Influences of Coagulum Maturation Time of Rubber Latex Coagulated with Formic Acid and Microorganism on the Effective Storage Time of Natural Rubber

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Fresh NR latex was coagulated using formic acid and microorganism. The resulting coagula were matured at various conditions, followed by creping, size reduction and drying at 115ºC for 5 hours. The dried coagula were then scanned using differential scanning calorimetry (DSC) and aged at various ageing times at 70ºC. The effective storage time (i.e. storage life) of the coagula was evaluated through heat accelerated storage ageing combined with the Doyle-Ozawa equation and the heat ageing life equation. The results showed that the effective storage time of natural rubber prepared by the coagulum of fresh latex coagulated with formic acid and matured for 6, 12, 18 and 24 h respectively increased to 45.6 years from 23.2 years at 30ºC, and increased to 100.5 years from 46.7 years at 25ºC. The effective storage time of natural rubber prepared by the coagulum of fresh latex coagulated with microorganisms and matured for 6, 12, 18 and 24 h respectively increased to 83.3 years from 57.7 years at 30ºC, and increased to 206.3 years from 132.8 years at 25ºC. Both effective storage time of natural rubbers coagulated with formic acid and microorganism increased with the prolonging of coagulum maturation time. The effective storage time of NR from the coagulum matured for 6−12 h increased fast, the effective storage time of NR prepared by the coagulum matured for 12−18 h increase slowly and the increase in the effective storage time of NR prepared by the coagulum matured for 18−24 h tend to be flat. The effective storage time of natural rubber coagulated with microorganisms is obviously longer than that of natural rubber coagulated with formic acid in the same storage conditions.

Keywords: Natural rubber; fresh latex; coagulum maturation; ageing; effective storage time

Natural rubber (NR) is prepared by processing of the latex of *Hevea brasiliensis* (rubber trees) through coagulation, maturation, creping, size reduction and drying, where each processing step will significantly affect the properties of NR[1]. There are three kinds of coagulation methods for fresh latex at present. The first is coagulation with acid (formic acid or acetic acid), the second is natural coagulation and the third is coagulation with microorganisms. The

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time for acid coagulation is shorter. However, the acid would destroy some non-rubber substances in fresh latex which will affect the rubber performance. The production cost of acid coagulation method is relatively high and the effluent produced during the production could also cause serious environmental pollution. The production cost of natural coagulation method is relatively low with a relatively good NR quality, but the coagulation time of fresh latex is longer than that of acid coagulation. It was reported[2–5] that fresh latex can be coagulated with microorganism.

However, the method of coagulation with microorganism has not been applied in production. The method of coagulation with microorganism developed in recent years has such advantages as shorter coagulation time, lower production cost, better product quality and less pollution[6]. The fresh latex after coagulation will form coagulum. The time of coagulum maturation has significant effect on the properties of NR. Previous studies showed[7–8] that by prolonging the coagulum maturation time, the nitrogen content decreased, the initial plasticity (P_0), Mooney viscosity and curing rate increased, the tensile strength increased at first and then decreased and the plasticity retention index (PRI) only slightly changed. Other non-rubber constituents will also change with the prolonging of coagulum maturation time. Such change will affect the mechanical, heat build-up and ageing properties of NR. The effective storage time (*i.e.* storage life) of NR depends upon its ageing resistance.

During the storage of NR at room temperature, the NR molecules will undergo degradation due to environmental factors, mainly light, heat and oxygen, causing the NR to depolymerise and become non-elastic and lose its performance characteristics. Zhang *et al.*[9] have studied the effective storage time of NR at different storage conditions. However, no report is available concerning the relationship between the coagulum maturation time and the effective storage time of NR.

The coagulum maturation time is generally 12–18 h during production and up to 24 h in special circumstances. Therefore, the investigation into the influences of coagulum maturation time on the effective storage time of NR will be useful in the production and application of NR.

In this work, fresh latex was coagulated with formic acid and microorganism, the coagulum was then matured for 6, 12, 18 and 24 h, respectively. The effective storage time of raw NR prepared from the matured coagulum was predicted by the use of hot air ageing combined with differential scanning calorimetry (DSC) according to the method[9].

EXPERIMENTAL

Materials

The fresh latex (Dry rubber content: 30%, ammonia content: 0.04%) was obtained from Fenyong Farm in Guangdong Province, P.R. China and the formic acid was of chemical grade. The microorganism coagulant was prepared by adding a type of microorganism into a solution of 5% molasses and cultivating for 24 hours.

Sample Preparation

NR coagulated with formic acid. Eighty kilogrammes of fresh latex was coagulated with formic acid and the level of formic acid used is 0.4% of the weight of dry rubber. The formic acid was diluted to a concentration of 5% before adding into the fresh latex. The formic acid for neutralisation of ammonia in fresh latex used is 0.04% of the weight of fresh latex added at the same time as coagulation.

The coagulum was matured for 6, 12, 18 and 24 h at room temperature respectively, then processed through creping, size reduction and drying. The drying was carried out in a convection oven at 115ºC for 5 hours. The maturation time was calculated once the formic acid was added into the fresh latex.

NR coagulated with microorganism. The microorganism was added into 80 kg of fresh latex for coagulation and the level of microorganism coagulant is 40% of the weight of dry rubber in the latex. The mixture was stirred well immediately after the microorganism coagulant was added into the fresh latex and then allowed to stand for coagulation. The coagulum was matured for 6, 12, 18 and 24 h respectively, then processed through creping, size reduction and drying. The drying was carried out in an oven at 115ºC for 5 hours. The maturation time was calculated once the microorganism was added into the fresh latex.

Method

The DSC tests of the NR samples were carried out by using a differential scanning calorimeter DSC-220 (Seiko Instruments Inc). The temperature rising rates were 4, 5, 6, 8 and 10ºC/min. The air flow rate was 50 ml/min.

The thermal ageing of the NR samples was carried out at the same time in a hot air oven at 70 ± 0.1ºC with an ageing time of 0, 5, 10, 15 and 20 days and their plasticity value was determined after ageing, respectively.

The initial plasticity of the NR sample was determined according to *ISO 2007:2007* Rubber, Unvulcanized — Determination of Plasticity-Rapid-Plastimeter.

The plasticity retention index (PRI) of NR sample was determined according to

ISO 2930:2009 Rubber, Raw Natural — Determination of Plasticity Retention Index (PRI).

RESULTS AND DISCUSSION

Thermal Ageing Life Equation of the High Molecular Weight Material

The thermal ageing life equation of the high molecular material is as follows:

$$\lg \tau = a + \frac{b}{T} \qquad \dots 1$$

Where: a − constant, the intercept of ageing life line

b − constant, the slope of ageing life line, $b = \frac{E}{2.303R}$, E is the activation energy of oxidation, R is the gas constant (R=8.314)

T − ambient temperature, K

τ − time needed when the properties of high molecular material reaching the out−of−service index, d.

The *Equation 1* can be rewritten as follows at ambient temperatures T_1 and T_2.

$$\lg \tau_2 + \lg \tau_1 + \frac{E}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad \dots 2$$

According to the *Equation 2*, if the life τ_1 of the material at temperature T_1 and the activation energy of oxidation E can be found out, then the ageing life τ_2 of the material at temperature T_2 can be calculated.

Hot Air Ageing Test of NR

The main index indicating the heat ageing resistance of raw NR is the plasticity retention

index (PRI). According to *ISO 2930:2009*, PRI is the ratio between rapid plasticity before and after heating for 30 min at 140ºC multiplied by 100,

$$PRI = \frac{P_{30\ min}}{P_0}\ 100 \qquad \ldots 3$$

PRI can also be used as a main indicator for heat ageing resistance of NR.

Considering that the ageing reaction is too vigorous at ageing temperature 140ºC, which may cause serious errors, the ageing test was carried out at 70ºC with prolonged time where the sample was taken out at certain intervals and the plasticity was determined. In order to make a distinction between the PRI listed in *ISO 2930:2009* and our experiment, the PRI in our experiment is presented as PRI′.

$$PRI' = \frac{P_i}{P_0} \times 100 \qquad \ldots 4$$

Where *i* is 0, 5, 10, 15 and 20 days.

The hot air ageing test results of NR coagulated with formic acid are listed in *Table 1*, and those of NR coagulated with microorganism are listed in *Table 2*.

TABLE 1. HOT AIR AGEING RESULTS OF NR COAGULATED WITH FORMIC ACID
AND MATURED AT DIFFERENT HOURS

Maturation time (h)	Item	Ageing time at 70ºC (d)					Regression equation	Correlation coefficient	τ value PRI′ =30 (d)
		0	5	10	15	20			
6	P_0	62.0	59.0	56.0	53.0	48.0			
	PRI′	100	95.2	90.3	85.5	77.4	PRI′=100.65–1.0968τ	0.9965	64.41
12	P_0	63.5	60.0	57.0	54.0	50.5			
	PRI′	100	94.5	89.8	85.0	79.5	PRI′=99.843–1.0079τ	0.9998	69.30
18	P_0	62.0	59.0	56.5	53.0	51.0			
	PRI′	100	95.2	91.1	85.5	82.3	PRI′=99.839–0.9032τ	0.9987	77.32
24	P_0	63.0	60.0	56.5	53.5	50.0			
	PRI′	100	95.2	89.7	84.9	79.4	PRI′=100.16–1.0317τ	0.9999	68.00

TABLE 2. HOT AIR AGEING RESULTS OF NR COAGULATED WITH MICROORGANISM
AND MATURED AT DIFFERENT HOURS

Maturation time (h)	Item	Ageing time at 70ºC (d)					Regression equation	Correlation coefficient	τ value PRI′ =30 (d)
		0	5	10	15	20			
6	P0	73.0	69.0	65.0	61.0	57.0			
	PRI′	100	94.5	89.0	83.6	78.1	PRI′=100–1.0959t	1.0000	63.87
12	P0	71.0	66.5	63.0	60.0	55.0			
	PRI′	100	93.7	88.7	84.5	77.5	PRI′=99.718–1.0845t	0.9983	64.29
18	P0	71.0	67.0	62.5	58.5	53.5			
	PRI′	100	94.4	88.0	82.4	75.4	PRI′=100.28–1.2254t	0.9996	57.35
24	P0	71.5	67.0	62.5	58.0	53.5			
	PRI′	100	93.7	87.4	81.1	74.8	PRI′=100–1.2587t	1.0000	55.61

The regression treatment for PRI′ data of all samples was conducted by the use of least square linear method, the equations obtained and the corresponding correlation coefficients are listed in *Tables 1* and *2*. It can be seen from data in *Tables 1* and *2* that the PRI′ was related to τ with good correlation coefficient. The least effective value of PRI′ for raw natural rubber in our test was set as 30 according to literature[11]. The PRI′ in the regression equations listed in *Tables 1* and *2* were substituted with this minimum acceptable value of 30 to calculate the effective storage times at 70ºC, which are listed in *Tables 1* and *2*.

Activation Energy of NR Oxidation

NR can oxidise slowly at ambient temperature and oxidation will be faster at hot air (hot oxygen) atmosphere. The hot oxygen resistance for NR is closely related to its oxidation kinetics. It is difficult to obtain oxidation data of NR at room temperature. The oxidation temperature of NR during heating can be obtained if the oxidation of NR can be accelerated in a shorter time through heating. The information of oxidation of NR can be obtained through analysis of these data. Zhang *et al.*[11] demonstrated that the first exothermic peak appearing at 185−205ºC is an oxidation exothermic peak of natural rubber in an air atmosphere. DSC can measure the temperature of the oxidation exothermic peak more accurately. The oxidation activation energy E of NR can be obtained by the Doyle−Ozawa Equation[10].

$$\frac{d \log}{d\,(1/T_p)} \quad \frac{0.4567E}{R} \qquad \dots 5$$

Equation 5 can be converted to

$$\log \beta = \frac{0.4567E}{R}\,\frac{1}{T_p} + C \qquad \dots 6$$

Where β is heating rate (K/min or ºC/min), T_p is the highest peak temperature (K) of the first oxidation exothermal peak, R is the gas constant (R = 8.314) and C is a constant.

When log β is plotted with $1/T_p$, a straight line is obtained by using the least square regression method, the slope of the straight line is –0.4567E/R and the value of E can be calculated and C is the intercept of the straight line.

The Oxidative Activation Energy of NR Coagulated with Formic Acid

The DSC curves for NR coagulated with formic acid are shown in *Figures 1* to *4*, respectively. The highest peak temperature of the first exothermal peak at heating rate 4, 5, 6, 8 and 10ºC/min and the oxidative activation energy calculated according to Doyle − Ozawa Equation are listed in *Table 3*.

The Activation Energy of Oxidation of NR Coagulated With Microorganism

The DSC curves for NR coagulated with microorganism are shown in *Figures 5* to *8*, respectively. The highest peak temperature of the first exothermal peak in heating rate 4, 5, 6, 8 and 10ºC/min and the oxidative activation energy calculated according to Doyle−Ozawa Equation are listed in *Table 4*.

Estimation of Effective Storage Time of NR and the Effect of Coagulum Maturation Time

According to lifetime and the oxidative activation energy of various samples during ageing at 70ºC (*Tables 1* to *4*), the effective storage time of various samples at ambient temperature of 30 and 25ºC can be obtained
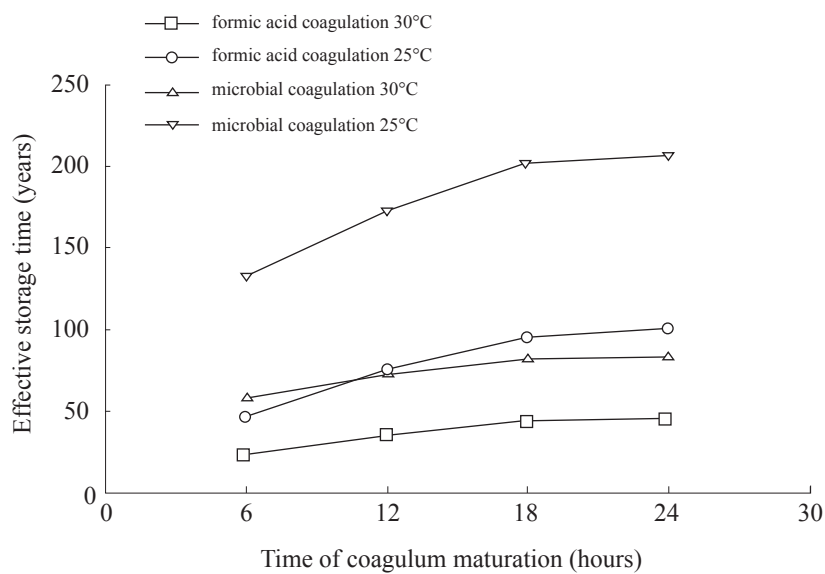
Figure 1. DSC curve for NR from coagulum matured for 6 h with formic acid.
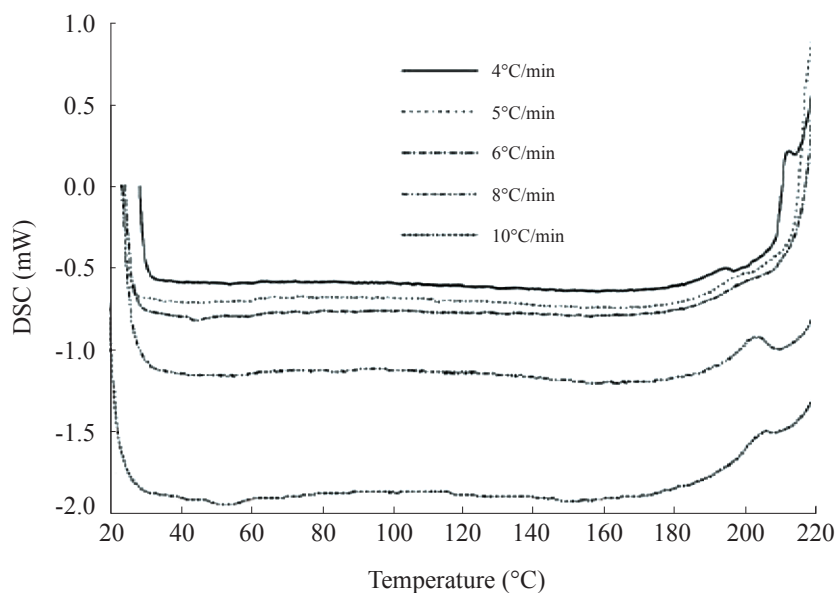

Figure 2. DSC curve for NR from coagulum matured for 12 h with formic acid.
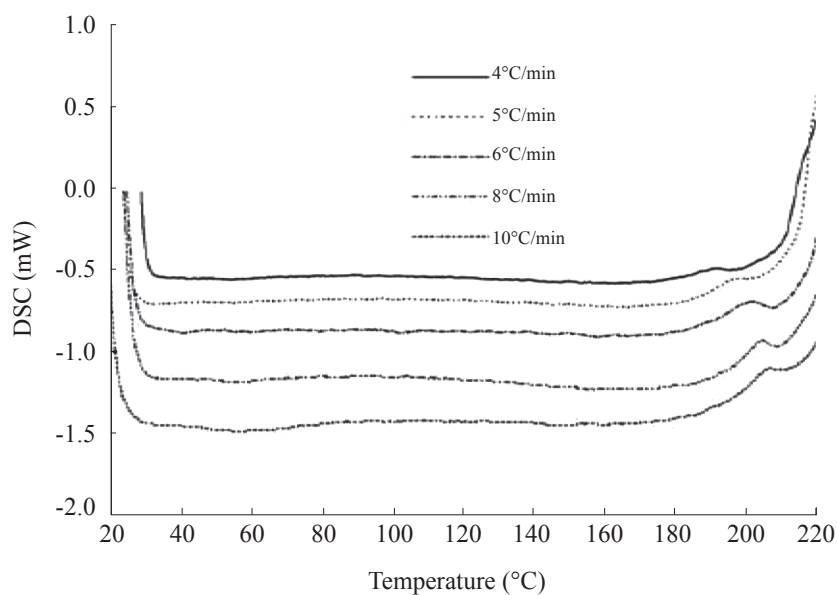
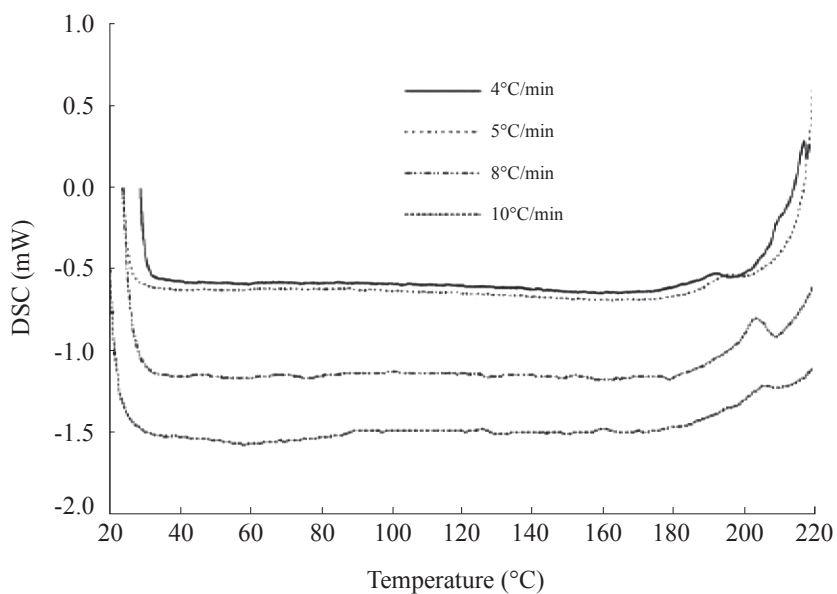*Figure 3. DSC curve for NR from coagulum matured for 18 h with formic acid.*

Figure 4. DSC curve for NR from coagulum matured for 24 h with formic acid.
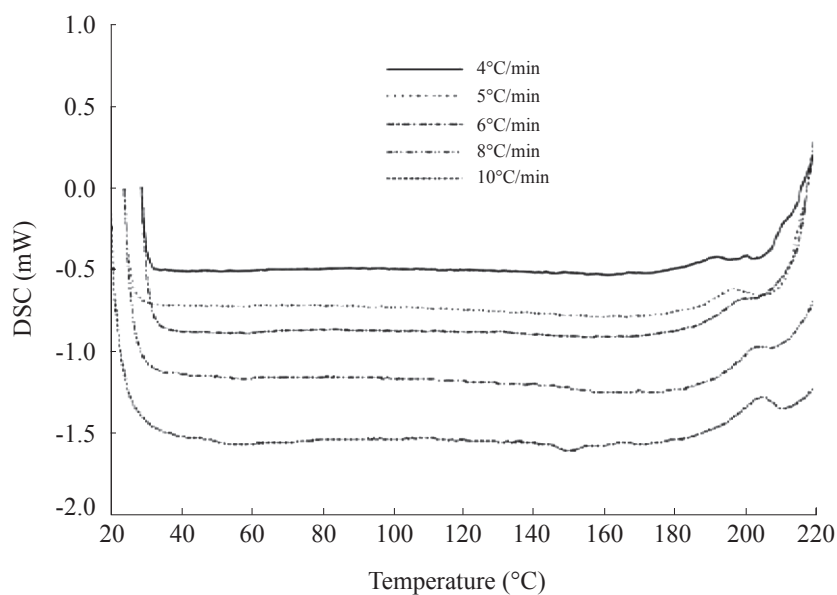
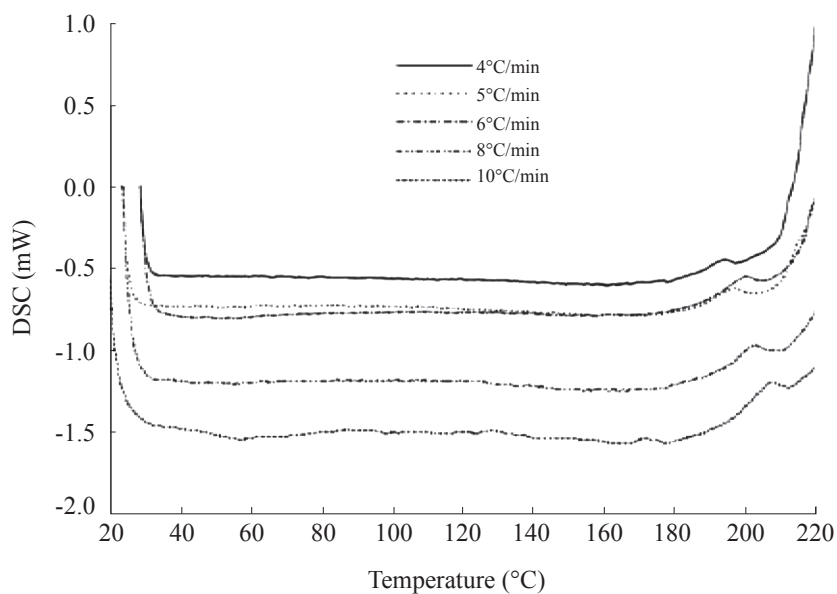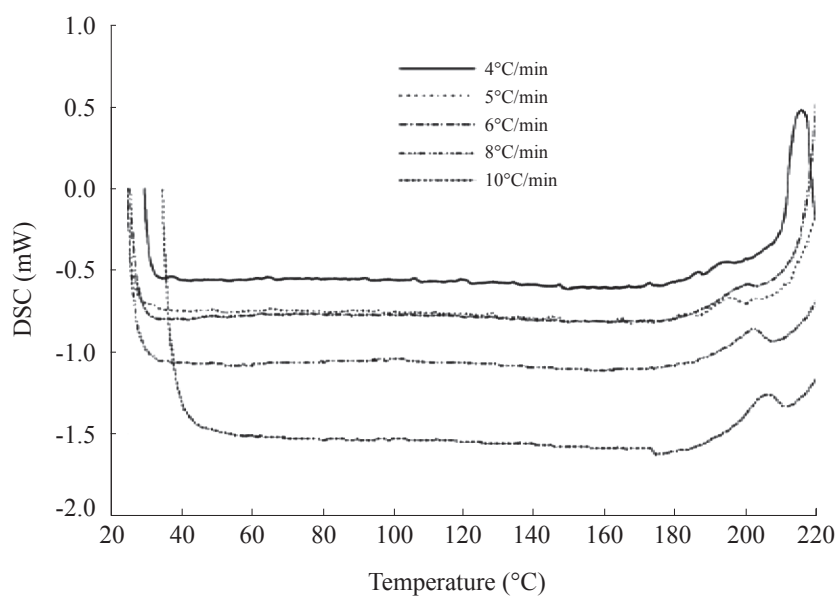*Figure 5. DSC curve for NR from coagulum matured for 6 h with microorganism.*

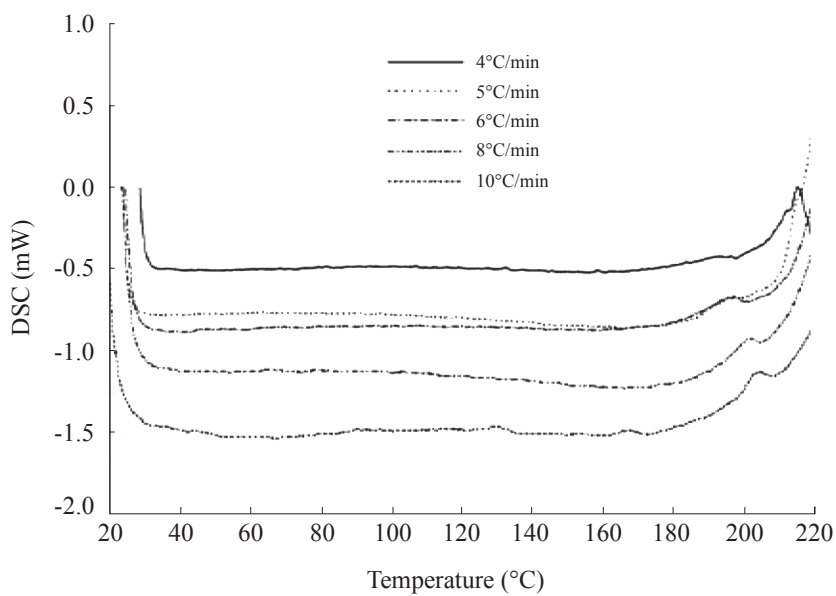*Figure 6. DSC curve for NR from coagulum matured for 12 h with microorganism.*

Figure 7. DSC curve for NR from coagulum 18 h with microorganism.

Figure 8. DSC curve for NR from coagulum matured for matured for 24 h with microorganism.

TABLE 3. THE HIGHEST PEAK TEMPERATURE OF THE FIRST EXOTHERMAL PEAK AND THE OXIDATIVE ACTIVATION ENERGY FOR NR COAGULATED WITH FORMIC ACID

| Maturation time (h) | Heating rate (ºC/min) | | | | | Activation energy (kJ/mol) | Correlation coefficient |
| | 4 | 5 | 6 | 8 | 10 | | |
	Highest peak temperature of the first exothermal peak (ºC)						
6	191.92	196.65	201.78	204.30	206.49	105.5	0.9849
12	194.63	196.70	203.89	204.69	206.97	113.1	0.9697
18	192.63	196.16		203.26	206.70	115.0	0.9999
24	192.31	196.66	199.96	203.99	205.21	118.9	0.9909

TABLE 4. THE HIGHEST PEAK TEMPERATURE OF THE FIRST EXOTHERMAL PEAK AND THE OXIDATIVE ACTIVATION ENERGY FOR NR COAGULATED WITH MICROORGANISM

| Maturation time (h) | Heating rate (ºC/min) | | | | | Activation energy (kJ/mol) | Correlation coefficient |
| | 4 | 5 | 6 | 8 | 10 | | |
	Highest peak temperature of the first exothermal peak (ºC)						
6	194.00	196.78	200.60	202.75	207.11	125.4	0.9954
12	193.72	195.52	200.10	202.01	205.75	130.2	0.9922
18	193.58	196.65	197.92	202.53	205.47	135.7	0.9980
24		196.16	199.62	202.83	205.28	136.3	0.9957

TABLE 5. PREDICTED DATA FOR EFFECTIVE STORAGE TIME OF NR

| Coagulum maturation time (h) | Formic acid coagulation | | | | Microorganism coagulation | | | |
| | Effective storage time (days) | | Effective storage time (years) | | Effective storage time (days) | | Effective storage time (years) | |
	30ºC	25ºC	30ºC	25ºC	30ºC	25ºC	30ºC	25ºC
6	8.46×103	1.71×104	23.2	46.7	2.11×104	4.85×104	57.7	132.8
12	1.29×104	2.74×104	35.4	75.2	2.65×104	6.31×104	72.6	172.8
18	1.61×104	3.47×104	44.1	95.1	2.99×104	7.36×104	81.9	201.6
24	1.66×104	3.67×104	45.6	100.5	3.04×104	7.53×104	83.3	206.3

by using *Equation 2*. The results are listed in *Table 5*. The curves in *Figure 9* show the change of the effective storage time at ambient temperature of 30 and 25ºC of NR coagulated with formic acid and with microorganism and matured for 6, 12, 18 and 24 h, respectively.

It can be seen from *Table 5* and *Figure 9* that both the effective storage time of NR prepared by microorganism and formic acid coagulation increase with the prolonged time of coagulum maturation. The effective storage time of NR maturated for 6 −12 h increases rapidly, the effective storage time of NR maturated for 12 – 18 h, increases slowly and the increase in the effective storage time of NR maturated for 18 – 24 h tends to be flat. The effective storage time of NR at ambient temperature of 25ºC increases faster than that of NR at ambient temperature of 30ºC. The effective storage time of NR prepared by microorganism coagulation is much longer than that of NR prepared by formic acid coagulation when NR is stored at the
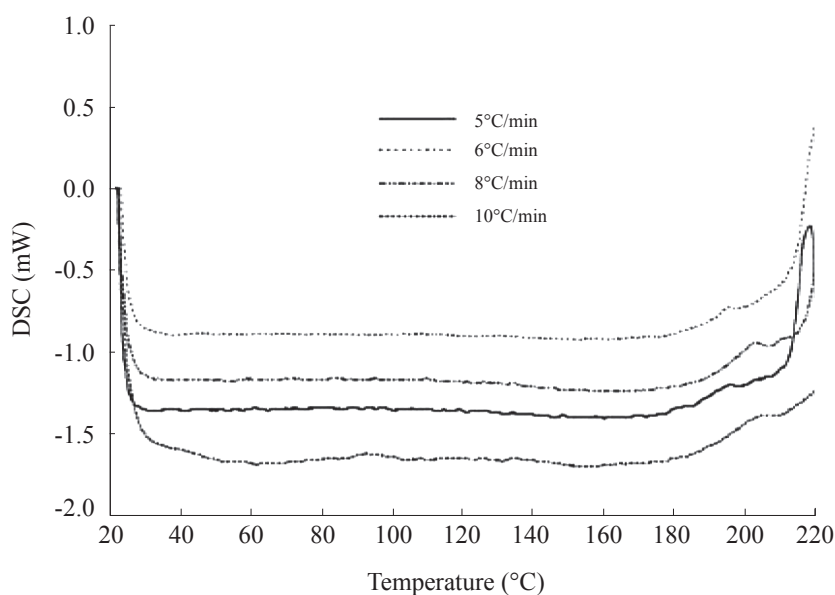
Figure 9. Relationship between the effective storage time and the time of coagulum maturation.

same condition. The non-rubber constituents especially the natural antioxidant contents will also change with the prolonging of coagulum maturation time, as a result of microbial action, changing the protein in NR latex metabolism into antioxidants. Temperature is also one of the factors affecting ageing of rubber. Higher temperature resulted in poorer ageing resistance of NR, causing the effective storage time of microorganism to be higher than that of acid and coagulum coagulated at 25ºC is higher than that of 30ºC. Meanwhile, acid coagulation at 25ºC is the same as that of microorganism at 30ºC and the storage time increases with maturation time.

CONCLUSION

The effective storage time of NR prepared by formic acid coagulation and matured for 6, 12, 18 and 24 h respectively is 23.2, 35.4, 44.1 and 45.6 years when NR is stored at 30ºC, and is 46.7, 75.2, 95.1 and 100.5 years when NR is stored at 25ºC. The effective storage time of NR prepared by microorganism coagulation and matured for 6, 12, 18 and 24 h respectively is 57.7, 72.6, 81.9 and 83.3 years when NR is stored at 30ºC and is 132.8, 172.8, 201.6 and 206.3 years when NR is stored at 25ºC. Both effective storage time of NR prepared by microorganism and formic acid coagulation increased with the prolonging of coagulum maturation. The effective storage time of NR prepared by the coagulum matured for 6 – 12 h increased rapidly, the effective storage time of NR prepared by the coagulum matured for 12 – 18 h increased slowly and the increase in the effective storage time of NR prepared by the coagulum matured for 18 – 24 h tended to be flat. In conclusion, the effective storage time of NR prepared by microorganism coagulation is longer than that of NR prepared by formic acid coagulation technology when NR is stored at the same condition.

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