Studies on the properties and the thermal decomposition kinetics of natural rubber prepared with calcium chloride

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Abstract: To evaluate calcium chloride coagulation technology, two kinds of raw natural rubber samples were produced by calcium chloride and acetic acid respectively. Plasticity retention index (PRI), thermal degradation process, thermal degradation kinetics and differential thermal analysis of two samples were studied. Furthermore, thermal degradation activation energy, pre-exponential factor and rate constant were calculated. The results show that natural rubber produced by calcium chloride possesses good mechanical property and poor thermo-stability in comparison to natural rubber produced by acetic acid.

Keywords: natural rubber, calcium chloride, coagulation, thermal degradation

Introduction

Natural rubber (NR) is an important regenerated resource. In 2005, its output was more than 8,000,000 and 700,000 tons in the world and China respectively. Traditionally NR is produced by acid coagulation or spontaneous coagulation [1-2]. Due to the production modes of Chinese small farms, the NR has been produced with a relatively complex procedure, which involves the latex stabilization and coagulation, followed by washing, granulating and drying. This is the standard acid coagulation technology (ACT). This technology has some disadvantages. To begin with, plenty of ammonia and acetic acid will be consumed during the stabilization and coagulating process. In addition, a large amount of water will be wasted during the process. Those may not only increase the cost of production but also cause heavy environment pollution. Calcium chloride (CaCl2) is an inorganic salt, which possesses low environmental burden and economic cost. It can also coagulate the latex effectively. However, CaCl2 coagulation technology (CCT) has not been popularized till recently. And there are few reports about the natural rubber coagulated by the CCT (NR-c). The current study aims to study the bulk properties and thermostability of NR-c and investigate the differences between NR-c and NR coagulated by the acid (NR-a).

Results and discussion

Bulk properties

PRI is used to rapidly assess the susceptibility of a raw natural rubber sample to heat and oxidative aging. The higher the PRI, the better resistance of the natural rubber...
Analysed to heat and oxidative aging [1, 2]. Table 1 shows the PRI of two samples. It indicates that PRI of NR-a is 22 units higher than that of NR-c, which clearly demonstrate that NR-c possesses poorer antioxygenic property. Meanwhile the $P_0$ and ML of NR-a are 10 and 24.7 units lower than NR-c respectively, indicating that NR-c possess better mechanical property than NR-a.

**Tab. 1.** Bulk properties of NR-c and NR-a.

<table>
<thead>
<tr>
<th>samples</th>
<th>$P_0$</th>
<th>PRI</th>
<th>ML(1+4) at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR-c</td>
<td>54.2</td>
<td>63.8</td>
<td>90.7</td>
</tr>
<tr>
<td>NR-a</td>
<td>44.5</td>
<td>86.5</td>
<td>66.0</td>
</tr>
</tbody>
</table>

**Differential Thermal Analysis**

Figure 1 and Figure 2 present the DTA curves of thermal degradation of NR-a and NR-c in air and nitrogen with a heating rate of 10 °C.min$^{-1}$. Generally, the thermal patterns of NR-a and NR-c in same atmosphere are similar especially when the temperature is below 300 °C.

**Fig. 1.** DTA curves of NR-a and NR-c in air.

**Fig. 2.** DTA curves of NR-a and NR-c in nitrogen.
**Thermal Degradation and Thermal Degradation Kinetics**

Figures 3 to 6 presents the TG curves of thermal degradation of two samples in air and nitrogen with a heating rate of 10, 14, 18, 22, 26, 30 °C.min⁻¹ respectively. There are two weight loss steps in both air and nitrogen, indicating that the thermal degradation of NR-a and NR-c in air and nitrogen is a two-step reaction. The first degradation occurs from 300 to 450 °C and the weight loss is about 90%. It may be the thermal decomposition of main chain. When the temperature is over 450 °C, the weight loss is very slow. It may be the carbonization process. In comparison with the degradation in nitrogen atmosphere, the degradation in air shift to a lower temperature. It is the oxidation of oxygen in air. Moreover, with the increase of the heating rate, all TG curves shift toward high temperatures. It’s the result of the heat hysteresis [3, 4].

![Fig. 3. TG curves of NR-c at different heating rates in air.](image1)

![Fig. 4. TG curves of NR-c at different heating rates in nitrogen.](image2)

The degradation kinetic analysis is very important for polymers as it can provide information on the energy barriers of the degradation process. The challenge for studying thermal degradation kinetics is to find a reliable approach. In the two major thermal degradation models in use, the shortcomings of the single heating-rate method have been reported by Vyazovkin [5], while the multi-heating-rate method has been extensively used to study the thermal degradation kinetics for polymers due to its reliability [6].
Using the multi-heating-rate method, the data in Figures 1 to 4 can be analysed with the Ozawa-Flynn-Wall (OFW) method [7]. In general, the reaction kinetic equation of solid polymer degradation can be calculated as follows:

\[
\frac{dX}{dt} = kf(X)
\]  

(1)

where \( X \) is degree of decomposition and \( f(X) \) is the function of \( X \), depends on the particular decomposition mechanism. And \( k \) is the decomposition rate constant, which can be expressed by the Arrhenius equation:

\[
k = A \exp\left(-\frac{E}{RT}\right)
\]  

(2)

where \( A \) is the frequency factor, \( E \) the activation energy (J.mol\(^{-1}\)), \( R \) is the gas constant (8.314J.mol\(^{-1}\).K\(^{-1}\)), and \( T \) is temperature (K). Substituting the Eq.(2) into Eq.(1), we obtain:

\[
\frac{dX}{dt} = A \exp\left(-\frac{E}{RT}\right)f(X)
\]  

(3)

If the temperature of a sample is changed by a constant value of \( B \), where \( B = dT/\text{d}t \), the variation in the degree of decomposition can be analyzed as a function of temperature. Therefore, the reaction rate is given as:
\[
\frac{dX}{dT} = \frac{A}{B} \exp\left(\frac{-E}{RT}\right) f(X)
\]

The Eq. (2) and (3) are the basic equations in the kinetic calculation. Separating the variable and rearranging and integrating Eq. (4), it can be obtained:

\[
g(X) = \frac{A}{B} \int_{x_0}^{x_f} \exp\left(\frac{-E}{RT}\right) dT
\]

If we define \(x = \frac{E}{RT}\) and integrate the right-hand side of Eq. (5), it can be obtained:

\[
\frac{A}{\beta} \int_{x_0}^{x_f} \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{\beta T} p(x)
\]

After taking logarithms, we obtain:

\[
\log \beta = \log \frac{AE}{g(X)R} + \log p(x)
\]

using the Doyle approximation [8], the function \(p(x)\) can be expressed as the following approximation:

\[
\log p(x) = -2.315 - 0.456x
\]

Substituting Eq. (7) to Eq. (6), it can be obtained:

\[
\log B = \log \frac{AE}{f(X)R} - 2.315 - \frac{0.4567E}{RT}
\]

Eq. (9) is the formula of Ozawa-Flynn-Wall method [6], Where \(B\) is the heating rate, from this equation, it is easy to obtain values for \(E\) over a wide range of decomposition by plotting \(\log B\) against \(\frac{1}{T}\) at constant values of \(X\).

**Fig. 7.** Activation energies (E) of NR-c and NR-a in air.

The relationships between \(E\) and \(f(X)\) during the thermal degradation are indicated in Fig 5 and Fig 6. Both the thermal degradation process can be approximately divided into two weight-loss phases: weight loss ranges 0-10% and 20-80%. For air atmosphere, at the first stage, \(E\) of NR-c increases sharply from 0 to 95 kJ·mol\(^{-1}\) and \(E\) of NR-a increases sharply from 0 to 120 kJ·mol\(^{-1}\). After that, \(E\) of NR-c increases
slowly from 110 to 157 kJ·mol\(^{-1}\) and \(E\) of NR-a increases slowly from 120 to 152 kJ·mol\(^{-1}\). During the degradation process, the \(E\) of NR-a is always higher than NR-c from 0 to 0.5, and the \(E\) of NR-a is similar to NR-c from 0.5 to 0.8. For nitrogen atmosphere, the tendency of \(E\) of NR-c and NR-a is similar. At the first stage, \(E\) of NR-c increases sharply from 0 to 160 kJ·mol\(^{-1}\) and \(E\) of NR-a increases sharply from 0 to 180 kJ·mol\(^{-1}\). After that, \(E\) of NR-c increases slowly from 160 to 210 kJ·mol\(^{-1}\) and \(E\) of NR-a increases slowly from 180 to 230 kJ·mol\(^{-1}\). During the degradation process, \(E\) of NR-a is always higher than NR-c from 0 to 0.3 and the \(E\) of NR-a is similar to NR-c from 0.3 to 0.8.

**Fig. 8.** Activation energies (\(E\)) of NR-c and NR-a in nitrogen.

Based on the results above, the two weight-loss phases in air and nitrogen is different, the first stage in air and nitrogen may mainly be the volatilization of low-boiling-point components and decomposition of unstable non-rubber components. And the second stage may be the degradation of NR-c main chain. Furthermore, comparing Fig. 5 to Fig. 6, we can find that both the \(E\) in \(N_2\) are larger than those in air. Finally, to the polymer stability, the \(E\) of initial stage is very important, so the stability of NR-a is higher than NR-c in both air and nitrogen.

**Fig. 9.** The pre-exponential factor of NR-c and NR-a in air.
The pre-exponential factor of NR-c and NR-a in nitrogen are also shown in Fig. 8 and Fig. 9. It indicates that the tendency of pre-exponential factor is similar to E. In order to describe the degradation process of NR-c and NR-a accurately. The rate constants of NR-c (Kc) and the rate constants of NR-a (Ka) at different degradation percentage are calculated as Eq.(2), and the ratios of Kc/ Ka at different degradation percentage are shown in Fig. 11.

**Fig. 10.** The pre-exponential factor of NR-c and NR-a in nitrogen.

**Fig. 11.** Kc/ Ka at different degradation percentage a: 5%; b:10%; c:20%; d:30%.
Experimental part

Materials and reagents
Fresh natural rubber latex (clone PR107), with total dry rubber content of 25%, was kindly provided by Shuguang Rubber Plantation (Maoming, GuangDong, P.R.China), acetic acid and CaCl₂, chemically pure reagents were obtained from Shanghai Chemical Co. (Shanghai, P.R.China).

Preparation of samples
Some fresh natural rubber latex was coagulated with 0.125% equivalent weight of CaCl₂ (w/w=1%) for a given period of time. After that, the coagulum was washed, granulated and dried on the production lines in Shuguang rubber factory, and then the sample NR-c was obtained. The contrast sample NR-a coagulated with 0.2% equivalent weight of acetic acid (w/w=2%) was produced with the same method.

Testing of the bulk rubbers
The bulk viscosity was measured on a Mooney shearing viscometer (model MK IV, Negretti Automation, Surrey, United Kingdom) operating at 100 °C. The large rotor (Type L, 38.10 mm diam. and 5.54 mm thickness) was used, and the Mooney viscosity (M) was recorded as the torque value after 1 min of preheating and 4 min of shearing [ML(1 + 4) at 100 °C]. The initial Wallace plasticity number (P₀) and the plasticity retention index (PRI) was determined by standardized method (ISO 2930), the plasticity (Wallace) of an NR disc of standard size (thickness 3–3.8mm) before and after 30 min of ageing at 140 °C was measured on a Wallace Plastimeter MKII010, Wallace Aging Oven 010. The PRI, the percentage of Wallace plasticity retained, is thus given by the relation:

\[
PRI = \frac{P_{30}}{P_0} \times 100\%
\]  

(10)

where \(P_0\) = plasticity before ageing, and \(P_{30}\) = plasticity after ageing in the oven.

Thermogravimetric analysis
Thermogravimetric analysis was performed with a NETZSCH STA 449C thermogravimetric analyzer (German). The mass of each sample was 5–6 mg. The carrier gas was air and nitrogen at a flow rate of 50 ml. The samples were heated from 30 to 650 °C at 10, 14, 18, 22, 26, 30 °C.min\(^{-1}\) respectively to record the thermogravimetry (TG) curves.

Differential Thermal Analysis
Differential thermal analysis (DTA) was performed with a NETZSCH STA 449C thermogravimetric analyzer (German). The mass of each sample was 5–6 mg. The carrier gas was air and nitrogen at a flow rate of 50 ml. The samples were heated from 30 to 650 °C at 10 °C.min\(^{-1}\) to record the DTA curves.

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