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Application of insoluble cross-linked starch particles as nucleation for foaming

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Abstract. Nucleation agents are important for foaming. Various mineral particles, such as calcium carbonate, talc etc, have been widely used as nucleation agents for starch foaming. However, incorporation of any additive is sensitive in developing fully biomaterials or edible materials, due to its safety issue or toxic concern. On the other hand, self-reinforced composites, in which a polymer matrix is reinforced with oriented fibers and tapes, or particles of the same polymer, have attracted greatly attentions since pure chemical functionality. In this work, we developed starch-based foam using cross-linked starch as nucleation agent, since the cross-linked starch is insurable in water and thermal stable up to 280°C. The cross-linked starch has successfully improved the uniform of starch foam.

1. Introduction

Nucleation agents have been widely used for various foaming processing since it can decrease the critical foaming energy and producing homogeneous cells. Various mineral particles, such as calcium carbonate, talc etc, have been widely used as foaming agents. However, incorporation of any additive is sensitive in developing fully biomaterials or edible materials, due to its safety issue or toxic concern. For, example, many starch-based materials not only require biodegradable but also edible [1-5]. On the other hand, self-reinforced composites (SRC), or single-polymer composites, in which a polymer matrix is reinforced with oriented fibers and tapes, or particles of the same polymer, have attracted greatly attentions since pure chemical functionality [6, 7]. The advantages of SRC systems include the ability to achieve perfect interfaces between composite components, their pure chemical functionality, and their higher value as recyclable products due to their relative homogeneity compared to composites composed of different classes of components.

Logically, we use same concept to develop modified starch as nucleation used for starch-based foam. In this work, we developed starch-based foam using cross-linked starch as nucleation agent, since the crosslinked starch is insurable in water and thermal stable.

2. Experimental

2.1. Materials

The cornstarch supplied by Hengrui Starch Company (Luohe, China, with moisture content 13%w) was used in this work. Cornstarch cross-linked by epichlorohydrin (Yifeng Company, Guangzhou, China) was used (2%w) as a nucleation agent. Tap water was used as plasticizer.

2.2. *Sample preparation*
In this works, the starch foams were prepared by two-step processing: 1) compounding starch-based pallets using a using a twin screw extrusion with co-rotating mixing screws (Keya, Nanjing, China) plasticized by injected water using a metering pump. 2) Starch foaming: the starch-based pellets with different moistures produced from first step were fed into a single screw extruder (Tongjia, Jining, China) with 35 mm diameter and 30 L/D ratio. A die nozzle with 3mm diameter connected with the single screw extruder was heated to 200°C.

2.3. *Characterization*
A differential scanning calorimeter (DSC), Perkin Elmer DSC 4000 equipped with a low-temperature accessory, was used to study the thermal properties of both normal starch and crossed starches. The samples (≈8 mg) were weighed in high-pressure stainless steel pans and sealed with a gold-plated copper seal to avoid moisture evaporation. The samples were heated from 50°C to 200°C at a heating rate of 10°C /min. The water contents in the samples were measured by a moisture content apparatus MB-35 from Hongji Instruments (Shanghai China) at 130°C. The cell structures of starch foams materials were studied using a SEM (ZEISS, Oberkochen, Germany) that was operated at a voltage of 10.0kV. The specimens were cut from cross-section and tuck on a circular metal stubs with double side adhesive tape and then coated with gold using an Eiko Sputter Coater under vacuum.

3. Results and discussions
Figure 1 shows the image of a water suspension (wt 5%) of native and modified starches respectively, heated to 95°C for 1 hr. It can be observed that there are two separated parts for the suspension of native starch: the top figure has a hazed (cloud) appearance, and the bottle part shows some un-dissolved starch. This indicates the starch was partly gelatinized at that temperature. The suspension of cross-linked starch shows two totally separated layers: water and starch, which indicates the cross-linking causes the starch to be insoluble under this condition.

Figure 1. Photos of the water suspension (5%) of native (lift) and cross-linked (right) starches heated to 95 °C for 1 hr.

Detailed thermal behaviors of various starches were studied by DSC. Figure 2 shows DSC thermograms of native and chemically modified starches. It is seen that there is a big endotherm was detected for native cornstarch, which represent gelatinization of the starch. No endothermic peak was detected for the cross-linked starch, which confirmed the cross-linked starch is unsolvable even at higher temperature [8-11]. The cross-linked starch showed water and thermal stability, which allow the granules to remain as rigid particles after thermal processing under moisture environment, thereby potentially act as the nucleation agents.

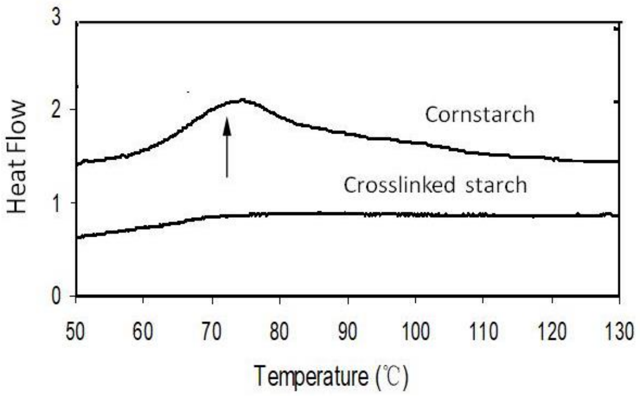

Figure 2. DSC thermograms of native and cross-linked starches (HF: mw).

Figure 3 shows the cell structures of starch foam without and with nucleation of cross-linked starch. All the foam showed the open cells. The sample without nucleation showed reasonable uniform and larger cell structures, and contains some lager cells. Additional of cross-linked starch as nucleation clearly decreased cell size with thinner wall. The diameter of the foam containing the nucleation is also slightly larger, which indicates the density of the foam is lower. The starch pellets containing nucleation of cross-linked starch showed better foams with more homogeneous size distribution. The results clearly indicated the cross-linked starch acted as nucleation for the starch foaming.

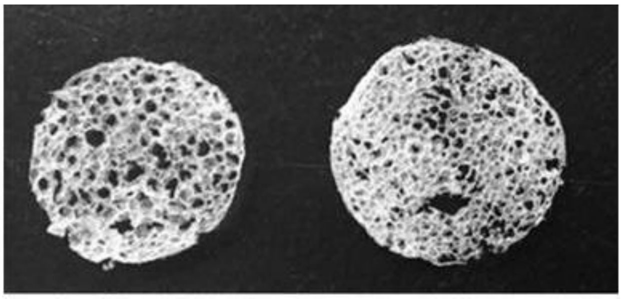

Figure 3. Cell structures of starch foam without (left) and with (right) nucleation of cross-linked starch (2 mm ——).

4. Conclusions

Starch-based foam nucleated with cross-linked starch particles was successfully developed. Since all the materials are natural, biodegradable with same chemical compound, the foam materials are not only environmentally friendly but also edible. The results showed that cross-linked starch had water and thermal stability, which allow the granules to remain as rigid particles after thermal processing under moisture environment, thereby acted as the nucleation agents. Additional of cross-linked starch as nucleation clearly decreased cell size with thinner wall. The starch pellets containing nucleation of cross-linked starch showed better foams with more homogeneous size distribution.

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