



Preparation of a novel agar/sodium alginate fire-retardancy film

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ABSTRACT

A novel flame retardant film of agar/sodium alginate/boric acid (AG/SA/BA) was prepared in presence of various concentration of BA (2.5, 5, 10, 15 wt%) through solution casting method. The result showed that C–O–B bonds were formed between BA and matrix. The addition of BA enhanced the limiting oxygen index (LOI), which might be related to the interaction formed between BA and matrix and excessive BA existing in molecular skeleton. The thermal stability of crosslinking film containing BA concentration above 5 wt% was improved when compared to that of the film without BA. Overall, the addition of BA enhanced flame retardancy and thermal stability at appropriate BA concentration.

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1. Introduction

Biopolymer has been gaining great interest in the past few years because they are renewable, biodegradable and environmentally friendly. Lots of polysaccharide materials have intrinsically flame retardancy because of existence of metal ions or the high oxygen barrier properties [1]. SA has the flame retardancy because of containing metal ions (sodium ions) [2], but AG has no flame retardancy. However, the blend of AG and SA has slight effect on improving the flame retardancy of AG. Adding flame retardants may improve the flame retardancy of polysaccharide material. Current Boron compounds are also widely used as the flame retardants and compounds, such as borax, BA, zinc borate, are well-known fire retardants because of their nontoxic, eco-friendly and high thermal properties [3]. However, the crosslinking of BA with AG and SA has not been reported so far.

The aim of this study was to prepare the AG/SA/BA films and investigate the effect of BA concentration on flammability, LOI and thermal stability.

2. Materials and methods

2.1. Materials

AG (Gel strength ≥ 1200 g/cm² at 1.5%) was purchased from Lanji technology development co., Ltd (Shanghai, China) and was used without further purification. SA (M/G = 2:1, Mw 2.1×10^6 g/mol)

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was purchased from Jiejing Seaweed co., Ltd (Rizhao, China). Glycerol and BA were all purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation of AG/SA/BA crosslinking films

AG (1 g) and SA (1 g) were dissolved in 100 mL distilled water with mixing vigorously for 30 min at 95 °C using the magnetic stirrer to obtain homogeneous solution with the concentration of 2 wt%. Glycerol, which mass was set to 30 wt% of total mass of AG and SA, was added into solution as a plasticizer. For the preparation of AG/SA/BA film, different mass BA (2.5, 5, 10, 15 wt% of total mass of AG and SA) was dissolved into distilled water at room temperature. Then AG (1 g) and SA (1 g) were dissolved in BA solution with stirring at 95 °C for 30 min and glycerol (0.6 g) was added in solution. Then homogeneous solutions were statically immovable at 95 °C for 30 min for crosslinking. The hot solution weighing 20 g was poured into a petri dish with a diameter of 10 cm and then left in the oven for 32 h at 50 °C.

2.3. Fourier transform infrared (FTIR) spectroscopy

The FTIR measurement was measured by the instrument (Thermo Fisher Scientific Nicolet iS 50, China) using 32 scans in the range of 4000–400 cm⁻¹ with the resolution of 4 cm⁻¹.

2.4. Flammability test and limiting oxygen index

The flammability of the prepared films was measured in the presence of air by using a vertical burning test similar to that

reported by Uddin [4]. The states of ignition and after burning 1 s were captured by the digital camera, respectively. All film samples were cut into the rectangle pieces (100 mm × 20 mm). Four film pieces were champed and fixed on the LOI instrument (HC-2, China).

2.5. Thermal stability

The thermal properties of films were determined using the thermogravimetric analyzer (TG209F3, Germany). All film samples were placed respectively and heated at the constant heating rate of 10 °C/min from 35 °C to 600 °C in nitrogen atmospheres.

3. Results and discussion

Fig. 1 showed the FTIR spectroscopy. The strong band at 1025 cm^{-1} had contributions from several vibration modes, namely to C–O and C–C stretching and to the C–C–O and C–O–H deformation [5]. The band at 1025 cm^{-1} of film containing 15 wt% was stronger than those of other AG/SA/BA film. Though there was no band at 653 cm^{-1} in the anomeric region of film containing 0 and 2.5 wt%, the intensity of the absorption band appearing at 653 cm^{-1} enhanced gradually as BA concentration rose from 5 to 15 wt%. This might be related to the formation of C–O–B chemical bonds. BA was the Lewis acid because of containing empty orbits [3]. But the mixture of AG and SA was Lewis base. This contributed to the formation of C–O–B. The C–O–B chemical bonds might be formed between oxygen elements of polysaccharide chains and boron elements of BA or between oxygen negative ions of carboxylate radicals and boron elements of BA.

The flammability of films was shown in Fig. 2. The snapshots with 1 s after ignition of film containing 0 (Fig. 2a2) and 2.5 wt% (Fig. 2b2) BA showed that two films continued to burn after removing the ignition source. But the flame of film containing 2.5 wt% BA was weaker than that of AG/SA film. As BA concentration further rose, the snapshots showed that there was no flame after removing the ignition source. At BA concentration above 2.5 wt%, these films showed self-extinguishing behavior after ignition. The films containing 10 and 15 wt% BA had no flammability in the ignition process. At BA concentration below 2.5 wt%, BA molecules might interact with polysaccharide molecules, but small amount of interaction was not enough to improve the flame retardancy of films. Upon further increasing BA concentration, the flame retardancy of film might be related to excessive BA existing in the molecular skeleton. BA or decomposition products of BA might hinder the further flammability of matrix.

The LOI values of all films were presented in Table 1. The LOI value of AG/SA film was 19%, lower than oxygen content in the air. As BA concentration rose, the LOI values of the films with BA increased gradually, indicating that the addition of BA enhance the flame retardancy of polysaccharide materials. But the LOI value of the crosslinking film containing 2.5 wt% BA was lower than 22%, indicating this film has inflammability. The LOI values of the crosslinking film containing 5, 10 and 15 wt% BA were between 22% and 27%, demonstrating that these materials were flammable. These results were consistent with the phenomenon of flame tests.

The TG and differential TG (DTG) curves were presented in Fig. 3, and the thermal stability data was shown in Table 1. The first stage of weight loss was 100–150 °C, related to the film dehydration. The second step, in the range of 190–350 °C, was ascribed to the thermal destruction of the glycosidic bond and the elimination of the adjacent hydroxyl group, which resulted in the formation of the intermediate material [6]. The last step occurred at 350–400 °C, due to the further decomposition reaction of intermediate material and the formation of char [7]. The decomposition onset temperature (T_{onset}) of films containing 2.5 and 5 wt% BA was lower than that of AG/SA film, demonstrating that a little BA caused early start of degradation. The reason might be that the interaction formed between BA and matrix accelerated loss of adsorbed and bound water. However, the T_{onset} of AG/SA film was lower than those of films with 10 and 15 wt% BA, which might be attributed to the evaporation of water from BA. T_{max} of AG/SA film was the lowest among all films. As BA concentration rose, the T_{max} increased gradually, which might be ascribed to the fact that the thermal annealing of BA with polysaccharide in presence of nitrogen caused the slower degradation [4]. Compared to that of AG/SA film, the significant decrease was observed for maximum degradation rate at BA concentration above 2.5 wt%, demonstrating that the addition of BA up to 5 wt% delayed formation of the volatile and combustible products [8]. Although the char production rose gradually with the increase of BA concentration, the char production of film containing 2.5 and 5 wt% BA was lower than that of film without BA. The intermediate material formed during thermal degradation might be more easily decomposed into volatile substance. Compared to AG/SA film, the char of films increased gradually at BA concentration above 5 wt%. BA existing in polysaccharide skeleton might undergo the esterification reaction with matrix molecules with increasing temperature up to 450 °C [9]. The resulting product formed by esterification reaction might be conducive to producing more char production. BA decomposed at high temperature and then generated boron oxide. The thermally degraded filler and product of intermediate material was bonded

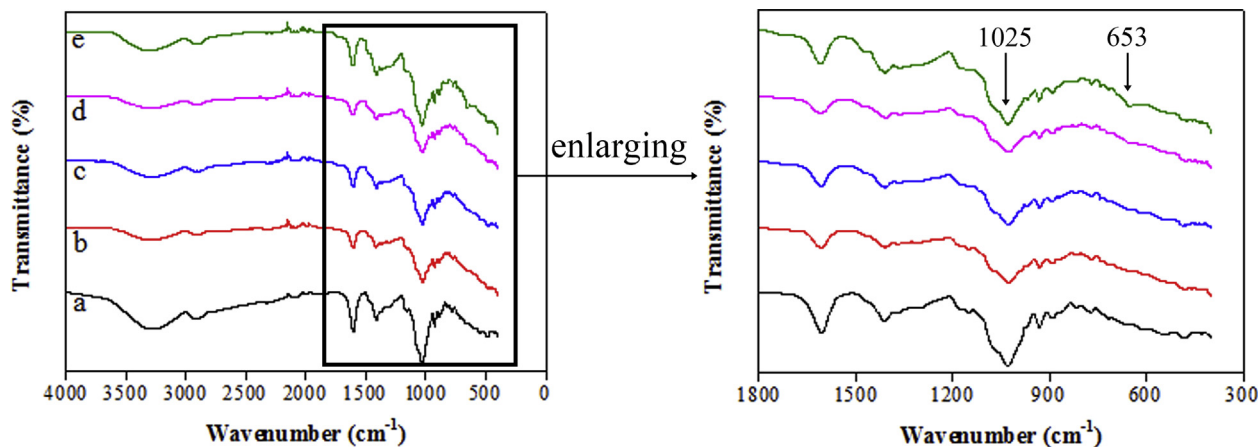


Fig. 1. FTIR spectra of AG/SA bicomponent film (a) and AG/SA/BA crosslinking films (b: 2.5 wt% BA, c: 5 wt% BA, d: 10 wt% BA, e: 15 wt% BA).

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