, size reduction, and drying. The drying temperature is 115–120°C; the drying time is 4 h.

Sample B is prepared with the fresh latex provided by State Farm B with the following procedure on the production line in rubber processing factory of the State Farm B: biological coagulation (i.e., the microorganism was added into the 10% sugar solution for inoculation of 24 h, then add the solution into fresh latex for coagulation, 3 g of sugar should be added to the latex for every 100 g of dry rubber), creping, size reduction, and drying. The drying temperature is 115–120°C; the drying time is 4 h.

Sample C is prepared with the fresh latex provided by State Farm C. The latex is preserved with 0.03% ammonia and coagulated with acetic acid. The coagulum are processed on the production line in rubber processing factory of the State Farm C through creping, size reduction, and drying in an air-blast thermostatically controlled oven at 100°C. The drying time is 5 h.

Property-test

Hot-air aging test

Hot-air aging test of test samples A-1-1 and A-1-2 was carried out at same time in electric heated air-blast oven at $70 \pm 1(^{\circ}\text{C})$. The experimental time is 0, 5, 10, 15, and 16 days, respectively; then, take the samples out and determine their plasticity value.

The hot-air aging test of test samples A-2 and B was carried out at the same time in an electric heated

air-blast oven at $70 \pm 1(^{\circ}\text{C})$. The experimental time is 0, 4, 8, 12, 16, and 20 days, respectively; then, take the samples out and determine their plasticity value.

The hot-air aging of test sample C was carried out alone in an electric heated air-blast oven at $70 \pm 1(^{\circ}\text{C})$. The experimental time is 0, 4, 8, 12, 16, and 20 days, respectively; then, take the sample out and determine its plasticity value.

The plasticity determination was carried out with the method specified in ISO 2007:1991 Rubber, unvulcanized—Determination of plasticity—Rapid—Plasticimeter method.

The plasticity retention index (PRI) determination was carried out with the method specified in ISO 2930:1995 Rubber, raw natural—Determination of plasticity retention index.

TG-DTA test

TG-DTA test of the samples was carried out by using TG-DTA-320 thermoanalyzer (Seiko, Japan). The temperature rising rates of the samples A-1-1 and A-1-2 are 5, 7, 10, 15, and 20°C/min; temperature rising rates of the samples A-2 and B are 4, 5, 6, 8, and 10°C/min; and the temperature rising rates of sample C are 2.5, 4, 6, and 10°C/min. The air flow rate is 50 mL/min.

RESULTS AND DISCUSSION

Principle of method

The heat aging life equation^{1,7} of the high molecular weight materials is usually as follows:

$$\log \tau = a + \frac{b}{T} \quad (1)$$

where a —constant, the intercept of aging life line; b —constant, the slope of aging life line, $b = \frac{E}{2.303R}$, E is the activation energy of oxidation, and R is gas constant ($R = 8.314$). T —ambient temperature, K; τ is the time needed when the properties of high molecu-

TABLE I
Test Results of Heat Aging of NR

Code	Item	Aging time at 70°C (days)					Regression equation	Correlation coefficient	τ -value PRI' = 30 (days)
		0	5	10	15	16			
A-1-1	P_i	44.0	39.5	38.0	37.0	34.5	$\text{PRI}' = 79.96 - 0.807 \tau$	0.9560	62.0
	PRI'	100	89.8	86.4	84.1	78.4			
A-1-2	P_i	43.5	38.0	34.0	31.5	30.5	$\text{PRI}' = 53.76 - 0.546 \tau$	0.9896	43.5
	PRI'	100	87.4	78.2	72.4	70.1			

A-1-1, acetic acid coagulation; A-1-2, natural coagulation of 7 days.

TABLE II
Test Results of Heat Aging of NR

Code	Item	Aging time at 70°C (days)						Regression equation	Correlation coefficient	τ -value PRI' = 30 (days)
		0	4	8	12	16	20			
A-2	P_i	36.0	36.5	33.0	30.0	27.5	23.0	PRI' = 105.0-1.885 τ	0.9718	39.8
	PRI'	100	101.4	91.7	83.3	76.4	63.9			
B	P_i	54.0	51.0	43.0	33.5	28.0	21.5	PRI' = 103.2-3.186 τ	0.9933	23.0
	PRI'	100	94.4	79.6	62.0	51.9	39.8			
C	P_i	56.0	53.5	51.0	47.5	45.5	41.0	PRI' = 100.7-1.309 τ	0.9947	54.0
	PRI'	100	95.5	91.1	84.8	81.2	73.2			

A-2 and C, acetic acid coagulation; B, biological coagulation.

lar weight materials reaching at the out-of-service index, d .

The eq. (1) can be written as follows; at ambient temperature T_1 and T_2 ,

$$\log \tau_1 = a + \frac{b}{T_1} \quad (2)$$

$$\log \tau_2 = a + \frac{b}{T_2} \quad (3)$$

Let eq. (3) minus (2), we get:

$$\log \tau_2 - \log \tau_1 = \frac{b}{T_2} - \frac{b}{T_1} \quad (4)$$

$$\text{i.e. } \log \tau_2 = \log \tau_1 + \frac{E}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

According to the eq. (4), if we find out the life τ_1 of the material at temperature T_1 and the activation energy of oxidation E , then the aging life τ_2 of the material at temperature T_2 can be calculated out.

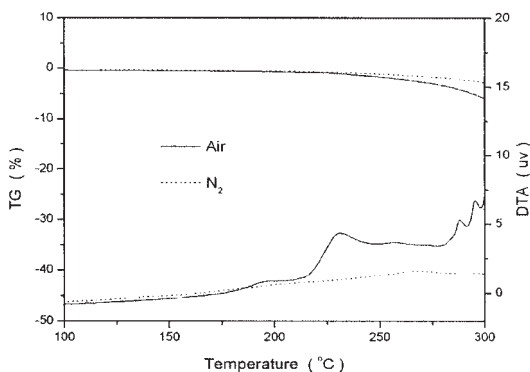


Figure 1 TG-DTA curves of acetic acid-coagulated rubber sample under air and nitrogen atmosphere with a heating rate of 6°C/min.

Hot-air aging test of NR

The main index indicating the heat aging resistance of raw NR is PRI. According to ISO 2930:1995 Rubber, raw natural—Determination of plasticity retention index (PRI), the PRI is determined by using rapid plastimeter. PRI is the ratio between rapid plasticity before and after heating 30 min at 140°C multiplied by 100, i.e.,

$$\text{PRI} = \frac{P_{30\text{min}}}{P_0} \times 100 \quad (5)$$

Considering that the aging temperature 140°C is too high, the aging reaction is too violent, which may arouse serious errors; therefore, the aging test is carried out in our experiment at 70°C with prolonged time; the sample is taken at certain interval and its plasticity is determined. To make a distinction between the PRI listed in ISO 2930:1995 and in our experiment, we use

$$\text{PRI}' = \frac{P_i}{P_0} \times 100 \quad (6)$$

where i for samples A-1-1 and A-1-2 is 0, 5, 10, 15, and 16 days, for samples A-2, B, and C is 0, 4, 8, 12, 16, and 20 days. The test results are listed in Tables I and II.

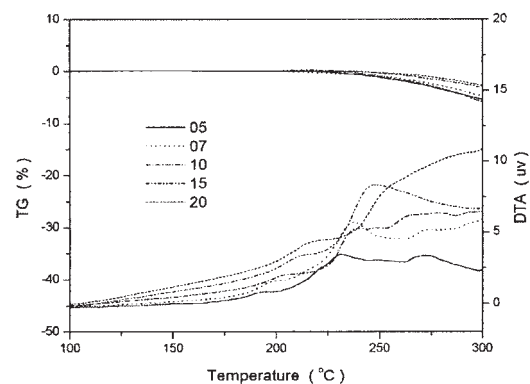


Figure 2 TG-DTA curves of sample A-1-1 under air atmosphere during various heating rates.

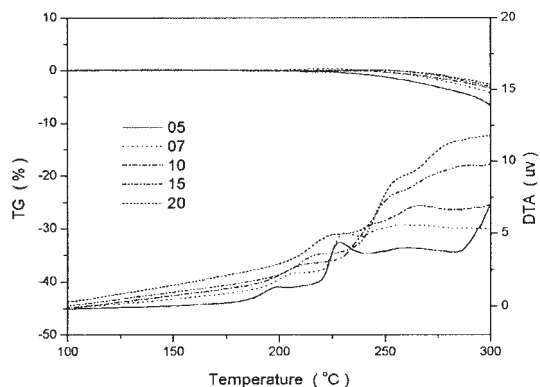


Figure 3 TG-DTA curves of sample A-1-2 under air atmosphere during various heating rates.

The regression treatment for PRI' data of all samples is conducted by the use of least square linear method. The equations obtained and the corresponding correlation coefficients are listed in Tables I and II, respectively.

According to the International Standard ISO 2000:1989 and Chinese Standard GB/T 8081-1999, the Standard Rubber 50 with PRI = 30 is still acceptable, which means the lowest value of PRI of the Standard Rubber 50 is 30 (i.e., $PRI \geq 30$). That is to say, the NR still maintains its usability when its PRI equals 30. Therefore, the least effective value of PRI for the raw rubber in our experiment is set as 30.

When the PRI is lower than that number, the NR is out-of-service. As we substitute PRI' with 30 in the regression equation, listed in Table I, the effective storage time τ of the samples at 70°C can be calculated out, which is listed in Tables I and II.

TG-DTA of NR

Determination of oxidation temperature of NR

As NR can oxidize slowly at ambient temperature, it is difficult to obtain oxidation data of NR at room tem-

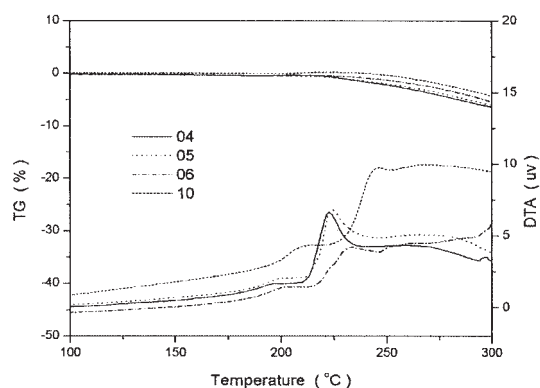


Figure 4 TG-DTA curves of sample A-2 under air atmosphere during various heating rates.

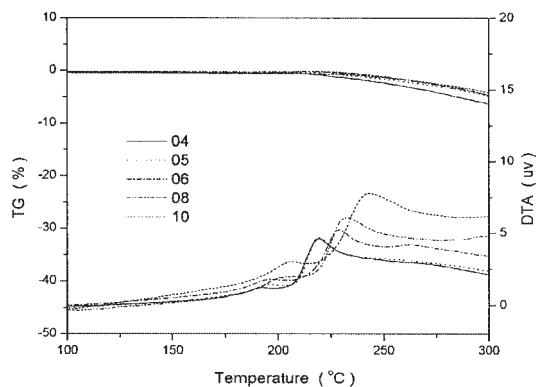


Figure 5 TG-DTA curves of sample B under air atmosphere during various heating rates.

perature. The oxidation of NR can be accelerated in a shorter time through heating, and the oxidation temperature of NR during heating can be acknowledged. The information of oxidation of NR can be obtained through analysis of these data. Figure 1 shows the TG-DTA curves of acetic acid-coagulated rubber samples under air and nitrogen atmospheres with a heating rate of 6°C/min. From Figure 1, it can be seen that the first exothermic peak of NR sample under air atmosphere appears at 185–205°C on the DTA curve, but the exothermic peak does not appear at the same place as stated earlier, on the DTA curve under nitrogen atmosphere. At the same time, there is a straight line on the TG curve, which indicates that the heat generation of NR within the scope of this temperature is an oxidative heat generation; the exothermic peak is the oxidative exothermic peak of NR.

Activation energy of oxidation reaction of NR

To solve the eq. (4), we must know the activation energy of oxidation E of NR. According to the temperature of the oxidation peak of NR found out by use

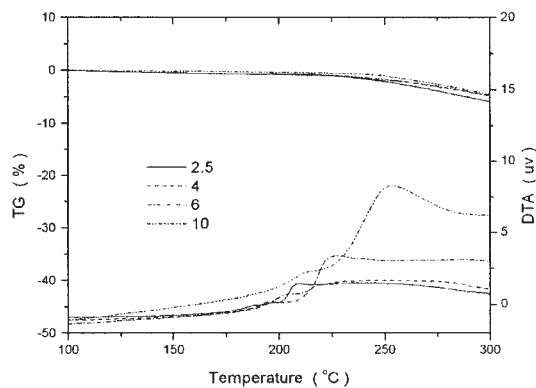


Figure 6 TG-DTA curves of sample C under air atmosphere during various heating rates.

TABLE III
Temperature T_p of Oxidative Exothermal Peak and Activation Energy of Oxidation Reaction of First Batch of Samples from State Farm A

Code	Temperature rising rate (°C/min)					Activation energy (kJ/mol)	Correlation coefficient
	5	7	10	15	20		
a-1-1	198.8	207.7	214.4	219.7	227.4	94.4	0.9923
a-1-2	195.8	200.8	207.4	214.4	219.8	104.8	0.9996

A-1-1, acetic acid coagulation; A-1-2, natural coagulation of 7 days.

of DTA method and according to Doyle–Ozawa equation,⁸

$$\frac{d \log \beta}{d(1/T_p)} = \frac{-0.4567E}{R} \quad (7)$$

Equation (7) can be converted to:

$$\log \beta = \frac{-0.4567E}{R} \frac{1}{T_p} + C \quad (8)$$

where β is heating rate (K/min or °C/min), T_p is the largest peak temperature (K) of the first oxidative exothermal peak, R is the gas constant ($R = 8.314$), and C is a constant. When a diagram is plotted with $\log \beta$ and $\frac{1}{T_p}$ as coordinates, a straight line is obtained by the use of least square regression method, the slope of the straight line is $\frac{-0.4567E}{R}$; from this, the value of E can be calculated out. C is the intercept of the straight line.

We can find out the activation energy of oxidation of NR. Figures 2–6 show the TG–DTA curves of samples A-1-1, A-1-2, A-2, B, and C. It can be seen from Figures 2–6 that, under various temperature rising rate, the TG curve is a straight line when the first exothermal peak appears on DTA curve, which indicates that the first exothermal peak on DTA curve is an oxidative exothermal peak. Following the highest peak temperature of the first exothermal peak on DTA curve at various temperature rising rate and the Doyle–Ozawa equation, the activation energy of oxidation

of various samples can be calculated out, and the results are listed in Tables III and IV.

Estimation of effective storage time of NR

According to the life time and activation energy of oxidation reaction of various samples during aging at 70°C, write the corresponding data into the eq. (4), then the effective storage time of various samples at ambient temperature of 30, 25, and 20°C can be obtained; the results are listed in Table V. From Table V, it can be seen that the effective storage time (i.e., storage life) of NR is related to rubber processing technology and ambient temperature during storage, but has little relation to P_0 and PRI. The effective storage time of the natural-coagulated and biological-coagulated NR is longer than that of the acetic acid-coagulated NR; the difference of the effective storage time between natural-coagulated and biological-coagulated NR is not obvious; the lower the storage temperature, the longer the storage life. The effective storage time of acetic acid-coagulated NR at ambient temperature of 30, 25, and 20°C is about 12.2–13.4 years, 23.8–25 years, and 47.4–47.9 years, respectively. The effective storage time of natural-coagulated NR and biological-coagulated NR at ambient temperature of 30, 25, and 20°C is 13.7–15.2 years, 29.6–30.4 years, and 62.5–65.8 years, respectively.

CONCLUSIONS

The effective storage time (i.e., storage life) of NR is related to rubber processing technology and ambient

TABLE IV
Temperature T_p of Oxidative Exothermal Peak and Activation Energy of Oxidation Reaction of Second Batch of Samples from State Farm A and Samples from B and C

Code	Temperature rising rate (°C/min)						Activation energy (kJ/mol)	Correlation coefficient
	2.5	4	5	6	8	10		
A-2		198.2	201.6	205.1		214.4	101.8	0.9995
B		192.4	195.8	197.4	202.5	206.3	116.3	0.9963
C	188.9	196.0		206.4		213.1	96.6	0.9917

A-2 and C, acetic acid coagulation; B, biological coagulation.

TABLE V
Predicted Data for Effective Storage Time of NR

Code	P_0	PRI	Storage life (days)			Storage life (years)		
			30°C	25°C	20°C	30°C	25°C	20°C
A-1-1	44.0	81.3	4.90×10^3	9.14×10^3	1.75×10^4	13.4	25.0	47.9
A-1-2	43.5	65.8	5.56×10^3	1.11×10^4	2.28×10^4	15.2	30.4	62.5
A-2	36.0	86.1	4.44×10^3	8.69×10^3	1.75×10^3	12.2	23.8	47.9
B	54.0	65.7	5.01×10^3	1.08×10^4	2.40×10^4	13.7	29.6	65.8
C	44.5	86.5	4.72×10^3	8.95×10^3	1.73×10^4	12.9	24.5	47.4

A-1-1, A-2, and C, acetic acid coagulation; A-1-2, natural coagulation of 7 days; B, biological coagulation. The values of P_0 and PRI were obtained before heat storage aging of the samples according to the method stipulated in ISO 2007 : 1991 and ISO 2930 : 1995.

temperature during storage, but has little relation to P_0 and PRI. The effective storage life of the natural-coagulated and biological-coagulated NR is longer than that of the acetic acid-coagulated NR. The difference of the effective storage time between natural-coagulated NR and biological-coagulated NR is not obvious; the lower the storage temperature, the longer the storage life. The effective storage time of the acetic acid-coagulated NR is 12.2–13.4 years at ambient temperature of 30°C, 23.8–25 years at 25°C, and 47.4–47.9 years at 20°C. The effective storage time of the natural- and biological-coagulated NR is 13.7–15.2 years at 30°C, 29.6–30.4 years at 25°C, and about 62.5–65.8 years at 20°C.

Calculation of effective storage time of raw NR is carried out through determination of PRI of NR at different heat aging time. The effective storage time of raw NR can be calculated out by the use of the method for determination of PRI of NR at different heat aging time and combined with DTA; the test results ob-

tained conform more truly to the practical conditions. This is a relatively accurate, economic, and convenient method for estimation of the effective storage time of NR. This method can estimate the effective storage time of NR with a more simple way in a shorter time, which possesses reference value in practical production.

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