

Thermogravimetric Analysis of Chitosan

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ABSTRACT: The thermal degradation of chitosan at different heating rates B in nitrogen was studied by thermogravimetric analysis. The results indicate that the thermal degradation of chitosan in nitrogen is a one-step reaction. The degradation temperatures increase with B . Experimentally, the initial degradation temperature (T_0) is $(1.049B + 326.8)^\circ\text{C}$; the temperature at the maximum degradation rate, that is, the peak temperature on a differential thermogravimetry curve (T_p), is $(1.291B + 355.2)^\circ\text{C}$; and the final degradation temperature (T_f) is $(1.505B + 369.7)^\circ\text{C}$. The degradation rates at T_p and T_f are not affected by B , and their average values are 50.17% and 72.16%, respectively, the maximum thermal degradation reaction rate, that is, the peak height on a differential thermogravimetry curve (R_p), increases with B . The relationship between B and R_p is $R_p =$

$(1.20B + 2.44)\% \text{ min}^{-1}$. The thermal degradation kinetic parameters are calculated with the Ozawa–Flynn–Wall method. The reaction activation energy (E) and frequency factor (A) change with an increasing degree of decomposition, and the variable trends of the two kinetic parameters are similar. The values of E and A increase remarkably during the initial stage of the reaction, then keep relatively steady, and finally reach a peak during the last stage. The velocity constants of the thermal degradation vary with the degree of decomposition and increase with the reaction temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 547–551, 2007

Key words: chitosan; thermal degradation; reaction kinetic; thermogravimetric analysis

INTRODUCTION

Chitin is abundant in the shells of animals such as shrimp, crab, insects, as well as in the cell walls of plants such as fungus and algae, and its output is just second only to the cellulose in nature. It is a natural organic macromolecule with positive charge and obvious alkali, and it is insoluble in water, dilute acid solution, dilute base solution, and other organic solvents due to its high crystallinity,¹ which becomes the major limiting factor in its utilization.

Chitosan, prepared from deacetylation of chitin under different degradation processes,^{2–5} is a non-toxic, biodegradable polysaccharide. Chitosan with different deacetylation degree and molecular weight has been explored widely due to its improving solubility.⁶ With the increasing interest to the scientific community, the importance of chitin, chitosan, and their derivatives motivates extensive research in many fields, which involve chitin resources;^{6,7} synthesis, extraction, and purification of chitin;⁸

chemical modification of chitosan,^{9–12} such as acylation, esterification, *N*-alkylation, and so on; oxidation,¹³ chelation,¹⁴ graft-copolymerization,^{15,16} cross-linking^{17,18} of chitosan, and so forth. With the improvement of modern analytical equipment, some researchers have promoted fruitful discussions on the structures and properties of chitosan, using Fourier transform infrared spectroscopy,¹⁹ X-ray diffraction,²⁰ nuclear magnetic resonance,^{21,22} differential scanning calorimetry, thermogravimetry (TG),²³ and so forth. But there are, unfortunately, few reports about systematical studies on the thermal degradation of chitosan.^{24,25} In this article, the thermal degradation of chitosan at different heating rates (B) in nitrogen has been examined with TG analysis. The effects of heating rates (B) on degradation temperature and degradation rate were discussed, and the kinetic parameters such as reaction activation energy (E), frequency factor (A) were calculated.

EXPERIMENTAL

Materials

After cleaning and then drying at 55°C , the fresh shrimp shell (obtained from Guangdong Hengxing Co., Zhanjiang, China) was dipped in 10% HCl solution at room temperature till no bubble was released. After neutralization and drying, the shrimp shell

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was further dipped in 8% NaOH solution for 24 h at room temperature and then it was washed to neutral and dried. This process was repeated till white chitin pieces were obtained.

Chitin obtained from the above-mentioned process was treated in 45% NaOH solution for 3 h at 90°C and then washed to neutral and dried. This process was repeated twice and white chitosan was obtained with the deacetylation degree of 84% and molecular weight of 1.7×10^5 .

TG analysis

TG analysis was performed with a NETZSCH STA 449C TG analyzer (Germany). The mass of each sample was 5–6 mg. The carrier gas was nitrogen at a flow rate of 50 mL min⁻¹. The samples were heated from 30 to 650°C at B (°C min⁻¹) = 10, 14, 18, 22, 26, 30, respectively, to record the TG and differential thermogravimetry (DTG) curves.

Data processing

The reaction kinetic factors were obtained by the processing of TG data through the Ozawa–Flynn–Wall (OFW) method.^{26,27} In general, the thermal degradation reaction of a solid polymer can be simply represented by: $B_{\text{solid}} \rightarrow C_{\text{solid}} + D_{\text{gas}}$, where B_{solid} is the initial material, C_{solid} and D_{gas} are the different products resulted from B_{solid} . In TG measurements, the degree of decomposition can be calculated as follows:

$$X = \frac{W_0 - W_t}{W_0 - W_f} \quad (1)$$

where X is degree of decomposition; W_t , W_0 , and W_f are the actual, initial, and final mass of the sample, respectively. A typical model for a kinetic process can be expressed as:

$$\frac{dX}{dt} = kf(X) \quad (2)$$

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

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where A is the frequency factor (s⁻¹), E is the activation energy (J mol⁻¹), R is the gas constant

(8.314 J mol⁻¹ K⁻¹), and T is temperature (K). Substituting the eq. (3) into eq. (2), we obtain:

$$\frac{dX}{dt} = A \exp\left(\frac{-E}{RT}\right) f(X) \quad (4)$$

If the temperature of a sample is changed by a constant value of B , where $B = dT/dt$, the variation in the degree of decomposition can be analyzed as a function of temperature. Therefore, the reaction rate gives:

$$\frac{dX}{dT} = \frac{A}{B} \exp\left(\frac{-E}{RT}\right) f(X) \quad (5)$$

The eqs. (4) and (5) are the basic equations in the kinetic calculation.

Separating the variable and rearranging and integrating eq. (5), it can be obtained:

$$g(X) = \int_{X_0}^{X_p} \frac{dX}{f(X)} = \frac{A}{\beta} \int_{X_0}^{X_p} \exp\left(\frac{-E}{RT}\right) dT \quad (6)$$

If we define $x = E/RT$ and integrate the right-hand side of eq. (7), it can be obtained:

$$\frac{A}{\beta} \int_{X_0}^{X_p} \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{\beta T} p(x) \quad (7)$$

After taking logarithms, we obtain:

$$\log \beta = \log \frac{AE}{g(X)R} + \log p(x) \quad (8)$$

using the Doyle approximation,²⁸ the function $p(x)$ can be expressed as the following approximation:

$$\log p(x) = -2.315 - 0.4567 \quad (9)$$

Substituting eq. (9) to eq. (8), it can be obtained:

$$\log B = \log \frac{AE}{f(X)R} - 2.315 - \frac{0.4567E}{RT} \quad (10)$$

Equation (10) is the formula of OFW method.^{26,27}

From this equation, it is easy to obtain values for E over a wide range of decomposition by plotting $\log B$ against $1/T$ at constant values of X . The slope of each line is $-0.4567 E/R$ and the intercept is $\log\{AE/R f(X)\} - 2.315$.

RESULTS AND DISCUSSION

Effect of B on the process of thermal degradation

Figures 1 and 2 are the TG and DTG curves of thermal degradation of chitosan in nitrogen at six different heating rates, respectively. It can be seen that the

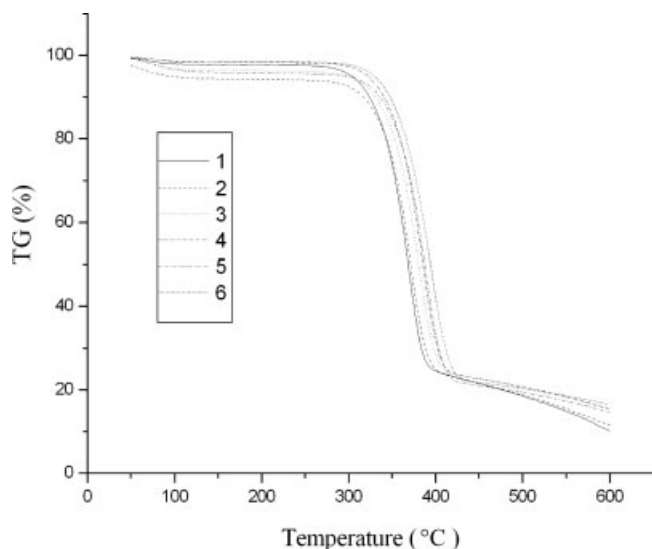


Figure 1 TG curves of the thermal degradation of chitosan. (Sample 1–6: $B = 10^{\circ}\text{C}/\text{min}$, $14^{\circ}\text{C}/\text{min}$, $18^{\circ}\text{C}/\text{min}$, $22^{\circ}\text{C}/\text{min}$, $26^{\circ}\text{C}/\text{min}$, $30^{\circ}\text{C}/\text{min}$).

TG curve is a smooth curve with only one weight-loss step and that there is only one peak on the DTG curve (Fig. 2), indicating that the thermal degradation of chitosan in nitrogen is simple and is a one-step reaction. Both TG and DTG curves shift toward high temperatures along with the rising of the heating rate. The trends seen in the TG and DTG curves at six different heating rates are similar.

Relationship between heating rate and thermal degradation temperature

Figure 3 shows the relation between the heating rates (B) and the thermal degradation temperature (T). The initial temperature of weight loss (T_0) and the final temperature of weight loss (T_f) are calcu-

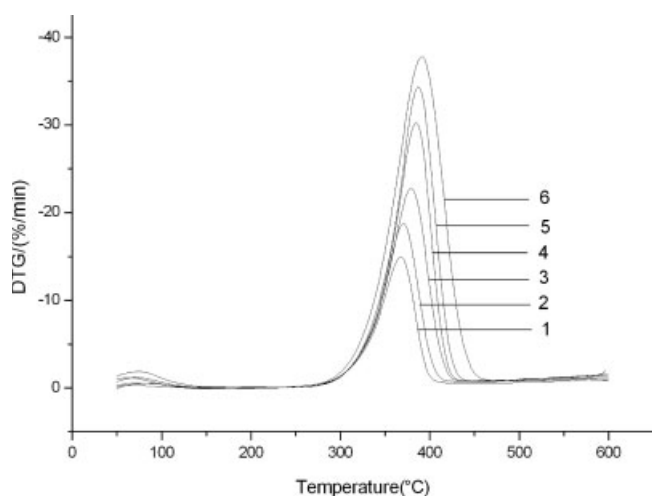


Figure 2 DTG curves of the thermal degradation of chitosan. (Sample 1–6: $B = 10^{\circ}\text{C}/\text{min}$, $14^{\circ}\text{C}/\text{min}$, $18^{\circ}\text{C}/\text{min}$, $22^{\circ}\text{C}/\text{min}$, $26^{\circ}\text{C}/\text{min}$, $30^{\circ}\text{C}/\text{min}$).

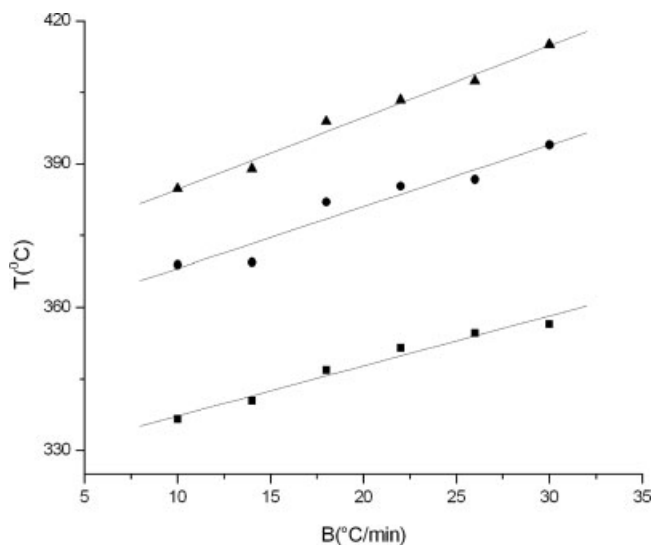


Figure 3 Relationship between B and the thermal degradation temperatures of chitosan. (\blacktriangle : T_f ; \bullet : T_p ; \blacksquare : T_0).

lated by a bitangent method from the TG curves, and the T_p is the temperature at maximum weight-loss rate. It can be seen that all the degradation temperatures increase linearly with the increasing of B , indicating that the degradation temperatures are mainly affected by B . The relations between B and T are as follows:

$$T_0 = (1.049B + 326.8)^{\circ}\text{C} \quad (r = 0.9858)$$

$$T_p = (1.291B + 355.2)^{\circ}\text{C} \quad (r = 0.9640)$$

$$T_f = (1.505B + 369.7)^{\circ}\text{C} \quad (r = 0.9922)$$

where r is the correlation coefficient. The linear increment of thermal degradation temperatures along with the increasing of B is a result of the heat hysteresis.^{29,30} To eliminate the heat hysteresis, the thermal

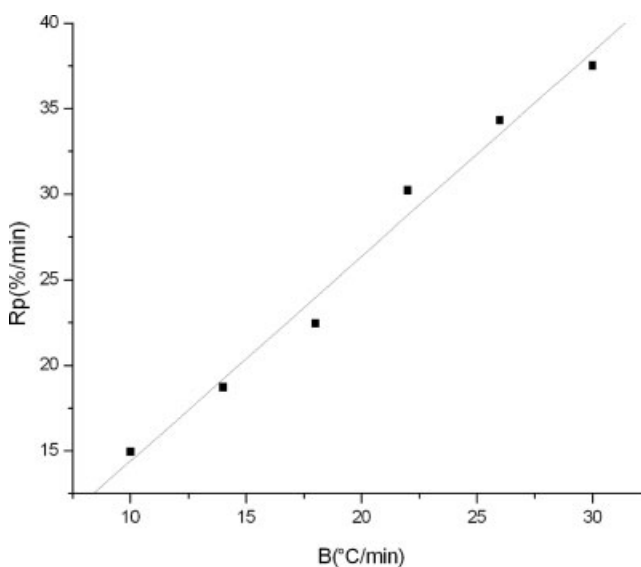


Figure 4 Relationship between B and R_p of chitosan.

TABLE I
Relationship between *B* and *C*

	<i>B</i> (°C min ⁻¹)					
	10	14	18	22	26	30
<i>C_p</i> (%)	50.87	44.83	56.02	50.22	49.33	49.74
<i>C_f</i> (%)	71.30	70.60	73.75	71.06	72.80	73.45

degradation temperatures should be expressed in equilibrium thermal degradation temperatures (T^0) which are the temperatures when B approaches 0. The equilibrium thermal degradation temperatures of chitosan are as follows:

$$T_0^0 = 326.8^\circ\text{C}, \quad T_p^0 = 355.2^\circ\text{C}, \quad \text{and} \quad T_f^0 = 369.7^\circ\text{C}$$

The peak width of DTG curve, which is expressed in $T_f - T_0 = (0.456B + 14.5)^\circ\text{C}$, increases with the increasing of B . The peak height of the DTG curve, that is, the maximum reaction rate of thermal degradation (R_p), increases with B , as shown in Figure 4. The relationship between B and R_p is as follows: $R_p = (1.20B + 2.44)\% \text{ min}^{-1}$ ($r = 0.9924$).

Effect of heating rate on the thermal degradation rate

Table I shows the relationship between heating rate (B) and the thermal degradation rate (C), in which C_p and C_f are the thermal degradation rates corresponding to T_p and T_f . It can be seen that the effects of B on C_p and C_f are not significant with the standard deviation of 5.85% and 1.59%, respectively. The average value of C_p is 50.17%, and that of C_f is 72.16%. The residual product is 27.84%, which is stable in the range of 30–600°C.

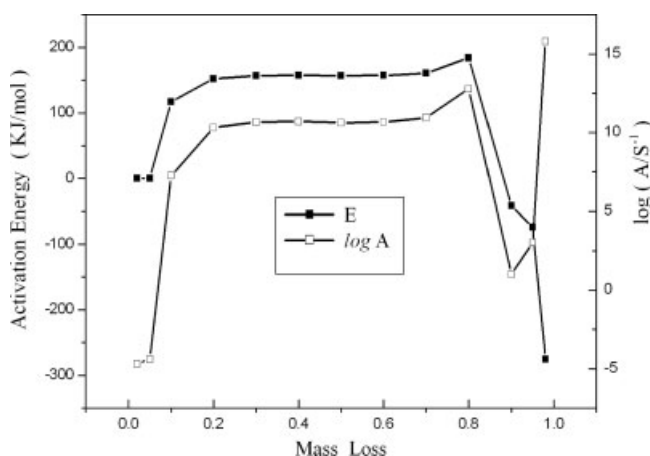


Figure 5 Activation energies and pre-exponential factor of chitosan by Ozawa–Flynn–Wall.

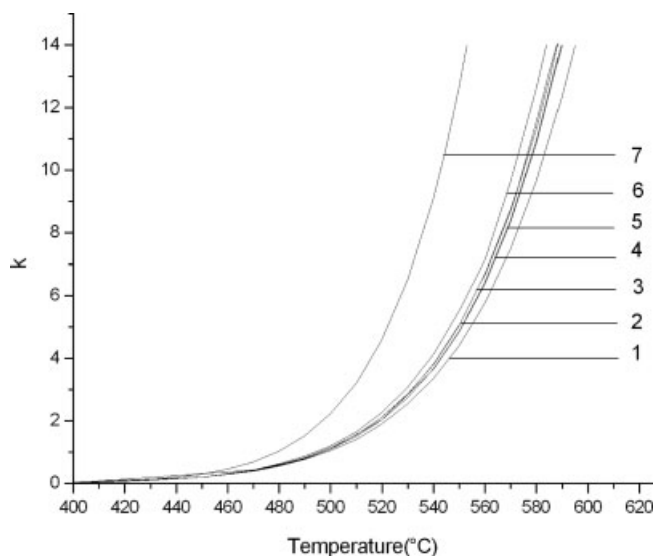


Figure 6 Relationship between k at different degree of decomposition (X) and the temperature (Samples 1–7: $X = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$).

Kinetics of thermal degradation of chitosan

The kinetic parameters were calculated with reference to eq. (6). Figure 5 illustrates that E of chitosan varies with $f(X)$ during the thermal degradation process, which can be divided into three weight-loss phases: 0–0.10, 0.20–0.75, and 0.80–0.95. At the first stage, E increases sharply (0–140 kJ mol⁻¹); this may be due to the volatilization of low-molecular-weight materials such as water. After that, E remains relatively steady (140–160 kJ mol⁻¹), and this may be caused by the thermal degradation of chitosan main chains. During the last stage, E increases with increasing degree of decomposition. This may be the decomposition of residual carbon from thermal degradation of chitosan becoming dominant. It can be seen that the variable tendency of A is similar to that of E (Fig. 5) when mass loss is between 0 and 0.8. Figure 6 shows the relationship of k at different degree of decomposition and the temperatures. There are different k values at different degree of decomposition, and k increases with the reaction temperatures.

CONCLUSIONS

The thermal degradation of chitosan in nitrogen is a one-step reaction. The degradation temperatures increase along with the increment of heating rate:

$$T_0 = (1.049B + 326.8)^\circ\text{C}, \quad T_p = (1.291B + 355.2)^\circ\text{C}, \\ \text{and} \quad T_f = (1.505B + 369.7)^\circ\text{C}.$$

The peak width of the DTG curve increases with increasing B . R_p increases with B : $R_p = (1.20B$

+ 2.44)% min⁻¹. The degradation rates are not affected significantly by *B*, and the average values of *C_p* and *C_f* are 50.17% and 72.16%, respectively. *E* and *A* vary with the increase degree of decomposition, and can be categorized into three phases corresponding to the volatilization of low-molecular-weight materials, the thermal degradation of chitosan main chains, and the decomposition of residual carbon. *k* varies with degree of decomposition and increases with the reaction temperatures.

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