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쌀 전분의 유동성을 함유한 영·유아용 조제분유의 공정 관리

허영석* · Gül Konuklar

글로벌 리서치서비스, 애보트 영양사업부, 3300 Sreler Rd Columbus, OH 43219

In-Process Control of an Infant Formula with Rice Starch using Rheology

Youngsuk Heo* and Gül Konuklar

Global Research & Services, Abbott Nutrition, 3300 Stelzer Rd. Columbus, OH 43219, USA

ABSTRACT

We studied the feasibility of monitoring and controlling the manufacturing process of an infant formula with rice starch by testing in-process samples using rheology. We used DSC to first determine the gelatinization temperature of the rice starch, a key ingredient of this product. With this characteristic temperature and the process design known, rheological measurements were conducted on the in-process samples for detecting the presence and extent of gelatinization and retrogradation of rice starch; in-process samples were collected from the carbohydrate tank, after the homogenizer, and the finished product tank. The correlation between the rheological measurements on these samples and manufacturing performance proved that rheology is a very sensitive tool for monitoring the structural development of this infant formula during main process, and their influence on sterilization efficiency. We observed that the lower degree of gelatinization during main process, a shorter residence time in the finished product tank, and using caustic flush rather than clean-in-place additively lead to higher sterilization efficiency. These findings can be utilized for a rational design and analysis of the manufacturing process for infant formulas containing rice starch.

Keywords : in-process control, infant formula, rice starch, gelatinization, retrogradation, rheology

INTRODUCTION

In manufacturing infant formulas, various analytical tests are performed at the final stage of process to ensure the product quality. Thus, problems can be discovered only after they have become almost impossible or much harder to fix than it would have been if detected earlier by testing in-process samples. Furthermore, the value of a product is determined not only by the quality of the product itself, but also by the manufacturing efficiency and regulatory compliance. To enhance this value, we need to first specify parameters that represent manufacturing efficiency and what dictates those parameters. Then, we should be able to identify batch to batch difference in product quality and verify regulatory compliance with the claims by monitoring and controlling these parameters.

The parameters that represent manufacturing efficiency are processing time per unit product, frequency of cleaning needs and amount of cleaning agents to remove residue in heat exchangers, and the product amount processed before the first cleaning. These parameters are dictated by ingredients, their interactions, and homogenizer efficiency when forming emulsion. In addition, the microstructural changes of emulsion droplets and suspended particles during main process can also affect the

* Corresponding author: Youngsuk Heo, Global Research & Services, Abbott Nutrition, 3300 Stelzer Rd. Columbus, OH 43219, USA. E-mail: Youngsuk.Heo@abbott.com

sterilization process.

The use of rice starch in an infant formula is clinically proven to help significantly reduce frequent vomiting of infants due to enhanced viscosity of the formula in an infant's stomach. In this study, we investigated the manufacturing parameters for an infant formula with rice starch. Thus, it is imperative to understand the microstructure of the rice starch that we use, and build the correlation between its microstructural change during manufacturing process, and the rheological behaviors of in-process samples containing rice starch. In doing so, we would be able to monitor main process using rheological measurements, and predict sterilization efficiency.

MATERIALS

Starches consist of two different types of glucose monosaccharide chains: linear amylose and branched amylopectin. The length and branching structure of amylose and amylopectin chains govern crystalline structure of a starch, and in turn, affect swelling rate (or hydration rate), gelatinization temperature, retrogradation rate, and resistance to shear flow. Because of the crystalline structure that amylopectin is mainly responsible for, starch granule itself is neither water-soluble nor digestible; however, if one adds water to starch, the water molecules penetrate into starch granules and start interacting with amylose and amylopectin chains, which leads to granule swelling. A small amount of amylose chains escape from starch granules at this stage. Upon heating, swelling of starch granules accelerates, and finally, at temperatures above its gelatinization temperature, all amylose chains are freed, and crystalline regions become amorphous (see Fig. 1). Another thermal transition of gelatinized starch occurs when it returns to room temperature or below. During this temperature reduction, amylose and amylopectin chains, which energetically favor interacting with water molecules at higher temperatures than its gelatinization temperature, tend to form firm and insoluble gel particles with collapsed or swollen starch granules. This occurs because the amylose and amylopectin chains no longer thermodynamically favor interaction with water; this is called regtrogradation, and is an irreversible process. To determine the gelatinization temperature of the rice starch for the infant formula with this ingredient, we first tested its thermal transition (see Fig. 2). Temperature was equilibrated at 25℃ for 5 minutes, and increased up to 110℃ with the heating rate of 5℃/minute. This thermogram tells us that the gelatinization temperature for this rice starch is 65.7℃. Next, we decided sample collection points from the main process based on the gelatinization temperature and process design. Finally, we conducted rheological measurements on these samples to track the changes of microstructure and flow property over the main process.

EXPERIMENTAL METHODS

We took samples from the carbohydrate tank, in which the main ingredients were rice starch, sugars, and water (sample A). According to the gelatinization temperature of the rice starch (65.7℃) and the process design, gelatinization was not expected to occur in sample A. However, several samples were found to

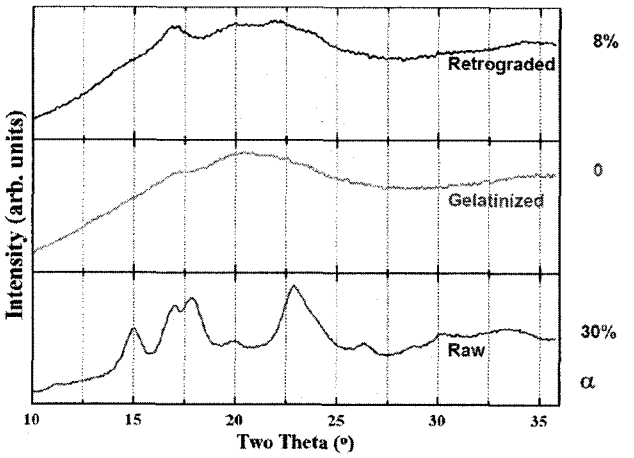

Fig. 1. X-ray diffraction patterns of raw, gelatinized, and retrograded starch samples. α denotes the degree of crystallinity in percentage [1]. See ref [2] for the experimental conditions.

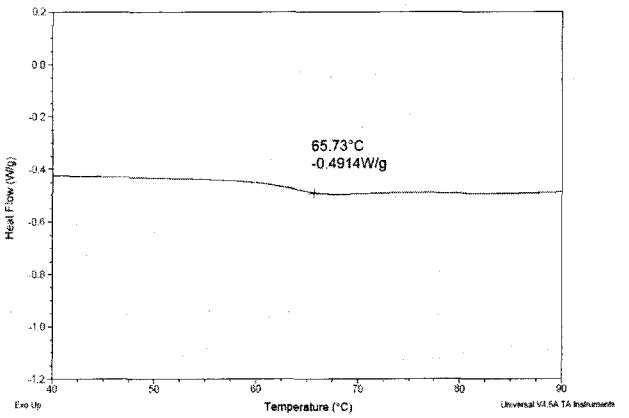

Fig. 2. DSC thermogram of the rice starch contained in the infant formula with rice starch. Q200 from TA Instruments was used. Gelatinization of starch, the first transition from order to disorder, is known to occur at the first endotherm [4].

be cloudy to some extent; light transmittance measurements on these samples using M-45 Agtron Process Analyzer were 74.5% and 72.7% respectively. This can be an indication of just starch granule swelling or gelatinization or both. Our rheometer, an ARES LS1 from TA Instruments with concentric cylinder geometry, confirmed no elasticity developed in these samples, which evidences no gelatinization. Note, however, that as an increasing number of amylose chains are freed in the carbohydrate tank before heating, starch will be more readily gelatinized for less time. This affects the degree of retrogradation upon cooling, and in turn, the sterilization efficiency and product quality as well. Second samples were collected after homogenization (sample B). Because of the higher temperature of homogenizer than that of gelatinization of the rice starch, rheology of these samples show well-developed elasticity (see Fig. 3). A dynamic strain sweep test with frequency 10 rad/s shows a pronounced linear viscoelastic region, and a dynamic frequency sweep test was done with the strain determined from this region. As shown in the dynamic frequency sweep in 〈Fig. 3〉, elastic modulus at low frequency was very noisy once it went below the limit of our rheometer, 0.001 Pa. Thus, keeping the record of elastic modulus at high frequency (50 rad/s) is more feasible. For viscous modulus, we selected low frequency (0.5 rad/s) because we can obtain zero-shear viscosity from $\eta_0 = G''/\omega$ at low frequency region as well. We also collected samples from finished product tank (sample C), and measured rheological properties along with the residence time before sterilization.

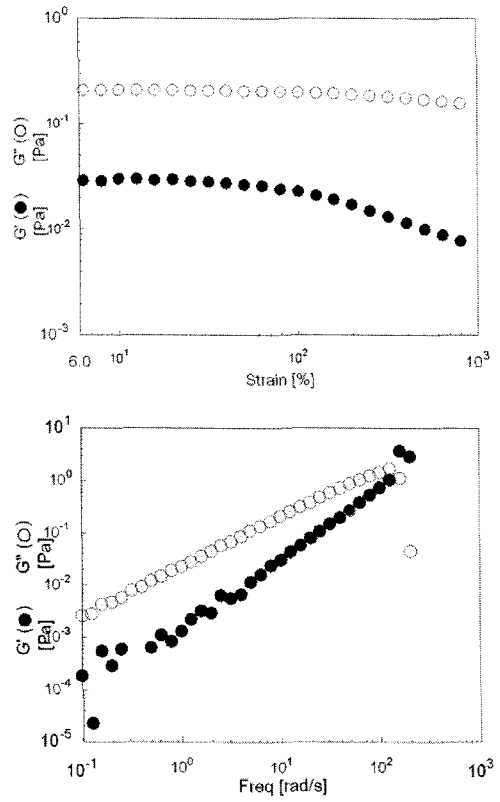

Fig. 3. Representative dynamic strain sweep test and dynamic frequency sweep test on a sample B. G' and G" respectively denote elastic modulus and viscous modulus.

RESULTS AND DISCUSSION

We examined the correlation between the events during main processing and the effects on sterilization efficiency. We measured the rheological properties of in-process samples (viscous and elastic moduli), cleaning agents used for heat exchangers, and residence time of sample C in the finished product (FP) tank. Then, we gathered information which represents sterilization efficiency, such as the amount of products before 1st cleaning, the number of cleanings, and the total processing time for an entire batch. In 〈Table 1〉, we recorded the average processing time per 1,000 lbs by dividing the processing time for each batch by the batch yield, and the cleaning frequency by dividing the number of cleanings by the batch yield. Finally, we listed the amount of product before the 1st cleaning by dividing the time before the 1st cleaning by the average processing time per 1,000 lbs.

1. Effect of Residence Time in FP Tank

Batches 3a and 3b: these two batches share the same rheological properties for the main process and cleaning agents, but have different hours of residence time (40 hrs vs. 55 hrs); 3a with shorter residence time shows better sterilization efficiency in terms of the product amount before 1st cleaning, the cleaning frequency, and the processing time.

Similar comparison was observed for the batches 4a and 4b.

2. Effect of Degree of Retrogradation

Batches 1 and 2: even though the residence time of batch 1 in FP tank (76 hrs) is shorter than that of batch 2 (90 hrs), batches 1 and 2 have very similar sterilization efficiencies in all aspects: the product amount before the 1st cleaning (37.5 vs. 43.5), the cleaning frequency (0.025 vs. 0.025), and the processing time (6.4 vs 6.9). This is presumably because the degree of retrogradation of batch 1 is a bit higher than that of batch 2,

Table 1. Rheological properties of the products stored in FP tank, cleaning agents, and residence time in FP tank, and batch yield, the amount of processed products before the 1st cleaning, cleaning frequency, and the average processing time per 1,000 lbs during sterilization

Batch number	G" [Pa · s]	G' [Pa · s]	Cleaning agent	Residence time [hours]	Batch yield [Klbs]	Amount before 1st cleaning [Klbs]	Cleaning frequency [1/ Klbs]	Processing time [mins/Klbs]
1	55	1289	Caustic	76	121.0	37.5	0.025	6.4
2	53	1244	Caustic	90	121.0	43.5	0.025	6.9
3a	N/A	N/A	CIP	40	88.9	17.9	0.022	6.7
3b	N/A	N/A	CIP	55	72.1	12.0	0.055	10.0
4a	44	999	Caustic	130	54.5	43.6	0.018	5.5
4b	44	999	Caustic	152	66.5	27.5	0.030	7.2
5a	33	714	Caustic	21	119.4	37.0	0.025	6.0
5b	33	714	CIP	42	41.6	27.7	0.024	6.5
6	51	1190	Caustic	79	121.0	37.5	0.025	6.4
7	43	959	CIP	111	161.0	4.0	0.037	7.6
8	44	984	CIP	28	161.0	9.0	0.037	6.7
9a	59	1338	CIP	29	68.3	8.6	0.073	7.0
9b	59	1338	CIP	118	52.7	32.4	0.019	7.4
10a	40	935	Caustic	52	77.7	24.2	0.026	6.2
10b	40	935	CIP	64.5	83.3	14.0	0.048	8.6

which compensates the difference in residence time, and, in turn, made the other parameters almost the same.

Similar comparison was observed for the batches 2 and 4a.

3. Effect of Cleaning Agents

Batches 10a and 10b: these two batches are essentially the same batch with different cleaning agents and residence time. even though residence time for batch 10a is a bit shorter than that for batch 10b, it does not seem sufficient to explain the large differences in parameters representing sterilization efficiency. Thus, caustic flush seemed to be affecting the sterilization efficiency in a positive way compared to clean-in-place (CIP).

Batches 7 and 10a: similar to the case of batches 10a and 10b, the two different cleaning agents exhibited drastic difference in sterilization efficiency.

Batches 4b and 5b: even though batch 4b has much longer residence time (152 hrs) than batch 5b (42 hrs), and higher degree of retrogradation indicated by rheological properties (viscous modulus=44 and elastic modulus=999 Pa.s) than batch 5b (viscous modulus=33 and elastic modulus=714 Pa.s), the sterilization efficiencies of these two batches are almost identical. This indicates the importance of the cleaning agent effect; caustic flush results in better aseptic performance than CIP does.

4. Integrity Check (We can Check the Integrity of Our Hypothesis that Two Different Samples with Similar Rheological Properties, Cleaning Agent, and Residence Time should show Similar Aseptic Performance)

Batches 1 and 6: These two batches have almost identical rheological properties, the same cleaning agents, and very similar residence time. This resulted in almost identical sterilization efficiencies, which ensures the integrity of our claims.

CONCLUSION

Heating rice starch with water during main processing is necessary to keep our ingredients sterile while residing in the FP tank before sterilization. Furthermore, we need to avoid excessive load on the heat exchangers with ungelatinized rice starch during sterilization. As a result, the rice starch becomes gelatinized during the main process, and it retrogrades upon cooling in the FP tank. The degree of retrogradation is dependent upon the profile of cooling over time and its pH; when a batch is more gelatinized, more retrogradation happens upon cooling. This retrogradation becomes more severe with time spent in the FP tank. Additionally, research has shown that higher retrogradation occurs at lower pH [3].

As discussed in the previous section, our experimental results tell us that the lower viscous and elastic moduli, the shorter residence time, and caustic flush rather than CIP additively lead to better sterilization efficiency in terms of the amount of processed products before the 1st cleaning, the cleaning frequency, and the processing time per 1,000 lbs.

Taken together, these results indicate that CIP causes higher retrogradation than caustic flush does. Thus, our main focus would be to find multiple ways to reduce the degree of retrogradation to a minimum.

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