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Effect of Water Vapor Sorption on Complex Formation in Amylose-lauric Acid Blend Powder

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Abstract: The purpose of this study was to understand the effect of relative humidity (RH) on amylose-lipid complex (ALC) formation in amylose-lauric acid blend powder held at 50 ºC (temperature slightly higher than the melting point of lauric acid) using differential scanning calorimetry (DSC) and X-ray diffraction. From DSC curves, the melting of crystalized lauric acid and two melting peaks of ALC were observed depending on RH. ALC formation was confirmed by X-ray diffraction pattern. The melting enthalpy (ΔH_m) of lauric acid in the sample held at RH 0 % was lower than that of lauric acid only though there was no ALC formation. This suggests that crystallization of lauric acid was prevented by amylose. The ΔH_m of lauric acid increased with an increase in RH up to 79.0 % because liquid lauric acid would have fused as the result of enhanced repulsive force between liquid lauric acid and hydrated amylose. The ΔH_m of ALC increased with an increase in RH between 79.0 and 95.0 %. For ALC formation, amylose has to be mobile in the system, but dehydrated amylose is in a glassy (immobilize) state. According to the glass to rubber transition behavior of amorphous polymer, amylose held at 50 ºC is suggested to become rubbery (mobile) state at RH 76.0 %. This interpretation will explain the reason why ALC formation began to be observed at the RH range between 72.4 and 79.0 %.

Key words: amylose, lauric acid, inclusion complex, water vapor sorption, differential scanning calorimetry

INTRODUCTION

Starch is mainly composed of amylopectin and amylose (AM). Amylopectin is a branched glucose polymer, and the segments have both a crystalline part (double helix) and an amorphous part. When starch is heated in the presence of excess water, the double helices of amylopectin unfold and are hydrated with water molecules (gelatinization). On the other hand, AM is essentially a linear polymer of glucose. AM commonly exists as an amorphous, semi-crystal, and/or AM-lipid complex (ALC) in starch granules. ALC is a single helix of AM that includes a fatty acid as a ligand. ALC can be also generated when starch is gelatinized and AM is released in the presence of fatty acid[1][2][3] and surfactant.[4] ALC is known to be more resistant to enzymatic dissociation than amorphous AM.[5][6] In addition, the retrogradation (recrystallization) of starch is suppressed by ALC.[7] Furthermore, ALC is useful as a molecular capsule.[8] It is, therefore, of practical interest as well as fundamental interest to understand the molecular mechanism of ALC formation.

In previous studies, ALC was formed by mixing fatty acid in gelatinized starch solution,[5][9] but ALC formation was inefficient because fatty acid is hydrophobic and thus shows poor dispersal in hydrophilic conditions. Powders, on the other hand, can be homogeneously blended independent of the hydrophilicity or hydrophobicity of materials, and AM-fatty acid blend powder can readily be produced. When the blend powder is held, water vapor sorption spontaneously occurs over time depending on the relative humidity (RH). Water vapor sorption likely causes spontaneous ALC formation during storage. However, to the best of our knowledge, there are no reports on the effect of water vapor sorption on the complex formation of AM-fatty acid in blend powder.

The purpose of this study is to understand the effect of RH on ALC formation in AM-fatty acid blend powder. Lauric acid (LA) was employed as a typical fatty acid. Since crystalline LA is thermodynamically stable, ALC formation was not expected in AM-LA blends. The melting temperature (T_m) of LA is reported to be 43.5−48.2 ºC,[10] and thus storage temperature was set be 50 ºC (temperature slightly higher than the T_m of LA). The storage period was set to 7 days; this period is almost enough to reach water vapor sorption equilibrium.[11][12] AM-LA was held at various RH conditions, and ALC formation of the sample was investigated using differential scanning calorimetry (DSC) and X-ray diffraction.

MATERIALS AND METHODS

Materials. AM from potato was purchased from Sigma-Aldrich Co., USA. Water content of the AM was determined to be 12.0 % (w/w) by oven-drying at 105 ºC for 16 h. LA was purchased from FUJIFILM Wako Pure Chemical Co., Osaka, Japan. The LA was manually ground using a mortar and pestle before using.

Preparation of AM-LA blend powder samples. AM and LA (total 15.8−17.9 mg) were prepared at 1 mmol-LA per g-dry AM according to a previous study[5] and mixed until homogeneous in a glass vial using a vortex mixer. The AM-LA (11.3−17.4 mg) was put into a DSC pan (internal diameter 3.9 mm), and then held at 50 ºC for 7 days in a container (diameter, 80 mm; height, 47 mm). RH in the container was adjusted by saturated salts (NaCl, KCl, $NH_4H_2PO_4$, and K_2SO_4). At 50 ºC, the RH generated by saturated salts was confirmed to be 72.4 ± 0.7 % for NaCl, 79.0 ± 0.9 % for KCl, 85.6 ± 3.2 % for $NH_4H_2PO_4$, and 95.0 ± 1.9 % for K_2SO_4 (mean ± SD, $n = 3$) using an RH logger (TR-72NW-S; T&D Co., Matsumoto, Japan). After 7 days, the DSC pan was hermetically sealed, and DSC measurement was carried out.

For the preparation of the anhydrous sample (RH 0 %), AM was vacuum-dried at 60 ºC for 6 h. The fully dried AM and LA were mixed as described previously in a glove box with dry air, and the AM-LA was hermetically sealed into the DSC pan. The sample was stored at 50 ºC for 7 days.

For comparison, AM only and LA only samples were also prepared according to the method explained above.

As another preparation of AM-LA sample, liquid water was rapidly provided to the AM-LA powder. Anhydrous AM-LA blend powder in the DSC pan was held at 50 ºC, liquid water pre-heated to 50 ºC (same amount of water as in the AM-LA held at RH 95.0 % at 50 ºC for 7 days) was added into the AM-LA using a pipette, and the DSC pan was hermetically sealed and then stored at 50 ºC for 7 days.

DSC measurement. Thermal properties of the samples were investigated using a DSC (DSC-60 Plus, Shimadzu Co., Kyoto, Japan). An empty aluminum DSC pan was used as a reference. Temperature and heat flow were calibrated with distilled water ($T_m = 0.0$ ºC) and indium ($T_m = 156.6$ ºC and melting enthalpy, $\Delta H_m = 28.5$ J/g). DSC was performed at 5 ºC/min over a temperature range of 20 to 160 ºC.

X-ray diffraction. To confirm ALC formation, X-ray measurement was carried out using an X-ray diffractometer (MiniFlexII, Rigaku Corp., Tokyo, Japan). As previously explained, AM-LA powder (1.13−1.63 g) was mixed at 1 mmol-LA/g-dry AM and put in an aluminum dish (diameter, 32.98 mm). The sample was held in the container at RH 95.0 % at 50 ºC for 7 days. The sample was defatted with diethyl ether at 60 ºC for 8 h using a Soxhlet extraction system. For comparison, AM powder was also prepared by the same method as was used for preparing the AM-LA powder. The sample was set on the sample holder, and X-ray measurement was obtained at 30 kV and 15 mA in the scanning range of 3º to 40º at 0.02º intervals.

RESULTS

Representative DSC curves for AM, LA, and AM-LA samples held at RH 0 % to 95.0 % at 50 ºC for 7 days are shown in Fig. 1. There was no clear thermal event in the AM samples (Fig. 1A). The LA samples showed an endothermic peak at approximately 42 ºC (Fig. 1B). The melting behavior of non-treated LA (as it is) was preliminarily confirmed, as shown in Supplemental Figure (Fig. S1; see J. Appl. Glycosci. Web site), and T_m (onset point) and ΔH_m were determined to be 43.2 ± 0.1 ºC and 34.4 ± 1.2 kJ/mol-LA, respectively (mean ± SD, $n = 3$). The LA samples were present as liquid state during the storage at 50 ºC. The liquid LA crystalized when the liquid LA was removed from the incubator, and the crystalized LA melted during DSC measurement. There was no major effect of RH on the T_m (40.9−42.9 ºC) and ΔH_m (33.8−36.2 kJ/mol-LA) of LA samples.

The AM-LA samples showed characteristic thermal properties depending on the RH (Fig. 1C). The AM-LA samples held at RH 0 % to RH 85.6 % showed a clear endothermic peak at 42 ºC due to the melting of LA. The AM-LA held at RH 95.0%, on the other hand, showed no or very little melting peak of LA. In addition, two endothermic peaks were observed, one at around 110 ºC and the other at around 136 ºC (Fig. 1D). The two endothermic peaks are suggested to be the melting of ALC.[9][10]

To confirm ALC formation in the AM-LA held at RH 95.0 %, the X-ray diffraction patterns of AM-LA and AM were compared (Fig. 2). To emphasize the diffraction peaks, the samples were defatted before the X-ray measurement. AM showed a diffraction peak at around 17º. This is in agreement with the largest diffraction peak observed for semi-crystal AM.[13] AM-LA, on the other hand, shows further diffraction peaks at around 7.6º, 12º, and 20º, and these peaks are in agreement with those of ALC having six glucose units per helical turn,[14][15][16][17] which indicates that ALC forms in the AM-LA held at RH 95.0 %.

The ΔH_m of LA in AM-LA samples is expected to decrease with an increase in the amount of ALC because a portion of the LA molecules contributes to ALC formation. As shown in Fig. 1, the melting peak of LA was clearly detected as a sharp endothermic peak. Thus, ΔH_m of LA is useful as an effective index of ALC formation. The ΔH_m of ALC, on the other hand, is expected to increase with an increase in the amount of ALC. The melting of ALC, however, was detected as multiple, small, and broad peaks. ALC is known to show multiple meting peaks depending on the storage condition.[14][18][19] For example, when LA was added in starch solution and the mixture was agitated, the formed ALC melted at approximately 90 ºC.[5] On the other hand, when starch-LA-water mixtures were extruded with a heating up to 120 ºC, the formed ALCs melted at 110−130 ºC.[20] When the extruded mixtures were re-scanned after cooling, they showed two melting peaks, one at around 90−110 ºC and the other at around 110−130 ºC.[20] It is known that the multiple melting peaks of ALC do not affect X-ray diffraction peaks.[14][16] It is suggested that the difference in T_m of ALC is originated not from crystalline structure of AM, but from crystalline lamellar thickness; the larger lamellar thickness, the higher T_m.[21] Since the multiple melting peaks of ALC were continuous in this study, it was experimentally difficult to individually determine the ΔH_m of the melting peaks. Thus, total ΔH_m of ALC (total area of endothermic peaks) was evaluated according to previous studies.[22][23][24]
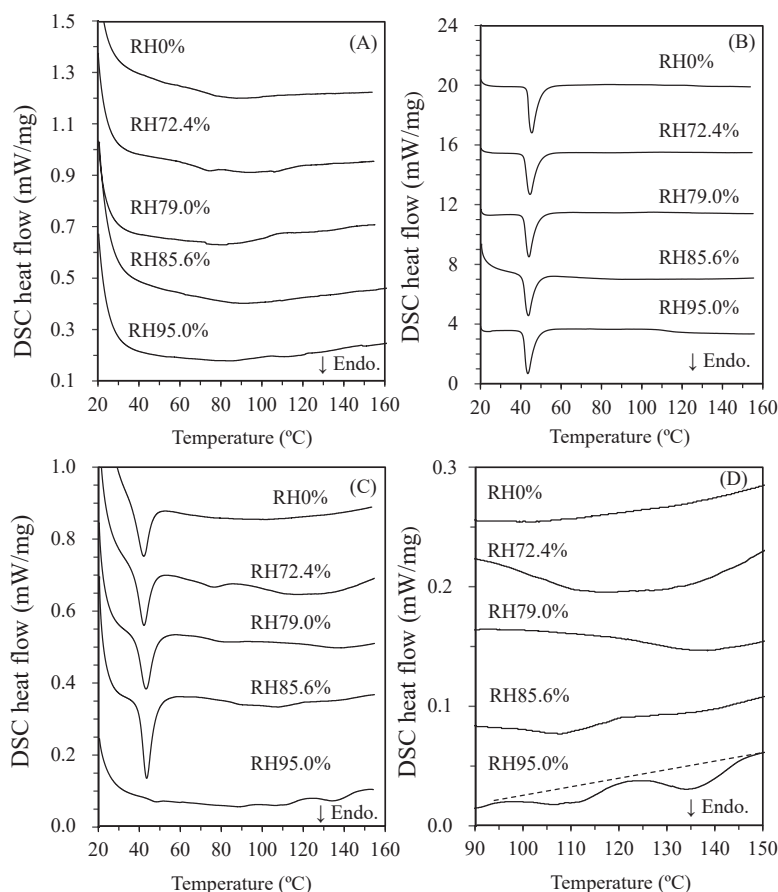
Fig. 1. DSC curves of (A) AM samples, (B) LA samples, and (C) AM-LA samples held at RH 0 % to RH 95.0 % at 50 ºC for 7 days.

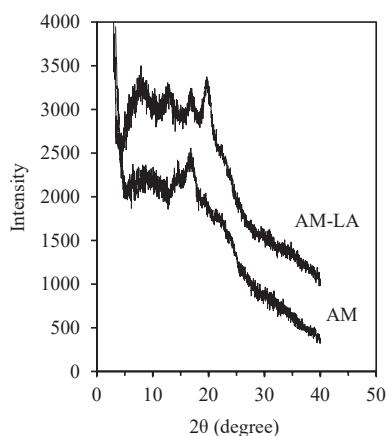The DSC curves of AM-LA samples are enlarged in the temperature range between 90 and 150 ºC (D).

Fig. 2. X-ray diffraction patterns of AM and AM-LA samples held at RH 95.0 % at 50 ºC for 7 days.

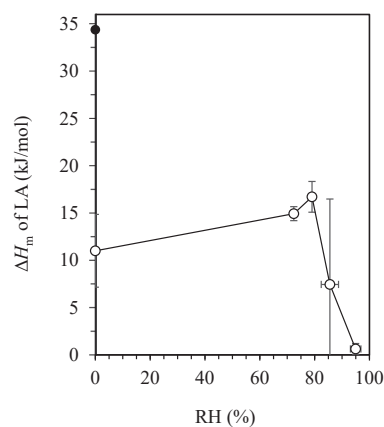The samples were defatted before measurement.

Fig. 3. Effect of RH on the ΔH_m of LA in AM-LA samples held at 50 ºC for 7 days.

Open and closed circles are AM-LA and LA only, respectively. Values are expressed as mean ± SD ($n = 3$).

The effects of RH on the ΔH_m of LA and the total ΔH_m of ALC are shown in Figs. 3 and 4, respectively. The ΔH_m of LA increased with an increase in RH up to 79.0 %, and then sharply decreased. The total ΔH_m of ALC increased with an increase in RH between 79.0 and 95.0 %. Notably, there was large deviation in the ΔH_m of LA and total ΔH_m of ALC at RH 85.6 %.

DISCUSSION

The ΔH_m of LA at RH 0 % was much lower than that (34.4 kJ/mol-LA) of LA only (Fig. 3). From the ratio of ΔH_m

(ΔH_m of LA in AM-LA samples per ΔH_m of LA only), crystallinity of LA in AM-LA was estimated to be 0.32. Although the lower ΔH_m of LA suggests the formation of ALC, there was no evidence of ALC formation (melting of ALC) in the DSC curve for AM-LA held at RH 0 % (Fig. 4). In the process of AM-LA preparation, crystal LA powder was dispersed in a large amount of AM powder. When the blend powder was held at 50 ºC, the crystal LA melted and then the liquid LA would have spread in the AM. When the AM-LA was cooled to room temperature, the liquid LA is expected to have crystalized. Crystallization of LA, however,
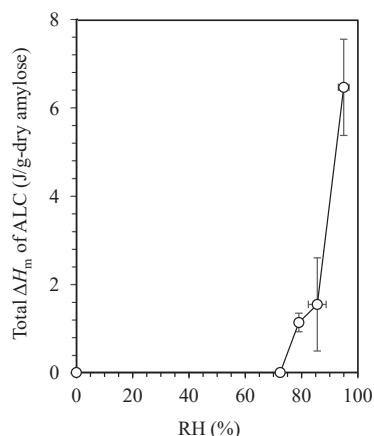
Fig. 4. Effect of RH on ΔH_m of ALC in AM-LA samples held at 50 ºC for 7 days.

The values are expressed as mean ± SD (n = 3).

was partially prevented because the spread liquid LA would have been confined in the gap spaces of AM powder.

The ΔH_m of ALC began to increase with an increase in RH from RH 79.0 % (Fig. 4). As explained above, the ΔH_m of LA is expected to decrease with an increase in the amount of ALC because a portion of the LA molecules contributes to ALC formation. The ΔH_m of LA, however, increased with an increase in RH and a maximum value (crystallinity 0.49) was observed at RH 79.0 % (Fig. 3). Water content of the samples basically increases with an increase in RH, and since water vapor interacts with AM through hydrogen bonds, repulsive force between liquid LA and hydrated AM is strengthened with the increase in RH. Then, spread liquid LA would translationally rearrange to avoid hydrated AM and thus force spread liquid LA to fuse in the system. When the system has cooled down to room temperature, the fused liquid LA readily crystallize unlike the spread liquid LA. Thus, crystallization of LA would be promoted with increasing RH.

For ALC formation, AM has to be mobile in the system. It is known that dehydrated biopolymer is in a glassy state, and the polymeric segments are immobilized.[25)26)] Thus, it would be intrinsically impossible for glassy AM to form ALC. To recover molecular mobility, glassy AM has to change to a rubbery (mobile) state by heating and/or hydration. Although there are no clear reports of the glass to rubber transition behavior of AM, it is suggested that AM held at 50 ºC becomes rubbery at RH 76.0 % as shown in the Appendix and Supplemental Figure (Fig. S2; see J. Appl. Glycosci. Web site). This interpretation will explain the reason why ALC formation began to be observed at the RH range between 72.4 and 79.0 %.

The ΔH_m of LA sharply decreased (Fig. 3) and the ΔH_m of ALC markedly increased (Fig. 4) with an increase in RH above RH 79.0 %, suggesting that ALC formation preferentially occurred rather than the fusion of spread liquid LA in this system. Since molecular mobility of AM increases with an increase in water content because of water plasticizing, ALC formation would be promoted. It should be noted that increasing water content does not simply promote the ALC formation because the fusion of spread liquid LA will also be promoted as the result of enhanced repulsive force between liquid LA and hydrated AM. In fact, there were large

deviations in the ΔH_m of LA and total ΔH_m of ALC at RH 85.6 %.

The glass to rubber transition of AM while suppressing the fusion of spread liquid LA is suggested to be necessary for the ALC formation, and this condition was gradually provided through water vapor sorption. However, there is a possibility that ALC is formed even if liquid water is rapidly provided to the AM-LA powder. For confirmation, liquid water preheated to 50 ºC (same amount of water as AM-LA held at 50 ºC and RH 95.0 %) was added by pipette to anhydrous AM-LA blend powder in a DSC pan held at 50 ºC, the DSC pan was hermetically sealed and stored at 50 ºC for 7 days. Representative DSC curve is shown in Supplemental Figure (Fig. S3; see J. Appl. Glycosci. Web site). DSC measurements confirmed that ALC formation was highly diminished; the ΔH_m of LA was 14.3 ± 2.1 kJ/mol-LA (re-crystallinity 0.42) and the total ΔH_m of ALC was 2.82 ± 0.93 J/g-AM (mean ± SD, n = 3). This will be because the fusion of spread liquid LA occurs preferentially over the glass to rubber transition of AM. When liquid water is added into AM-LA using a pipette, excess water will be partially provided to the AM-LA. At the part, repulsive force between liquid LA and water is enhanced and strongly promotes the fusion of spread liquid LA. On the other hand, water vapor sorption exclusively proceeds with hydration of AM, and thus the glass to rubber transition of AM occurs preferentially over the fusion of spread liquid LA. Thus, water vapor sorption has a positive effect on ALC formation.

CONCLUSION

The effect of RH on ALC formation was examined for AM-LA blend powder held at 50 ºC for 7 days. The ΔH_m of ALC (amount of ALC) increased with an increase in RH between 79.0 and 95.0 %. For ALC formation in AM-LA blend powder, the glass to rubber transition of AM while suppressing the fusion of spread liquid LA is suggested to be necessary conditions, but this is satisfied only by water vapor sorption and not by adding liquid water. Strictly speaking, the effect of water vapor sorption on the powder depends on the surface area of the powder and the generating velocity of water vapor for RH control in the incubator. In addition, storage temperature and time, types of ligand, and the ratio between AM and ligand are expected to affect ALC formation induced by water vapor sorption, and the effects of these will be examined in the future.

APPENDIX

Since the glass to rubber transition temperature (T_g) of anhydrous AM is high, thermal decomposition will occur before the glass to rubber transition during DSC measurement. Although T_g of AM decreases with an increase in water content, the thermal response of the glass to rubber transition is too small and broad, making it is very difficult to judge the response as an endothermic shift due to glass to rubber transition. Thus, there are no clear experimental reports on the T_g of AM. According to existing knowledge on the glass to rubber transition behavior of amorphous polymer, the T_g of AM can be predicted as follows.

Effect of molecular weight (MW) on the anhydrous T_g of

amorphous materials is described by the stretching exponential equation (Eq. (A1))

$$1 - \frac{T_g}{T_g^{max}} = \exp\left(-\left(\frac{MW}{\alpha}\right)^n\right) \quad \text{(A1)}$$

where T_g^{max} (K), α (dimensionless), and n (dimensionless) are constant. In the case of α-1,4-glucan (Fig. S2A; see J. Appl. Glycosci. Web site), $T_g^{max} = 517.2$ K, $\alpha = 225.6$, and $n = 0.49$ are reported.[26] The T_g increases with increasing MW but cannot increase without limit. T_g^{max} indicates the maximum T_g of α-1,4-glucan. Since AM is of sufficiently high MW, anhydrous T_g of AM can be assumed to be T_g^{max} (517.2 K = 244.1 ºC).

The effect of water content on the T_g of hydrophilic amorphous materials can be described by the Gordon-Taylor model (Eq. (A2)),

$$T_g = \frac{X_1 T_{g1} + kX_2 T_{g2}}{X_1 + kX_2} \quad \text{(A2)}$$

where X and T_g are the weight fraction (dimensionless) and T_g (K), subscripts 1 and 2 are solid and water, and k is a constant. According to the approximated Couchman-Karasz model, k can be described as

$$k = \frac{\Delta C_{p2}}{\Delta C_{p1}} \quad \text{(A3)}$$

where ΔC_p (J/(g·ºC)) is the heat capacity change induced by the glass to rubber transition. The T_{g2} and ΔC_{p2} of water are set to 136 K[27] and 1.94 J/(g·K),[28] respectively.

Effect of anhydrous T_g (ºC) on the $1/\Delta C_p$ (g·ºC/J) of α-1,4-glucan can be described as follows:[29]

$$1/\Delta C_p = 0.008 T_g - 0.843 \quad \text{(A4)}$$

From the linear proportion (Fig. S2b; see J. Appl. Glycosci. Web site), the ΔC_p at T_g^{max} (assumed T_g for anhydrous AM) was calculated to be 0.35 J/(g·ºC).

According to Eq. (A3), the k of AM was determined to be 5.53. The estimated anhydrous T_g and k for AM were in good agreement with anhydrous T_g (516 K) and k (5.2) for starch reported in a reference.[30] From the GT model with anhydrous T_g and k for AM, the glass transition of AM at 50 ºC was determined to occur at water content of 18.8 g/100 g-dry AM (Fig. S2c; see J. Appl. Glycosci. Web site).

Equilibrium water content of the AM-LA samples depends on RH. From the weight gain with consideration of the initial water content of AM, the equilibrium water content of the AM-LA samples was calculated at each RH (Fig. S2d; see J. Appl. Glycosci. Web site). Since LA is a hydrophobic material, it can be assumed that the water vapor exclusively interacts with AM in AM-LA samples. According to the assumption, the equilibrium water content of AM in the AM-LA samples (g-H_2O/100 g-dry AM) was evaluated. The water content at which the glass transition of AM occurs at 50 ºC (18.8 g/100 g-dry AM) showed a range of equilibrium water content of 17.4 g/100 g-dry AM at RH 72.4 % and 20.0 g/100 g-dry AM at RH 79.0 %. From the linear approximation in the RH range between 72.4 and 79.0 %, it was estimated that the water content at which the glass transition of AM occurs at 50 ºC is equivalent to the equilibrium water content at RH 76.0 %. That is, the glass to rubber transition of AM held at 50 ºC is suggested to occur at RH 76.0 %.

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