

Thermal Degradation Study of Sodium Alginate-Zeolite 4A Composites

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Abstract: Natural biodegradable materials have now received ever-increasing attention in the food industries as they provide an alternative as green packaging materials to conventional non-degradable plastic films, and their utilizations once commercialized will extremely reduce the dependence and consumption of nonrenewable fossil resources. Thus, there is imminent need to develop highly-performed biodegradable materials for food packaging applications. In this work, a few zeolite 4A modified sodium alginate films have been fabricated using the solution casting method. The aqueous dope with different zeolite loadings was cast on clean glasses, followed by ambient drying treatment before obtaining final hybrid films. Then the membrane thermal properties have been characterized in detail to investigate the pyrolysis characteristics and kinetics in the course of heating process. The experiments were performed at the air flow rate of 30 ml/min with temperature from ambient up to 1050 K. From experimental results, thermal degradation of the sodium alginate composites could be clearly separated into several stages based on the weight loss and the weight loss rate. The kinetic parameters for the main degradation phase thus were estimated by using the pseudo first-order assumption. The heating rates used for sodium alginate hybrid membranes ranges from 5 to 30 K/min so as to evaluate its influences on the thermal degradation. The results have also shown that the introduced zeolite as well as its content has obviously affected the thermal properties of the sodium alginate composites. These pyrolysis investigations will be useful for better understanding the thermal stability of these sodium alginate biocomposites and provide necessary information for thermally processing packaging wastes from these biodegradable materials.

Keywords: Sodium alginate; zeolite 4A; thermal decomposition; degradation kinetics

1. Introduction

The significant progress in developing environment friendly and biodegradable polymers and composites for various industrial applications has been made in recent years as a result of increased worldwide concern about sustainability issues and environmental concerns. In the meantime, the problems of overflowing landfills and living plastic wastes have also accelerated the need to develop polymers with controllable lifetime taking into consideration environmentally acceptable manufacturing, application, recycling and disposal methodology [1-3]. Thus the main driving force for developing degradable polymers is economic and environmental necessity rather than academic curiosity [4]. As an alternative to solve the environmental problems caused by the massive use of synthetic materials for various packagings, notable efforts have been made in the last decade in developing packaging materials based on biopolymers.

Nowadays, the demand of natural biopolymer from renewable sources has greatly increased, due to huge amount of plastic waste produced from synthetic polymer every year and the reduced availability of landfills. These biodegradable polymers like alginate can be used in many fields instead of synthetic polymers. Alginate is a naturally occurring polysaccharide obtained from marine brown algae, comprising linear chains of (1,4)-b-

Dmannuronic acid and (1,3)-a-L-guluronic acid. Sodium alginate (SA), a polyelectrolyte having rigid molecular chain, has been extensively exploited and studied in detail on many potential applications [5-8]. Besides being biodegradable and renewable, SA possesses good film forming ability. Hence, it could be developed for food packaging in place of conventional synthetic polymers.

With increasing environmental concerns from plastic packaging wastes, there is imminent need to develop new recycling techniques to avoid huge accumulation of plastic wastes. Thus, thermal pyrolysis may provide a sustainable way of recycling organic wastes which offers the possibility of transforming packaging wastes into fuel oils for the petrochemical industries or decomposing these wastes for thermal power generation [9,10].

However, the low thermal conductivity of plastics as well as the endothermic character of the decomposition reactions involves high power consumption in the pyrolysis process. The use of solid acid catalysts permits the temperature of the process to be decreased and also provides a narrower product distribution, which allows control of the type of products obtained with a lower cost of production [11,12]. According to the bibliography [13], zeolites may act as catalysts in the cracking of polymers, making their transformation into a fuel product easier. Thus, in this work, zeolite 4A, usually used as adsorbent or as catalyst in some industrial processes, were selected

to act as catalyst in the thermal disposal of SA. Some researches [14,15] have reported that thermal decomposition of a few pure metal alginate compounds has proceeded through the formation of metal oxalates as intermediate fragments.

The objectives of this work are: (i) to examine thermal behavior of the SA composites; (ii) to investigate the influences of the zeolite on the thermal degradation, and (iii) to analyze thermal degradation kinetics.

2. Experimental

In present work, a few different zeolite 4A (self-synthesized)-incorporated sodium alginate (SA, Tianjin Letai Chemical Co. Ltd., China) composites were fabricated by using the solution casting method, similar to that reported in our previous work [16]. The procedure for preparing composite membranes can be briefed as follows. A desired amount of dried zeolite 4A powder was weighed and dispersed in 45 g deionized water under agitation for 20 min, followed by adding a small portion of 5 g SA into the zeolite-liquid mixture. After stirring for another 4 h, the remained polymer was added into the resultant mixture and continuously stirred for 12 h to result in a homogenous suspension. Note that the polymer addition method used was to keep zeolite particles stirred in a dilute polymer solution for longer time and thus make the polymer molecule chains better attached to the zeolite surface and form good zeolite-polymer interactions [17]. The resultant suspension was spread out onto a 30cm×40cm clean glass wafer and flattened with a casting knife, then placed into an oven that was pre-heated to around 400 K for the solvent evaporation. The composites at a zeolite loading of 0, 10, 20 and 40 wt% were named as SA-0, SA-10, SA-20 and SA-40, respectively.

Thermal behaviors of the composite samples were characterized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) with a simultaneous module on a Shimadzu DTG-60 analyzer. For thermal analyses, dried samples with a mass of 5-6 mg were placed in a silica crucible and then heated from ambient up to 960 °C with temperature programmed at certain heating rates in air at a flow rate of 30 ml/min.

3. Results and discussion

3.1. Thermal decomposition of SA composites

Fig. 1 shows the TGA and DTA curves of the SA-0 sample heated at 10 K/min up to 1200 K. Besides initial weight loss of around 10% up to 400 K due to the physical water loss, the sample has experienced two major weight-loss stages with distinct separation, as noted in Fig. 1. At this heating rate, the maximum rate of weight

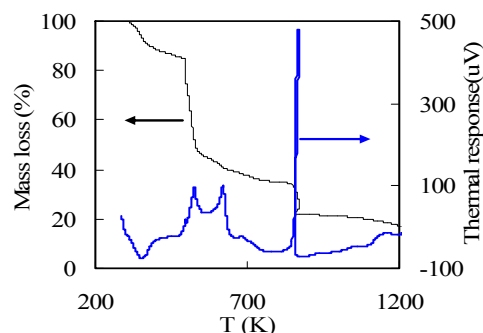


Fig. 1 TGA and DTA curves of the SA composites at a heating rate of 10 K/min.

loss occurs in the range of 500-700 K for the second stage by primarily chain scission, subsequent side-reactions like cyclization, crosslinking and partial carbonization without enough oxidative atmosphere, final formation of stable metal oxalates as intermediate fragments [14,15]. Around 820 K for the third stage is primarily involving decomposition of the carbonized products and formation of metal oxide from further decomposition of stable metal oxalates at high temperature.

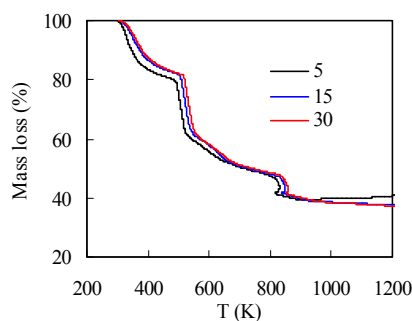


Fig. 2 Influence of heating rate on the TGA curves of the SA-40 sample.

The DTA curve shows the thermal response features are consistent with the TGA results as reflected by the DTA peaks. It can be seen from the DTA curve show that the first stage was endothermic whereas the other two stages were exothermic. The endothermicity in the first peak indicates that the energy is required to vaporize the adsorbed water molecules. The exothermicity observed means that the energy released from burning or forming new chemical bonds was greater than the energy absorbed for bond scission during decomposition. The energy produced from decomposing these wastes may be collected for other energy applications.

The three-stage decomposition features for the SA are identical to those of the other samples with the zeolite addition; one of example can be referred to Fig. 2, where the TGA curves obtained at three different heating rates are presented for the SA-40 sample. With the addition of zeolite, the decomposition could become more easily, as

the activation energy required for thermal degradation decreases, which is discussed in the later section.

3.2. Effect of the heating rate

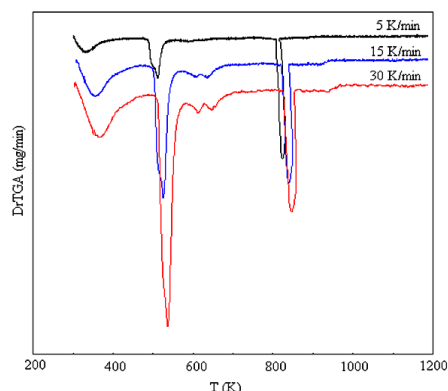


Fig. 3 Influence of heating rate on the weight loss rate for the SA-40 sample.

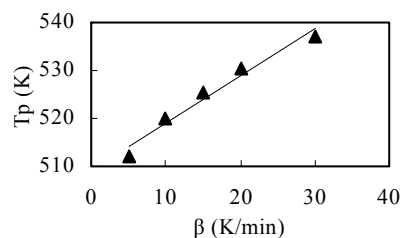


Fig. 4 Variation of the peak temperature of the SA-40 sample with the heating rate.

The derivative TGA curves obtained at various heating rates for the SA-40 sample are shown in Figure 3. As seen from this figure, the sample experiences three weight loss peaks and the second peak is the main one, being very well consistent with the TGA three-stage classification. As the heating rate increases, the peak becomes stronger and wider. It can be seen from both Figs. 2 and 3 that, by increasing the heating rate, the decomposition temperature shifts to the higher values. These shifts in the second-stage peak temperature are shown in Fig. 4. Clearly as shown in Fig. 4, the decomposition temperature almost increases linearly with the increase of the heating rate. These shifts in the temperature may indicate that the gasification rate of reaction products slows down as heating rate increases. Further, at higher heating rates, the time required to reach the decomposition temperature becomes shorter, possibly resulting in better thermal decomposition. But the temperature difference between inside and outside the huge sample becomes larger and cause thermal lagging that may delay the inside thermal degradation.

3.3. Thermal decomposition kinetic

Kinetic analysis is of importance for better understand-

ing the materials thermal degradation reactions and providing necessary information for thermally processing packaging wastes from these biomaterials. From the derivative TGA curves shown in Fig. 3, it can be seen that the second-stage is the main weight loss for the SA samples and thus is considered only in this work. The kinetic parameters like activation energy and pre-exponential

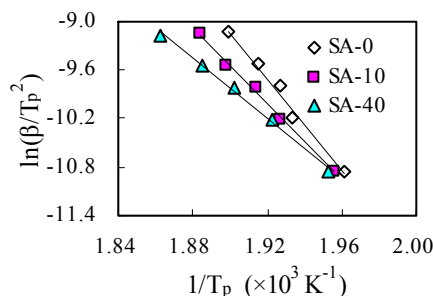


Fig. 5 The plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the samples.

factor value for the thermal decomposition of the samples are abstracted from TGA data, using the Kissinger method [18]. In order to conveniently calculate the pre-exponential factor (A) according to the Arrhenius equation, it is usually assumed that the decomposition follows the first-order reaction kinetics. Following this method, the relationship between the heating rate (β) and the peak temperature (T_p) can be plotted in Fig. 5. It could be found that the $\ln(\beta/T_p^2)$ against $1/T_p$ is straight lines for the sample, indicating that the mechanism of thermal decomposition of these compounds is the first order. The slope of the line was equal to $-E_a/R$. Therefore, the activation energy (E_a) was obtained from the slope of the graph while the pre-exponential factor $\ln(A)$ was calculated from the following expression [19].

$$A = \beta(E_a/RT_p^2) \exp(E_a/RT_p) \quad (1)$$

Table 1 Calculated pre-exponential factor.

β (k/min)	T_p (K)	$\ln(A)$ (s^{-1})
5	507	37.47
10	516	37.39
15	521	37.37
20	524	37.41
30	528	37.49
Average		37.43

From (1), it can be seen that the Arrhenius equation pre-exponential factor seems to relate to the peak temperature and heating rate. For evaluating its validity, the experimental data are analyzed by using this equation and the calculated results are shown in Table 1 for the SA-20 sample. Promisingly, the values of $\ln(A)$ obtained at different heating rates are very close to each other.

The calculation results are summarized in Table 2 for these materials. As can be seen, after adding into the zeolite, the activation energy for the SA thermal degradation turns to decrease and its value decreases with the zeolite amount, indicating that the zeolite addition may render the materials processing temperature decrease and possibly allow low treatment cost [11-12].

Table 2 Calculated results by using Kissinger method.

	$\ln(A)$ (s ⁻¹)	E_a (kJ/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/K·mol)
SA-0	47.6	221.72	219.03	173	83.91
SA-10	41.3	196.38	193.69	165	53.02
SA-20	37.4	178.88	176.19	158	33.89
SA-40	31.3	154.94	152.25	150	3.84

Based on the kinetic parameters (E_a and A), the thermodynamic parameters of decomposition could be calculated from the following equations [19]:

$$A \exp(-E_a/RT) = v \exp(-\Delta G/RT) \quad (2)$$

$$\Delta H = E_a - RT \quad (3)$$

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

where ΔG , ΔH and ΔS were free energy, enthalpy and entropy of the activation, receptivity; $v = k_B T/h$ (where k_B and h are Boltzmann and Plank constant, respectively). Thermodynamic parameters obtained for SA composites are also listed in Table 2.

4. Conclusion

The thermal decomposition of sodium alginate with the zeolite 4A addition was investigate in this work, and the results show that the main thermal decomposition process is in the range of 500-700 K, resulting from the chain scission of macromolecular framework and the formation of stable intermediates. The decomposition shifts to higher temperature as the heating rate increases.

Kinetic analysis shows that the main thermal degradation may follow the first order reaction mechanism. Through the Kissinger method, the kinetic and thermodynamic parameters can be abstracted from the weight loss data. The calculations reflect the activation energy for the SA thermal degradation decreases a lot after the zeolite addition.

5. Acknowledgment

The authors would like to thank the partial financial support of Tianjin University of Commerce through the SRT Project 2009024.

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