Thermal and rheological properties of starch-based materials

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Abstract. From application-oriented point of view, in order to decrease the cost of transportation the starch-based form was prepared by two steps: 1) compounding; and 2) foaming. That is because the foamed materials consist of more than 90% gas, the transportation cost could be higher than foam itself. In this work, starch-based pallets used for foaming were developed by extrusion. This presentation focuses on thermal and rheological properties of the starch-based materials. Cornstarch was used in this work. The results showed that the gelatinization temperature of the cornstarch was about 68°C with excess water content. The shear thin rheological behavior was observed for the cornstarch. Based on these the extrusion condition were designed and developed. In order to avoid foaming during compounding the temperature should be controlled less than 100°C. The higher screw speed can reduce the processing energy.

1. Introduction

Recently, more and more countries have started to ban foam packaging materials from non-biodegradable resources [1-7]. Starch-based foam is an ideal replacement for these non-biodegradable materials, in particular application as loss fill. From application-oriented point of view, in order to decrease the cost of transportation the form was prepared by two steps in this work: 1) compounding; ad 2) foaming. That is because the foamed materials consist of more than 90% gas, the transportation cost could be higher than foam itself. The compounded particles can be easily transport to anywhere near customer, then increase volume through foaming using a simple single screw extruder. In this work, thermal and rheological properties of starch-based materials were investigated to design the processing conditions for compounding.

It has been recognized that the processing properties of starch based materials are much more complex than conventional polymers since the processing (in particular extrusion) of starch-based polymers involves multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization [8-12]. In this work, starch-based pallets used for foaming were developed by extrusion. This presentation focuses on thermal and rheological properties of the starch-based materials, in particular the knowledge used for compound (extrusion).
2. Experimental

2.1. Materials
The cornstarch supplied by Hengrui Starch Company (Luohe, China, with moisture content 13% w) was used in this work. The calcium carbonate (Yifeng Company, Guangzhou, China) was used (2% w) as a nucleating agent to ensure the uniformity of foaming cells. Tap water was used as plasticizer.

2.2. Sample preparation
Pallets compounding: cornstarch and calcium carbonate were homogeneously mixed in a High Speed Mixer before processing. Mixtures were compounded using a twin screw extrusion with co-rotating mixing screws (Keya, Nanjing, China) plasticized by injected water using a metering pump. Diameter and L/D ratio was 65mm and 40 for twin-screw extruder respectively. The screw speed of 150rpm and a temperature profile of 30, 30, 80, 110, 110, 110, 80, 80°C (8 barrels) were set for the twin screw extruder, and a 3mm diameter die nozzle (heated to 80°C) with 9 holes connected with the twin screw extruder to produce cylindrical pallets. The feed rate of the mixtures and injection speed of water were matched up to steadily and continuously produce starch-based pellets with different water contents.

2.3. Characterizations
A differential scanning calorimeter (DSC), Perkin Elmer DSC 4000 equipped with a low-temperature accessory, was used to study the thermal properties of the starch-based pellets with different moisture. The samples (≈8mg) 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.

A Haake Torque Rheometer (Rheomix 600) with a twin-roll mixer was used in the experimental work. Sample materials were introduced into the mixer through a top-mounted loading hopper, and torque and temperature were recorded immediately after loading. Various roller speeds (15–90 rpm) and initial temperatures (30–90°C) were used in the experimental work.

3. Results and Discussions
One of the unique characteristics of starch-based polymers is their thermal processing properties, which are much more complex than conventional polymers, due to the multiple chemical and physical reactions that may occur during processing, as discussed above. Raw starches have no plastic behavior due to the intra- and intermolecular hydrogen bonds between the hydroxyl groups in starch molecules, which represent their crystallinity. Thermal processing is used to disrupt and transform the semi-crystalline structure of starch granules to form a homogeneous and amorphous material. This transformation is usually accomplished using small amounts of molecular substances commonly known as gelatinization agents or plasticizers. The transformed materials is normally called thermoplastic starch (TPS), and the techniques used to produce TPS products include extrusion, injection/compression molding, intensive mixing and hot pressing.

Figure 1 shows the DSC thermograms of corn starch with various water contents. It is seen that with decreasing water content, the endotherm G, gelatinization temperature of starch, almost remained at the same temperature when the water content water was higher than 40% and moved to higher temperature when the water content was lower than 40%. The endotherm M1 moved to higher temperature with decreasing water content. When the water content decreased to about 50% four endotherms were observed. Based on the results discussed above these four endotherms were identified as G, M1, M2 and Z respectively. The endotherm G disappeared when the water content was lower than 30%.
Figure 1. DSC endotherms of corn starch with different water content. The moisture content (from top) is: (a) 74.57%; (b) 65.3%; (c) 51.8%; (d) 40%; (e) 29.9%; (f) 16.15 %; (g) 9%;

The most commonly used technique for studying the rheological properties of TPS is capillary rheometry, which also represents the phase transition of starch under shear stress. For most TPS, the dependence of apparent viscosity on shear rate is linear on double-logarithmic plots, indicating that the power-law model could describe the rheological behavior of TPS as:

$$\eta = K\gamma^{n-1}$$

where $\eta$ is the molten viscosity, $K$ is the consistency, $\gamma$ is the shear rate, and $n$ is the power-law (pseudo-plasticity), index. The power-law behavior of TPS is mainly ascribed to the gradual reduction of starch intermolecular bonds. As expected, the apparent viscosity of TPS normally decreases with an increase in plasticizer (and/or water) content at constant temperature; it also decreases with increasing temperature at the same plasticizer weight content. Figure 2 shows the effect of mixer speed on torque with increasing time. As expected, the loading peak increased with increasing rpm, and the time to achieve the second peak decreased with increased rpm, since higher speeds enhanced the mechanical reactions and reduced packing time. The highest final temperature and the lowest torque were produced by the highest rpm. Figure 3 shows a plot of the variation of torque and temperature versus time at different rpm. It can be seen that with increasing rpm, the final torque decreased and the final temperature increased linearly on the logarithmic plots.

Figure 2. Effect of mixer speed on the variation of torque and temperature with time, as measured by the Rheometer Rheomix (30% water content, initial temperature 40°C): (a) 15 rpm, (b) 30 rpm, (c) 45 rpm, (d) 60 rpm, (e) 75 rpm, and (f) 90.
Figure 3. Plot of the variation of torque and temperature versus time at different rpm.

4. Conclusions
The phase transition of starch during gelatinization under shear stress conditions was studied by DSC and Rheomix. The DSC results correspond with torques measured by Rheomix. The results indicate that the processing conditions depend on multi-factions, such as water content, temperature, and extrusion speed etc. When compounding or extrusion of starch-based materials, an optimized conditions are important since the starch-based materials showed shear thin rheological behaviors.

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