Thermal Degradation of Sodium Alginate- Incorporated Soy Protein Isolate/Glycerol Composite Membranes

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Abstract: Soy proteins are one of the most important natural biopolymers used to produce biodegradable materials, and thus have received ever-increasing attention in the food packaging materials, for compromising packaging materials and environmental protection so as to satisfy the requirements of the green packaging. In this work, a few new glycerol-plasticized soy protein isolate (SPI) composite membranes, modified by the incorporation of sodium alginate, were fabricated by using the solution casting method. The obtained films were examined with a thermogravimetric analyzer for thermal treatment consideration. The thermal characterization was conducted in detail to investigate the pyrolysis characteristics and kinetics of obtained SPI composites. The experiments were performed at the air flow rate of 30 ml/min, under different heating rates of 5, 10, 15, 20 and 30 K/min and from ambient temperature up to 1050 K. Thus the influences of heating rate and membrane composition on the thermal degradation of SPI composite have been evaluated, respectively. Based on TGA and DTG results, thermal behaviour of the SPI composites could be clearly separated into several degradation stages. The pseudo first-order kinetic parameters for the main degradation phase thus were estimated by means of certain conventional methods. These thermal investigations will be useful for better understanding the thermal stability of these SPI bio-composites and provide necessary information for thermally processing packaging wastes from these composite materials.

Keywords: soy protein isolate; sodium alginate; thermal degradation; kinetics

1. Introduction

In recent years, the development of environment friendly and biodegradable materials based on natural polymers has received increasing attention in an attempt to substitute petroleum-based plastics, which present important concerns in terms of pollution and sustainability [1, 2]. The problems of overflowing landfills, polluted marine waters and plastics wastes have also accelerated the need to develop polymers with controllable lifetimes taking into consideration environmentally acceptable manufacturing, application, recycling and disposal methodology [3]. Thus the main driving force for developing degradable materials is economic and environmental necessity rather than academic curiosity [4].

Recently, many researchers have provided overviews of various partially and completely biodegradable resins and composites [1, 5, 6]. Among various cellulose, protein and starch based materials, soy protein has been studied extensively as a potential replacement for petroleum-based products due to its low cost, easy availability and biodegradability [1]. It is usually obtained from soybean seeds by a separation method based on chemical reactivity and solubility [1]. Soy protein isolate (SPI) is a cream-colored powder with 90-95% protein content [1,7]. Its wide applications may include adhesives, plastics, films, coatings, glazing agents and emulsifiers in food chemistry, therapeutics, agricultural equipment, automobiles, marine infrastructure and civil engineering [2,8].

At present, soy proteins are thought to be one of the most important natural biopolymers that can be used to produce biodegradable materials, and their utilization will reduce the dependence and consumption of nonrenewable resources. Therefore soy proteins possess great potentials in the food packaging industries, for compromising packaging materials and environmental protection in order to satisfy the ever-increasing requirements of the green packaging. As such, there is an immediate need to develop or commercialize soy protein-based biodegradable materials for food packaging applications.

However, SPI materials without other secondary components may not have, in most cases, satisfactory physico-chemical and mechanical properties for industrial applications [9]. In general, the secondary, tertiary and quaternary structures of these macromolecules can be modified by denaturation, enhancing the interaction between amino acid side chains without breaking peptide bonds and consequently improving gel and film-forming, and mechanical properties [1]. For this reason, methods such blending with other biodegradable polymers [1,10-13] and chemical [1,7,14,15] or enzymatic [1,16,17] modifications have been developed.

In this work, we have attempted to incorporate sodium alginate (SA), a naturally occurring polysaccharide obtained from marine brown algae, into soy protein isolate (SPI) for preparing new composite materials. Thus, studying their thermal behavior and understanding deg-
radation kinetics are very important. The objectives of this work are: (i) to examine thermal behavior of the resultant SPI/SA composites, (ii) to investigate the influences of heating rates on the composite thermal degradation, and (iii) to analyze thermal degradation kinetics.

2. Experimental

2.1. Materials used

Commercial soy protein isolate (SPI) was provided by Harbin High-technology Soy Protein Co. Ltd. It has been prepared by acid precipitation and contains over 90% protein and less than 5.0% moisture. Sodium alginate (SA) is a sodium salt of alginic acid which is a linear polysaccharides containing 1,4-linked b-D-mannuronic (M) and a-L-guluronic (G) acid. Analytical grade glycerol (1, 2, 3-propanetriol) with 95% purity was used as a plasticizer. Analytical grade sodium hydroxide (NaOH) pellets were used to prepare a 1.0 mol/L solution at room temperature. These materials were purchased from Tianjin Letai Chemical Co. Ltd., China.

2.2. Preparation of SPI/SA composite films

The Fabrication of SPI/SA films was based on a solution casting and evaporation process. In this work the dope with a weight ratio of SPI/SA as 5:1 was prepared as follows. Firstly, 20 wt% SPI aqueous solution was prepared by adding 10g SPI powder to 40g of deionized water, in which the pH value was dropwise adjusted to 10.0 by 1mol/L NaOH solution. The dissolution was carried out at 353 K and under stirring for 1 h. Secondly, 4 wt% SA aqueous solution was prepared by adding 2g SA solid to 48g deionized water and stirred for 4 h. Then, the SA solution was added into the SPI solution. To the resultant mixture glycerol was added by 0, 6, 10 and 12g respectively and stirred with 200 rpm for 5h, yielding a series of the casting dopes with different compositions. The dope was cast on a Teflon sheet and dried in room temperature for 24 h. After dried, films were peeled from the sheet smoothly. The films obtained were named as M1, M2, M3 and M4, respectively. Besides, the pure SPI and SA films were also prepared for comparison.

2.3. Thermogravimetric analysis

Thermal analyses of dried samples with a mass of 5-6 mg were performed on the Shimadzu DTG-60 apparatus with a simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The samples were heated from ambient up to 1050 K with temperature programmed at certain heating rates in air at a flow rate of 30 ml/min.

3. Results and discussion

2.1. TGA measurements

Fig. 1 is presenting the weight variations at different temperatures calculated from TGA curves for pure SPI, pure SA and SPI/SA composites to evaluate the exact variation in degradation trend of SPI with change in the glycerol content and the SA introduction.

Fig. 1 TGA curves of different SPI/SA composite samples obtained at 10 K/min.

During the thermal degradation in oxidative atmosphere, the SPI, SA and SPI/SA biomaterials all exhibit a three-stage decomposition. Initial weight loss up to 400 K has been seen due to the physical water loss from the sample. Main weight loss for the biopolymer degradations is seen in the second stage but the temperature range is different for these SPI/SA composites. For pure SPI, its main weight loss is the in the temperature range from 540 to 630 K whereas for the SA its rapid degradation occurs in the narrower and lower range of 490-560 K. For the SPI/SA composite without glycerol, it can be seen that the main weight loss happens in the range of 480-600 K. Once plasticized by glycerol, the composite becomes less thermally stable and its decomposition starts from around 410 K. It is worth noticing that, SA has a typical and rapid degradation in the final stage, due to the formation of sodium oxide around 650-800 K, and this remarkable feature has retained for all the composites. Very interestingly, for binary SPI/SA, its rapid degradation in the third stage shifts to higher temperature than neat SA. But after added by glycerol, the third-stage rapid degradation of the SA moves to lower temperature range.

Fig. 2 presents the DTA curves for pure SPI, pure SA and SPI/SA composite samples. It can be seen that the DTA features are consistent with the TGA results as reflected by the DTA peaks. These DTA curves 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 used for thermal power generation.

Fig. 2 DTA curves of different SPI/SA composite samples obtained at 10 K/min.

Fig. 3 Variation of TGA curves with the heating rate for the SPI/SA samples.

Fig. 3 shows the effect of heating rate on the TGA curve features. It was found that, by increasing the heating rate, the decomposition temperature shifted to the higher values. 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.

3.2. Kinetic analysis

Kinetic analysis performed on thermal degradation reactions is useful for better understanding the thermal stability of these SPI bio-composites and provides necessary information for thermally processing packaging wastes from these composite materials. The Coats-Redfern integral method [18] was used to calculate the kinetic parameters like, activation energy and pre-exponential factor value of thermal degradation reaction for SPI/SA composites. The whole process of thermal degradation was divided into three suitable steps as discussed above, and each step might be assumed as 1st order reaction. Here, only the main thermal degradation, i.e., the second step, was considered. The kinetic reaction equation can now be written simply by the following expression:

\[ \frac{dx}{dt} = A \exp(-E/RT)(1-x) \]  

In this expression \( A \) is pre-exponential factor, \( E \) is activation energy, \( T \) is temperature, \( t \) is time and \( x \) represents the weight loss fraction of the sample which can be calculated by:

\[ x = (W_i-W_f)/(W_i-W_T) \]  

where \( W_i \), \( W_f \) and \( W_T \) are representing the initial weight and weight at temperature \( T \) and final weight of the test sample, respectively. At a constant heating rate \( \beta \) (=\( dT/dt \)) during thermal degradation, (1) can be rearranged and after integration it can be written as:

\[ \ln\left[-\ln(1-x)/T^2\right] = \ln\left[\frac{A\beta}{2RT}\left(1-2RT/E\right)\right] - \frac{E}{RT} \]  

In (3), the expression \( \ln[A\beta/E(1-2RT/E)] \) is constant for the most \( E \) values and for the temperature range used during the thermal degradation process [19]. Therefore, for a first order reaction a straight line should be obtained if the left side of (3) is plotted against \( 1/T \). More reasonably, (3) can be applied separately by calculating the value of \( x \) separately for each heating rate, and thus essentially parallel line will come for each heating rate. This method was taken in present study. Taking 450 K as the onset temperature of the second stage for all the samples, the temperature values for \( x = 0.10, 0.15, 0.20, 0.25 \) and 0.30 were readily abstracted from the TGA data for the heat rates of 5, 10, 15, 20 and 30 K/min. These temperature data then were used to obtain the Coats-Redfern plot. Thus for each constant heating rate, one Coats-Redfern line can be plotted and five lines for each sample considered. Figure 4 is showing the typical Coats-Redfern plots of \( \ln[-\ln(1-x)/T^2] \) vs. \( 1/T \) for the samples and the heating rate used in this case includes 5, 10, 15, 20 and 30 K/min. As can be seen, all the five lines for each sample are generally parallel to each other, further indicating that the decomposition may follow the first-order reaction mechanism. Otherwise, no parallel lines can be resulted for these samples.

The values of slope and intercept were obtained from the graph for all SPI/SA composite samples for the main degradation stage. The value of slope is used to calculate the activation energy \( E \). Similarly, pre-exponential factor can also be calculated from the intercept value by putting the temperature at which \( x = 0.20 \) in the place of \( T \) and \( \beta = 20 \) K/min [19-20]. The kinetic parameters calculated by using the above method for all the samples are presented.
in Table 1. It can be found that after plasticized by glycerol the composite needs less activation energy for thermal decomposition, indicating that the composite thus obtained may become less thermally stable than before the glycerol addition.

Fig. 4 Coats-Redfern plots for the M4 samples Table 1 Calculated kinetic parameters

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E$ (kJ/mol)</th>
<th>log $A$ (s$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>SPI</td>
<td>141.88</td>
<td>44.58</td>
</tr>
<tr>
<td>M1</td>
<td>119.83</td>
<td>39.07</td>
</tr>
<tr>
<td>M2</td>
<td>76.41</td>
<td>34.56</td>
</tr>
<tr>
<td>M3</td>
<td>73.52</td>
<td>32.61</td>
</tr>
<tr>
<td>M4</td>
<td>73.73</td>
<td>32.48</td>
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4. Acknowledgment

The authors gratefully acknowledge Tianjin University of Commerce for financially supporting this research through the SRT Project 2009106.

References