The Effects of the Modified Starches on the Melting Flow and Biodegradation of the Starch/Glycerol Blend

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Summary: The purpose of this study was to improve the melting flow of starch/glycerol(GA) blends by modified starches. A variety of modified starches, which was treated by hydrolysis and acid hydrolysis, with and without ultrasonic treatment were used. The MFI (melt flow index) of blends increased from 0.5g/10min to 300g/10min when the addition of acid hydrolysis starch (0.3M CA-starch) was 70wt%. Their crystalline behaviors were analyzed by XRD results. The ultrasonic treatment has been proved to have the effect of hydrolysis without acids and synergistic effect on recrystalline. The SEM micrographs of the blend with the ultrasonic treatment starch gave the cleaving surface with comparison to the other blends. The weight loss of the blends with acid hydrolysis starches reached to 60~80% after one week biodegradation as the ultrasonic treatment was used.

Keywords: acid hydrolysis; biodegradable; crystallization; ultrasonic treatment

Introduction

Much research had recently been developing biodegradable materials because of the world environment and resources problem resulted from petroleum derived plastics. Starch, a renewable polysaccharide from a great variety of crops, was one of raw materials for biodegradable plastics. Yu et al.[1] indicated that glycerol were used as a plasticizer on thermoplastic starch (TPS), the TPS was tended to recrystallinization, which resulted in embrittlement. Then, the poor mechanical properties and melting flow ability limited its applications.

This research was to study the properties of starch/glycerol blends with modified starch in order to improve melt flow ability of blends. Besides, ultrasonic was also applied to treat above modified starch, and the analysis of the change of crystallinity morphology and biodegradation was investigation.

Experimental Part

Materials

Tapioca starch (food grade) was product of Thailand. Citric Acid (CA, reagent grade, Katayama Chemical Co., Ltd.) was used without any treatment. Glycerol (GA, reagent grade, Wako Pure Chemical Co., Ltd.) was applied to plastic starch.

Procedures

The Modified Starches

Tapioca starch was hydrolyzed with de-ion water and then denoted as hydrolysis starch. A variety of modified starches, which were treated by the citric acid of 0.1M, 0.3M, 0.5M are denoted as 0.1M, 0.3M, 0.5M CA-starch, respectively. All these modified starches were prepared by mixing the native starch to the corresponding

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solution with a weigh ratio of 1:1. Then, mixtures were stirred for 5 min and dried at 100 °C of oven temperature for 20min. If the above mixtures processed by an ultrasonic oscillator at 46 KHz for 10 minutes, it is denoted as S10 to imply to 10 minutes of ultrasonic treatment for comparison.

Blends

In this study, a variety of blends were manufactured by compounding the native starch with the modified starches, by 30wt%, 50wt%, 70wt%, respectively. The native starch was mixed with GA for 10 min before compounding with a modified starch. After that, the modified starch was added into starch/GA blends to blend for 10 min. For all the blends in this research, the amount of GA was fixed at 30phr based on the overall starches, native starch and modified starches. A single-screw extruder($\psi = 25$mm, L/D = 32) at four step temperatures of 100, 90, 70, 40 °C and the rotating speed was 20rpm was used to compound the blends.

XRD Measurement

The structure was characterized with an x-ray diffractometer, PANalytical Model X'PERT PROMPD, using Cu Kα radiation. The voltage and current of x-ray diffractometer were 45KV and 40mA, respectively. The measurement were perform in the range of 2θ from 10 to 40°.

Melt Flow Index (MFI) Measurement

The MFI measurements were carried out with a tester (Kayeness, Inc., model 7050HT) and the load was 9 kg at 125 °C. The average value was obtained from four test specimens.

SEM Observation

The morphology observations of starch blends were observed by a scanning electron microscope (JEOL JSM5600). Their specimens were fractured freezing and coated with a thin layer of gold (coating 120 seconds). The voltage of above SEM was used to be 10KV in this measurement.

Biodegradation Test

The size of each sample was 3cm × 3cm × 0.3cm, placed in the yeasty composting at ambient temperature. The humidity of composting was kept between 40% and 50%. Each sample was degraded for one week at the same condition, and dried with vacuum treatment for 48 hours, the weight loss of samples were obtained after drying.

Results and Discussions

Acid Hydrolysis of Starch

The structure of tapioca starch was composed of amylose and amylopectin. Amylose, mainly composed of $\alpha(1 \rightarrow 4)$ bonds, formed a double helix structure and higher crystallinity. Neverthless, amylopectin, was composed of both $\alpha(1 \rightarrow 6)$ bonds and $\alpha(1 \rightarrow 4)$ bonds [Figure 1], $\alpha(1 \rightarrow 6)$ bonds were amorphous regions of starch. Some studies [2–3] have shown that the acid preferentially hydrolysis starch chains in the amorphous regions of starch granule, and the crystalline regions was slowly degraded at the second stage. In this research, the applied citric acid will attack starch chains of both amorphous and crystalline regions. Beside, the degree of $\alpha(1 \rightarrow 4)$ bonds breaking will increase as increasing the concentration of citric acid.

XRD

Tapioca starch present a x-ray pattern of type A, with the main peaks in 15°, 17°, 18°, 20°, 23°,respectively. It is similar to the XRD structure of cassava starch (polvilho azedo) reported by Gomes et al.[4]. The $\alpha(1 \rightarrow 6)$ branch chains of starch would be preferentially broken during the process of acid hydrolysis. Then, the reordering of the part with chain-breaking would change the crystallinity of acid hydrolysis starch. Besides, $\alpha(1 \rightarrow 4)$ chain ensued breaking as the acid concentration increased. Figure 2 showed the XRD diffraction pattern of the native and modified starches. The significant drops of the diffractive peaks of the hydrolysis starch with respect

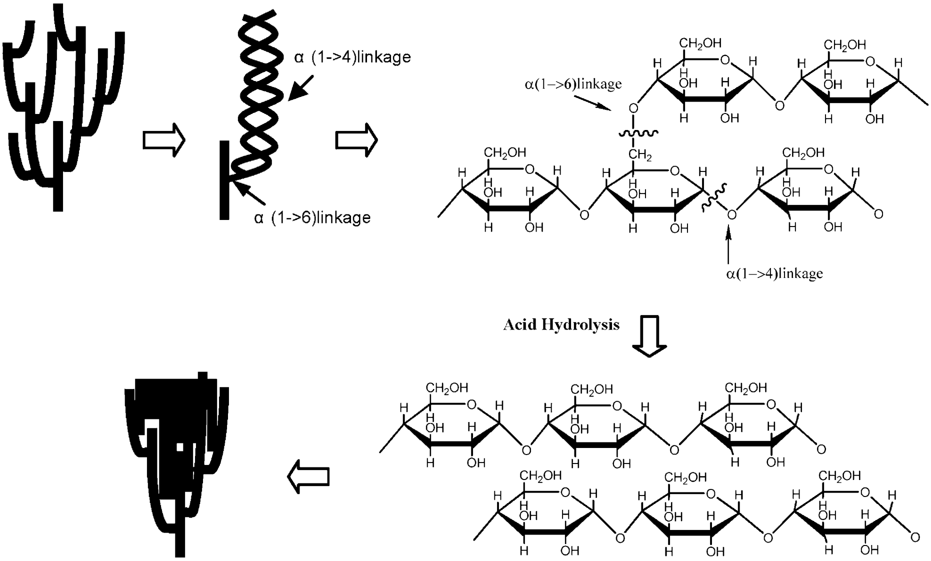

Figure 1.
Degradable diagram of tapioca starch with critic acid.

to native starch implied a decrease of crystallinity resulted from $\alpha(1\rightarrow6)$ chain breaking. The peaks of 0.1M CA-starch showed a serious drop. It showed be resulted from $\alpha(1\rightarrow4)$ chain breaking. The breaking had severely damaged the helix structure; however, the re-ordering effect did not occur. Consequently, the crystallinity was significant lowered down. As the concentration of acid hydrolysis increased to 0.3M and 0.5M, the broken chains became shorter. It accelerated the reordering and the re-crystalline effect occurred as shown in the presence of diffractive peaks in 0.3M CA-starch and 0.5M CA-starch. These results coincide with previous literatures.[5–7] They reported that a few starch chains allow the reordering of the chain segment to give a more crystalline structure with a sharper x-ray pattern. In this study, the ultrasonic treatment was provided to enhance the effect of hydrolysis without acids. It was confirmed by that the XRD pattern of S10-hydrolysis starch was similar to that of 0.1M CA-starch. On the other hand, it was also demonstrated by the synergistic effect shown in XRD pattern of S10-0.1M CA-starch,

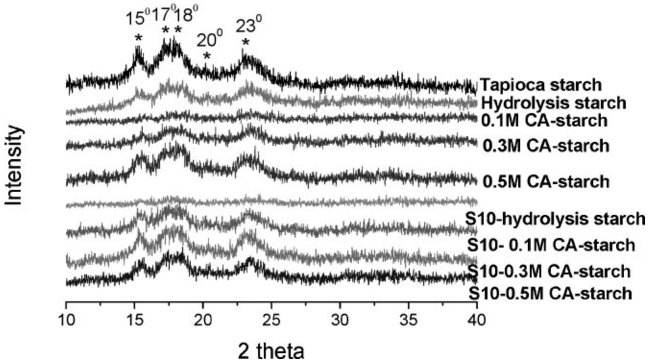

Figure 2.
XRD of various modified starch without and with ultrasonic treatment.

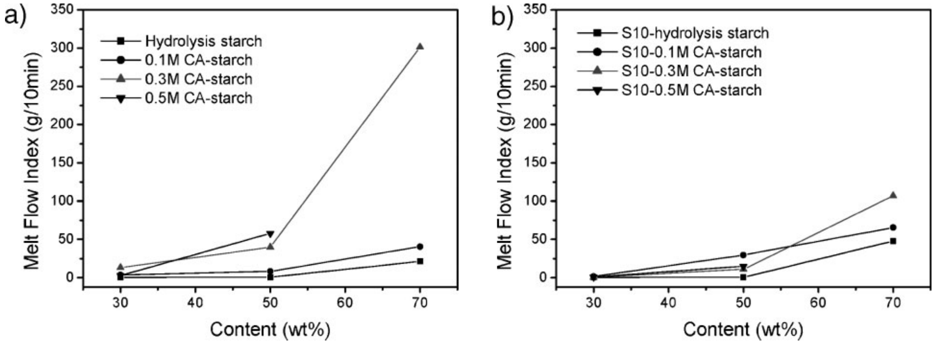

Figure 3.
MFI of starch/GA blends added modified starch (a) without ultrasonic treatment (b) with ultrasonic treatment for 10 min.

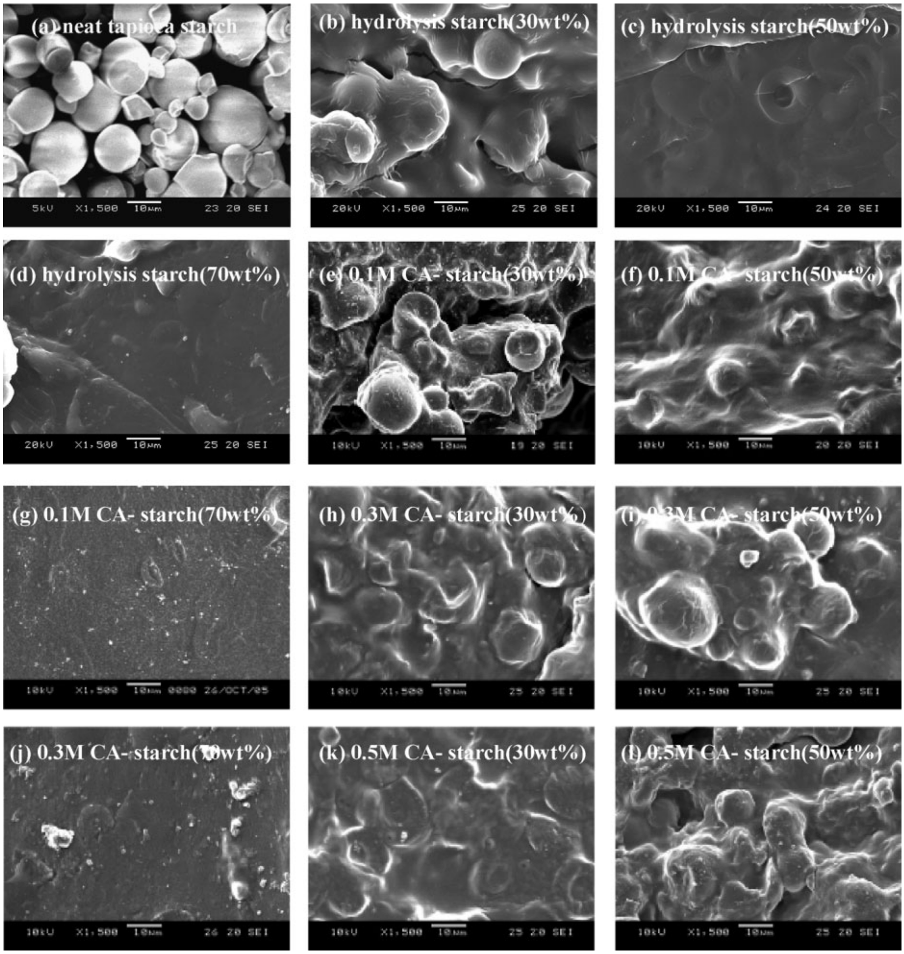

Figure 4.
SEM of starch/GA blends composed of modified starches with and without ultrasonic treatment.

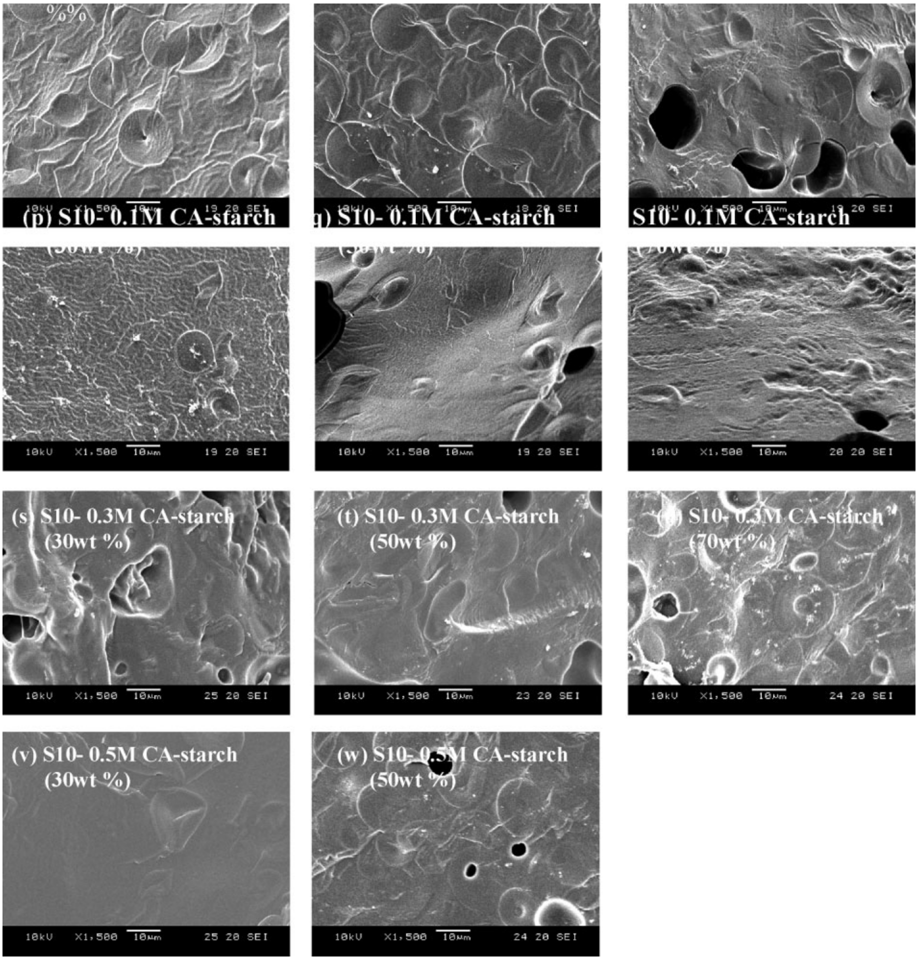

Figure 4.
(Continued)

S10-0.3M CA-starch, and S10-0.5M CA-starch.

MFI

The long chains of tapioca starch entangled itself to prevent its flow. Therefore, this research used the modified starches to improve the MFI of starch/GA blends. The effects on MFI by blending different modified starches with and without the ultrasonic treatment were showed in Figure 3(a) and (b). MFI of blends present an obviously increase as the addition of modified starches exceed 50wt%. Especially, as the addition of 0.3M CA-starch was 70wt%, the MFI of blend could reach to 300g/10min in Figure 3(a). Nevertheless, it decreased to 100g/10min with the addition of modified starch with the ultrasonic treatment in Figure 3(b). On the other hand, in the cases that the blends with 70wt% modified starch, the MFI of S10-0.1M CA-starch and S10-hydrolysis starches obviously increased with respect to that without ultrasonic treatment. These results were also consistent with the illustration of the previous XRD analysis.

SEM

The average particle size of neat tapioca starch was about 15∼20 μm showed in

Figure 4(a). The morphology of blends with modified starch showed in Figure 4(b~l). The morphology of blends present a smooth and compatible surface as addition of modified starch increased. This effect for the blends with acid hydrolysis starches was more significant than those with hydrolysis starches. The smooth cryo-fractured surfaces gave evidence that our modified starches have good plasticization. This results was consistent with the work of Roberta et al.[8] for corn starch/sodium alginate blends. On the other hand, the morphology of blends with ultrasonic treatment starches present a cleaving surface as observed in Figure 4(m~w). The cleaning surface should be resulted from the recrystalline of the modified starches with the ultrasonic treatment.

Biodegradation

Weight loss of blends was 50~65% for the hydrolysis starches after one week degradation in Figure 5(a), and was 20~40% for the acid hydrolysis starches in Figure 5(b~d). The blends with acid hydrolysis starches had a lower degradation, and it decreased as the concentration of critic acid increased. Weight loss of blends with acid hydrolysis starch increased to 60~80% when the ultrasonic treatment was applied. The blends had shorter chains to degrade by fungi as the ultrasonic treatment was used.

Conclusion

A variety of modified starches was applied to improve the melting flow behaviors of starch/GA blends successfully. The starches were modified by hydrolysis, acid hydrolysis, as well as the ultrasonic treatment. The analysis of the crystallinity was studies by XRD. The SEM morphology of the blends with modified starches showed the compatible interface; moreover, the SEM micrograph of the blends with ultrasonic treatment gave a cleaving surface. Therefore,

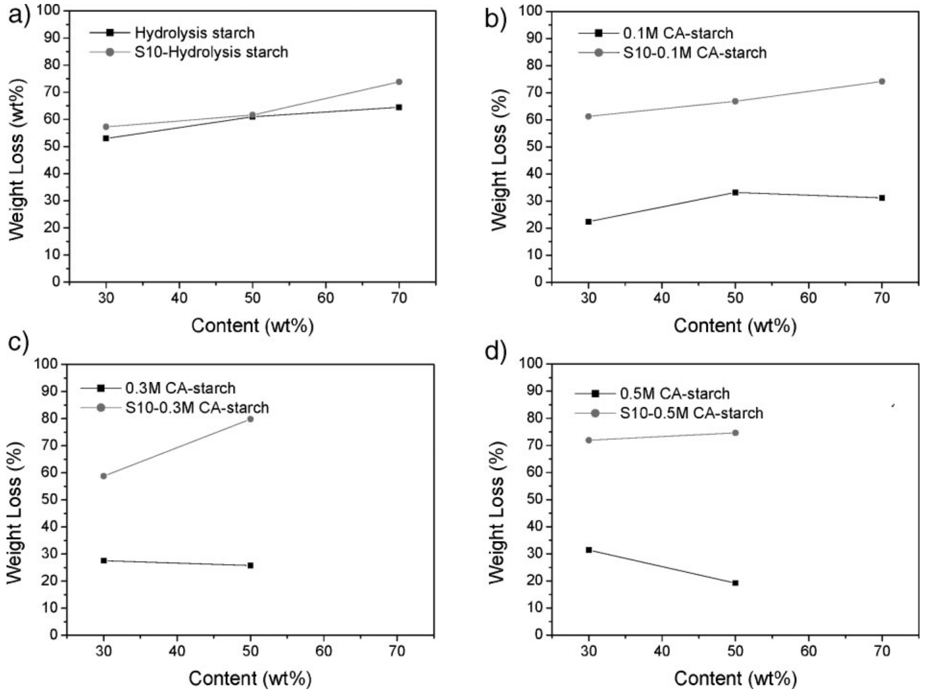

Figure 5.

Weight loss of starch/GA blends added different content (a) hydrolysis starch (b) 0.1M CA-starch (c) 0.3M CA-starch (d) 0.5M CA-starch after the biodegradation for one week.

it should be a tradeoff between the melting flow and biodegradation of the blend.

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