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Drying Characteristics and Dynamic Model of Chlorinated Natural Rubber from Latex

YANG LEI*#, ZHONG JIE-PING**, CHEN JING***, CHEN QU-YUN* AND FU XIN**

Drying characteristics of chlorinated natural rubber (CNR) from latex were analysed through drying experiments by suspending CNR cubes in an air chamber at different drying temperatures, air velocity and granularity. Two different models were adopted to predict the two drying phases of CNR. It was found that the two drying models could accurately represent the drying characteristics of CNR SAS was used to estimate parameters in the drying model and a drying constant. Chemical and viscosity methods were also used to measure the effect of drying temperature on physical and chemical properties

Key words: drying; temperature; dynamic model; chlorinated natural rubber; latex; physical properties; chemical properties

Chlorinated Natural Rubber (CNR), which is traditionally prepared by the chlorination of natural rubber in CCl_4 solution, has excellent film formation, penetrance, inflammation resistance, corrosion resistance properties, and thermal stability[1]. It has been broadly applied as raw material for paints, inks, adhesives and acid- and alkali-proof products. The traditional CCl_4-solution process is prohibited in many countries because of its many disadvantages, including high equipment investment cost and hazard to the environment and health of workers. This makes the production of CNR from latex an attractive alternative process. Zhong and others[2–6] studied the preparation of CNR in aqueous media. There were also studies conducted on the molecular structure of CNR by IR spectroscopy and NMR[7–12]. The applications and chlorination mechanism of CNR has been studied in detail[13–20]. However, until now, there have been few reports on the drying characteristics of CNR from latex. In this article, we report on a study of the drying processes of CNR from latex by suspending CNR granules in a drying chamber.

The objectives of this study are to develop an equation for drying and determine parameters such as drying constants in the equation; and to analyse the effect of drying temperature on its physical and chemical properties.

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EXPERIMENTAL

Materials

Distilled water was added to a three-necked, round-bottom flask. The temperature was kept constant with a water bath. Chlorine gas was passed into the water until saturation was reached. Natural rubber (NR) latex, which was stabilised with Vulcanstab LW®, was added while the mixture was being stirred. At the same time, chlorine gas was continuously passed into the flask. CNR with preliminary chlorination was produced. The chlorine gas continued to pass into the flask for a predetermined reaction time, thereafter the reaction was stopped. The product was neutralised with dilute sodium hydroxide solution, filtered and washed with distilled water. The chlorine content of the resulting wet CNR sediment was 65% (by the method of *Q/HG6-012-87*[21]).

The CNR product from the same batch was shaped into rectangular cubes with three different measurements of 30×30×30 mm, 22.5×22.5×22.5 mm and 16×16×16 mm (by pushing through cubic moulds). These cubes were then put into an air-tight vessel partly filled with water and kept for two days, at least.

Experimental Apparatus

In the drying experiments, a drying chamber with an air circulation system was used. A piece of CNR cube was suspended in the chamber with a steel wire from a balance on the chamber. The experimental apparatus is shown in *Figure 1*.

Changes in the weight of CNR cube were determined using the electric balance (Shanghai Precision Science Instrument Ltd.,

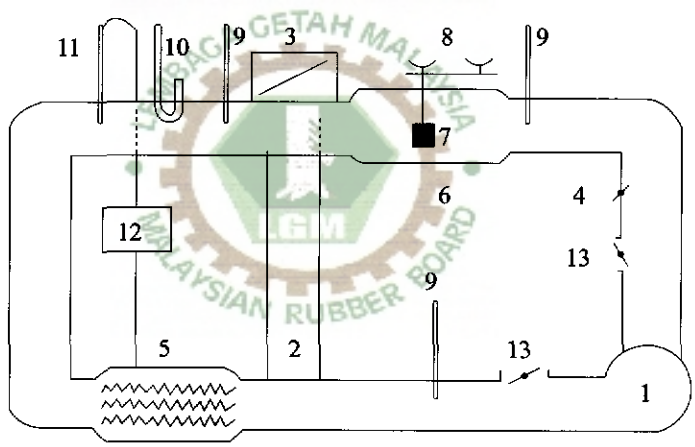

Figure 1. Experimental apparatus.

1: Blower; 2: Oriffice meter; 3: Differential pressure meter; 4: Valve; 5: Heater; 6: Drying chamber; 7: Sample; 8: Weighing balance; 9: Dry bulb thermometer; 10: Wet bulb thermometer; 11: Thermometer ; 12: Contact; 13: Valve.

FA2004, linear error ±0.0005 g) without interrupting the drying. Air temperature was controlled by thermometer. Air velocity was calculated and determined with the values of differential pressure meter.

Methods

Experiments were carried out using three different sizes of CNR cubes under different air temperatures and velocity. After experimental conditions were set and kept constant, the sample was taken from the air-tight vessel and weighed by an electric balance (Shanghai Precision Science Instrument Ltd., FA2004, linear error ±0.0005 g). The sample was then suspended in the drying chamber and the weight of the sample and the string was cleared out from the LED of the electric balance (Shanghai Precision Science Instrument Ltd., FA2004, linear error ±0.0005 g) above the chamber. The time spent for the moisture loss were recorded continuously until the moisture was constant. The initial moisture was determined by the method[21] of *Q/HG6-012-87*.

The effect of drying temperatures on physical and chemical properties of CNR was measured using chemical and viscosity methods.

Solubility and viscosity, chlorine content and initial moisture content of the cubes (%, d.b) were determined by the method[21] of *Q/HG6-012-87*.

RESULTS AND DISCUSSION

Effect of Temperature on Drying Characteristics

It has been reported that the emitting temperature[22] of hydrogen chloride was about 123°C; so experiments on cubes with measurements of 30×30×30 mm were carried out at air temperatures of 50°C, 60°C, 70°C, 80°C, 90°C and 98°C, respectively, and in a constant air velocity of u=2.44 m/s. The changes in moisture content and drying rate corresponding to air temperature are shown in *Figures 2* and *3*, respectively. X represents average moisture content of the cubes (%, d.b), X_0 represents initial moisture content (%, d.b) and X^* represents equilibrium moisture content (%, d.b).

Effect of Air Velocity on Drying Characteristics

Experiments on the cubes with measurements of 30×30×30 mm were carried out at a constant air temperature of 55°C and different air velocities of 1.84 m/s, 2.43 m/s and 3.32 m/s, respectively. The changes in moisture content and drying rate corresponding to air velocity are shown in *Figures 4* and *5*, respectively.

Effect of the Size of CNR Cubes on Drying Characteristics

Experiments were carried out at an air temperature of 60°C and air velocity of 2.44 m/s on the cubes with three different measurements of 30×30×30 mm, 22.5×22.5×22.5 mm and 16×16×16 mm, respectively. The changes in moisture content and drying rate corresponding to the measurements of the cubes are shown in *Figures 6* and *7*, respectively.

Analysis of Drying Mechanism and Derivation of Dynamic Model

The curves of drying rate (*Figures 3*, *5* and *7*) show two different drying phases during the drying period. In the first phase, the drying rate

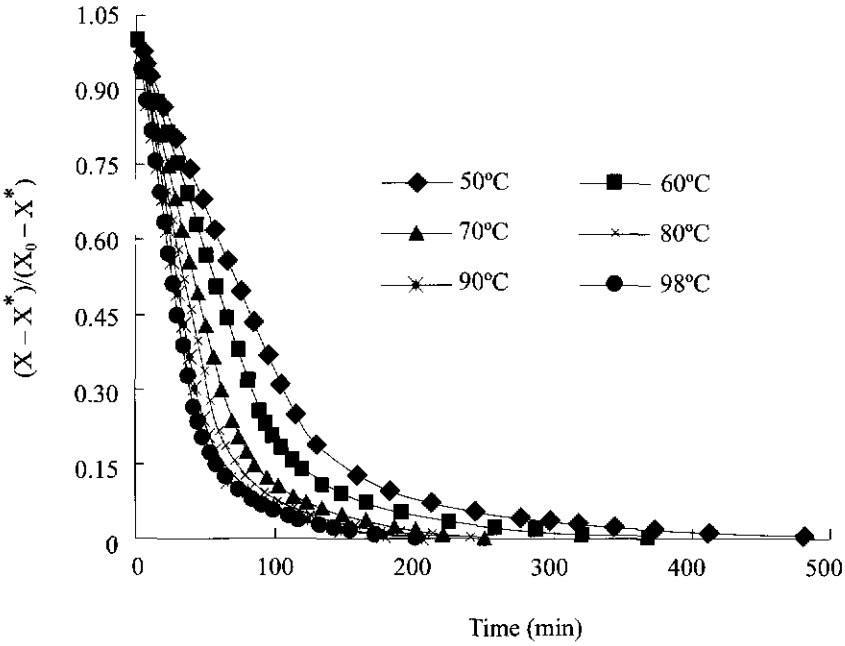

Figure 2. Changes in moisture content at varying temperature.

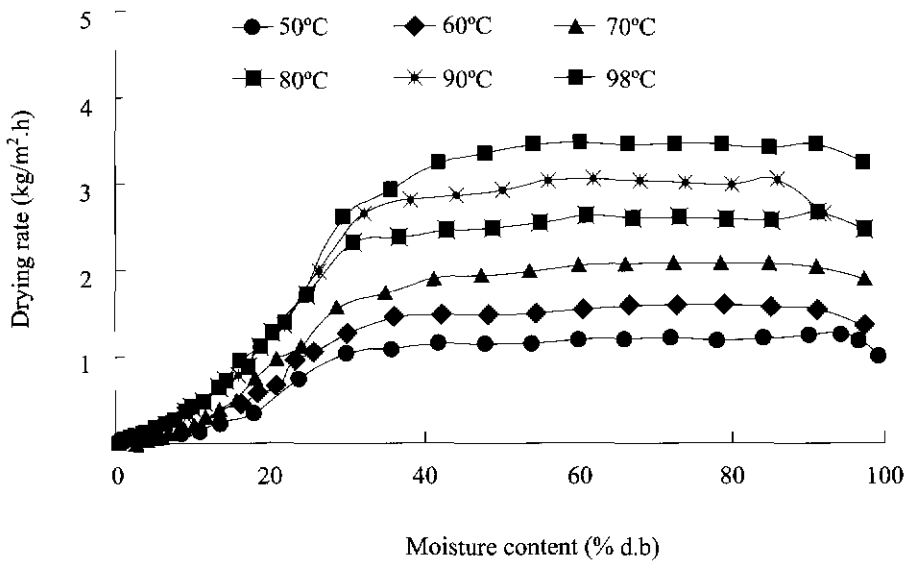

Figure 3. Changes in the drying rate at varying temperatures.

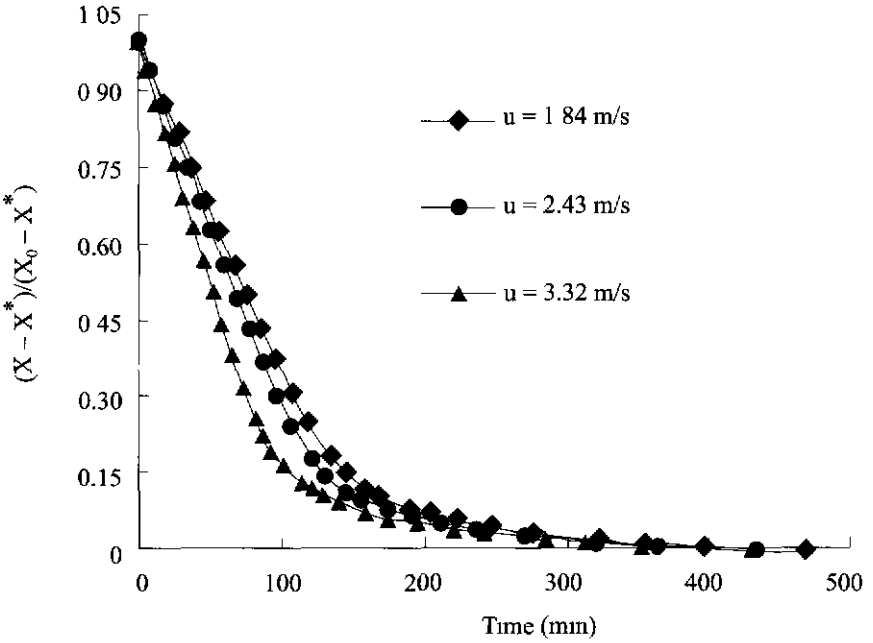

Figure 4 Changes in moisture content at varying air velocity

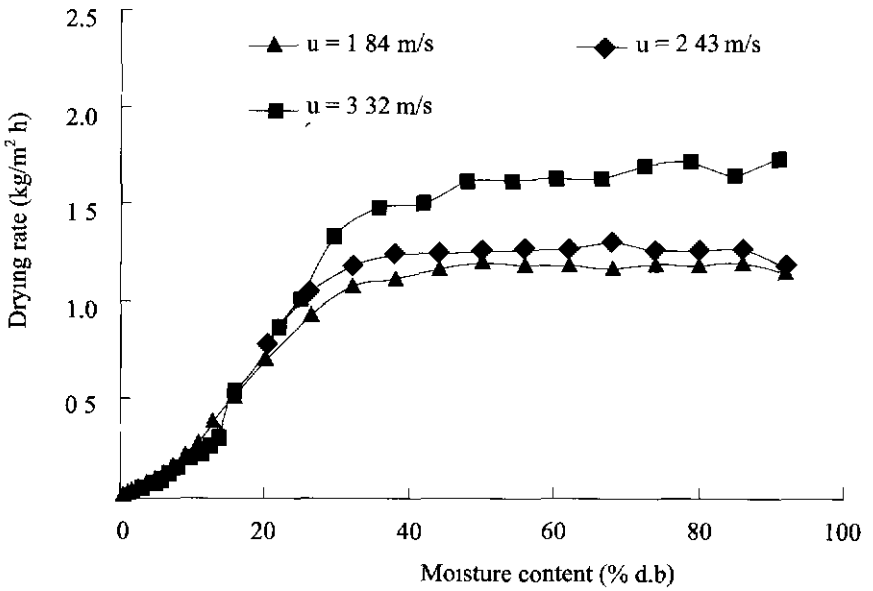

Figure 5 Changes in the drying rate at varying air velocity

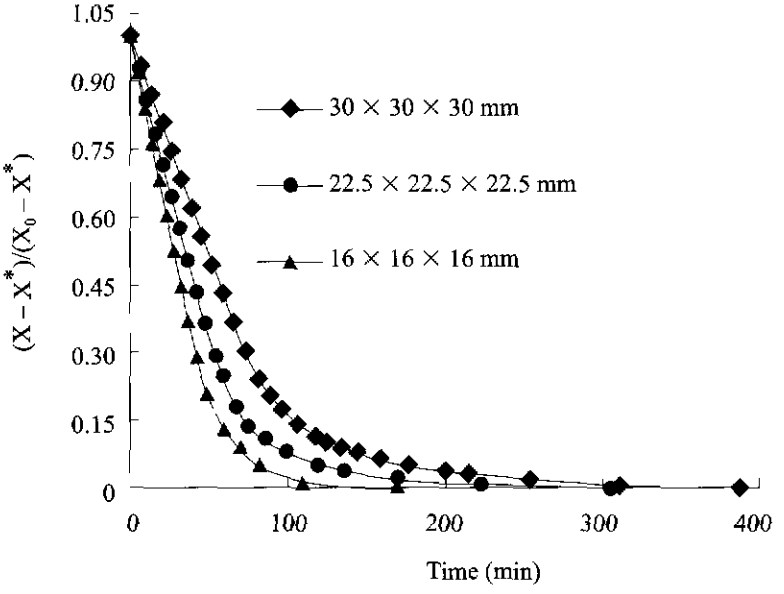

Figure 6. Changes in moisture content at varying granularity.

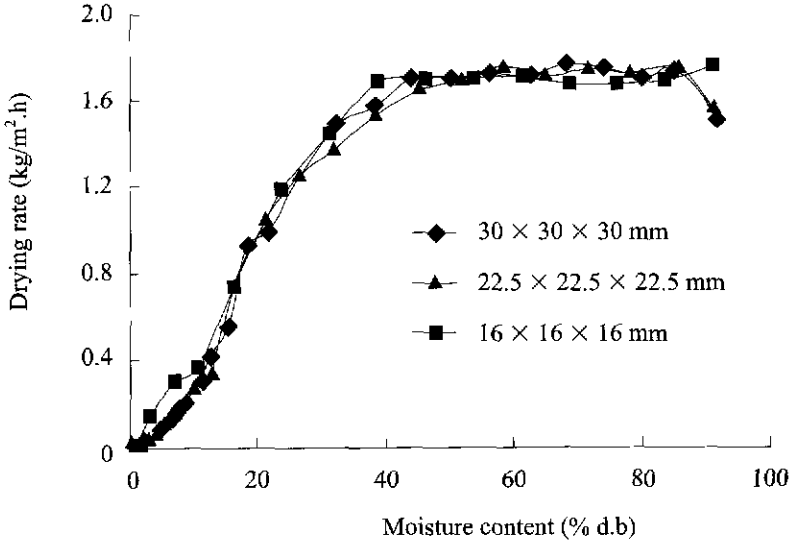

Figure 7. Changes in the drying rate at varying granularity.

almost keeps constant with the declining moisture content, the curves of drying characteristics are similar to linearity functions (*Figures 2, 4* and *6*). In the second phase, the drying rate reduces sharply with the declining moisture content and the curves of drying characteristics are similar to exponential functions. The turning point between the first and second phases was set as critical moisture content (*Xc*). We can see from *Figures 3, 5* and *7* that the *Xc* changed only slightly in the drying conditions and it is around 40% (d.b).

In the first phase, weight loss is mainly caused by moisture vaporising from the surface of the sample. The drying rate is constant and related to drying temperature, air velocity and the measurements of the cubes. The drying rate can be expressed as[23]:

$$\frac{dX}{dt} = k' \quad (k' \text{ is drying rate constant, } t \text{ is drying time.}) \qquad \ldots 1$$

By integrating *Equation 1*, the following equation can be obtained:

$$\frac{X_0 - X}{X_0 - X^*} = kt \; (k = \frac{k'}{X^* - X_0}) \; X \geq X_c \qquad \ldots 2$$

Statistical Analysis System (SAS)[24] was used to test *Equation 2* with the experimental data by regression analysis. Results are shown in *Table 1*. The result shows that the model agrees well with the drying characteristics of the CNR cubes during the first phase. The drying constant (k) was affected by drying conditions such as drying temperature (T), air velocity (u) and sample measurement R_i (R_i is the spherical equivalent radii of the cube, calculated by the equation $^4/_3 \pi R_i^3 = a^3$; a is the length of the rectangular cube[25]). It also has been found that the k influenced by $1/T$ and u exponentially and by R_i linearly. Thus the equation can be expressed as follow:

$$\ln k = x_1 + x_2 / T + x_3 u + x_4 \ln R_i \qquad \ldots 3$$

By regressing *Equation 3* adopting the least squares fitting method, the relationship between drying constant k and $1/T$, u, R_i can be expressed as:

$$\ln k = 3.623 - 2738.9/T + 0.2373 u - 1.186 \ln R_i \; (r = 0.992; \text{probability} = 0.0001).$$

In the second phase of drying, the moisture diffusion rate inside the CNR cube is slower than the vaporising rate of moisture on the surfaces of CNR granule. With the drying process going on, the dry areas on the surfaces extend inwards gradually and form a spherical wet core inside the cubes. During the experiments, some cubes of CNR samples were cut into two and after being dried to some extent, a spherical wet core was clearly seen in the sections as shown in *Figure 8*. The spherical wet core became progressively smaller with the drying process. The drying process ceased when the moisture content of CNR cubes were in balance with the relative humidity of the drying air. The drying behaviours of CNR cubes can be similarly expressed by the following equation[26]:

$$\frac{X - X^*}{X_0 - X^*} = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D}{R_i^2} t\right) \quad X < X_c \qquad \ldots 4$$

Suppose $B = \frac{\pi^2 D}{R_i^2}$; where, D = average diffusion coefficient ($cm^2.min^{-1}$) and t = drying time (min). When a modification factor A is introduced, then we get the following equation:

$$\frac{X - X^*}{X_0 - X^*} = A \exp(-Bt) \qquad \ldots 5$$

Both sides of the *Equation 5* are treated by logarithm. We get:

TABLE 1 REGRESSION OF THE DRYING MODEL IN THE FIRST DRYING PHASE

No	Air velocity (m/s)	Temperature (°C)	Side length of the cube, a (cm)	Equivalent radii of the cubes, R_i (cm)	Regression results Drying constant (k)	Correlation coefficient (r)
1	2 44	50	3 0	1 86	0 006699	0 9999
2	2 44	60	3 0	1 86	0 08590	0 9999
3	2 44	70	3 0	1 86	0 011655	0 9999
4	2 44	80	3 0	1 86	0 014070	1 0000
5	2 44	90	3 0	1 86	0 017011	0 9999
6	2 44	98	3 0	1 86	0 019043	0 9999
7	1 84	55	3 0	1 86	0 006393	0 9999
8	2 43	55	3 0	1 86	0 007174	0 9999
9	3 32	55	3 0	1 86	0 009164	0 9999
10	2 44	60	2 25	1 40	0 013557	0 9999
11	2 44	60	1 6	0 99	0 017258	1 0000

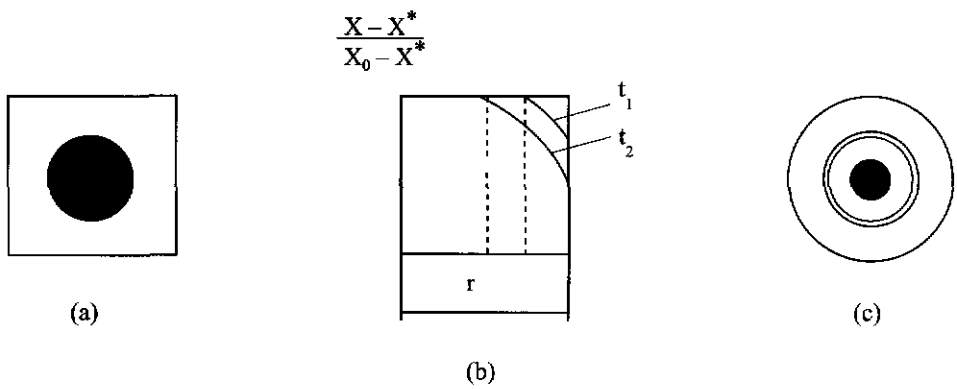

Figure 8 CNR samples were cut into two pieces after being dried (a) spherical wet core, (b) changes in moisture content on drying, (c) thin shell of the wet core

$$\ln \frac{X-X^*}{X_0-X^*} = \ln A - Bt \qquad 6$$

SAS was used to test *Equation 6* with the experimental data by regression analysis Results are shown in *Table 2*

Table 2 shows that the values of A are nearly the same in different drying conditions Assuming that the average values of A are the drying constant of the exponential model, the *Equation 5* can be expressed as follows

$$\frac{X-X^*}{X_0-X^*} = 1\,044 \exp(-Bt) \qquad 7$$

The correlation analysis methods (using SAS) have been used to determine the relation between D and air velocity u, and D and granularity R_i

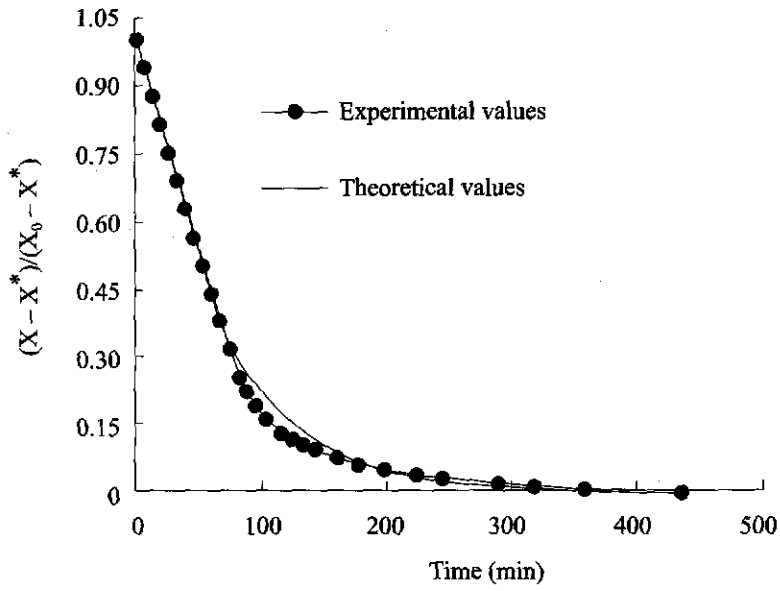

Figure 9. T = 55°C; u = 3.32 m/s and R_i *= 1.86 cm.*

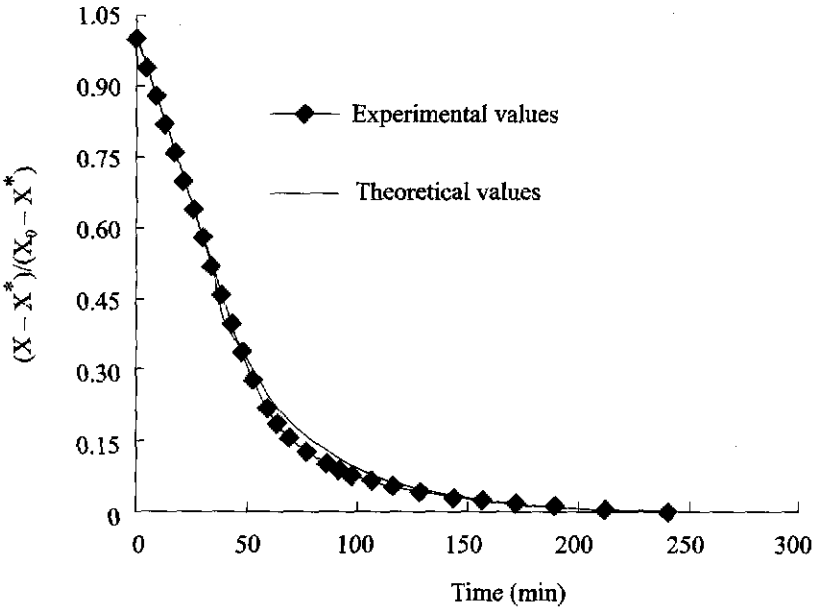

Figure 10. T = 80°C; u = 2.4 m/s and R_i *= 1.86 cm.*

The result are as follows:

- $|r|_u = 0.08124 < |r|_{0.05}$, $P_r = 0.9482$, which shows that the effect of air velocity on D is not obvious.
- $|r|_{R_i} = 0.41035 < |r|_{0.05}$, $P_{r_i} = 0.7308$, which indicates that the effect of granularity on D is not obvious.

The moisture diffusion coefficient (D) as a function of air temperature (T) can be expressed by the Arrhenius equation $D = D_0 \exp(-\frac{E}{RT})$, which was tested in regression analysis by SAS with the experimental data. The results obtained were: D_0 = 4.760; E/R = 2251 (r = 0.967; probability = 0.0001).

Two groups of experimental data were selected for a comparison between experimental and theoretical values. The results are shown in *Figures 9* and *10*. They agree well with each other. This shows that the models can precisely describe the drying characteristics of CNR

Effect of Drying Conditions on Physical and Chemical Properties

The samples of CNR dried under different air temperatures were analysed to measure properties as solubility, viscosity and chlorine content. The results are shown in *Table 3*.

According to the data measured by chemical and viscosity tests, no obvious variation of the physical and chemical properties of CNR appeared. The samples dried at the temperature 120°C become a little harder and the colour tended to become yellow, which may be caused by oxidation. This indicated that degradation of CNR occured if drying temperature was too high.

TABLE 2. REGRESSION RESULTS OF THE DRYING MODEL IN THE SECOND DRYING PHASE

No	Air velocity (m/s)	Temperature (°C)	Side length of the cube, a (cm)	Equivalent radii of the cubes, R_i (cm)	Regression results B	R	A	D
1	2.44	50	3.0	1.86	0.011794	0.995	1.066	0.004148
2	2.44	60	3.0	1.86	0.015323	0.997	1.093	0.005377
3	2.44	70	3.0	1.86	0.022322	0.995	1.008	0.007827
4	2.44	80	3.0	1.86	0.023906	0.994	0.947	0.008388
5	2.44	90	3.0	1.86	0.027931	0.995	1.004	0.009801
6	2.44	98	3.0	1.86	0.028503	0.996	1.017	0.010001
7	1.84	55	3.0	1.86	0.012416	0.997	0.983	0.004357
8	2.43	55	3.0	1.86	0.013842	0.996	1.014	0.004857
9	3.32	55	3.0	1.86	0.012703	0.995	1.070	0.004457
10	2.44	60	2.25	1.40	0.022446	0.990	1.043	0.004462
11	2.44	60	1.6	0.99	0.050853	0.993	1.583	0.005073

TABLE 3. RESULTS OF SOLUBILITY, VISCOSITY AND CHLORINE CONTENT

Temperature (°C)	Solubility	Viscosity (mPa.s)	Chlorine content (%)
50	Good	10.5	66.68
55	Good	10.0	64.76
60	Good	9.2	66.70
65	Good	9.2	63.37
70	Good	9.2	63.31
75	Good	9.2	67.19
80	Good	9.0	66.91
90	Good	8.8	64.89
98	Good	8.6	67.34

CONCLUSION

The drying process of CNR product prepared from latex consists of two different drying phases under experimental conditions. In the first phase, T and u influenced drying rate exponentially and R_i linearly. In the second phase, the diffusion coefficient was mainly related to drying temperature and granule sizes and air velocity had no obvious effect on the drying rate.

The dynamic model was proved to agree well with the drying characteristics of CNR, and the relative coefficient was up to 99%. There were no obvious variation in its physical and chemical properties when the drying temperature was not higher than 100°C.

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