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Original Article

Impact of hydrogenated starch hydrolysate on glass transition, hygroscopic behavior and crystallization of isomalt-based systems

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Abstract

Glass transition behavior, adsorption isotherm and crystallization of isomalt-hydrogenated starch hydrolysate (HSH) mixtures (0-20% HSH) and pure HSH were investigated. At similar solid content, T_g decreased as HSH concentration increased. T_g data at different solid contents were well-fitted with Gordon-Taylor equation ($R^2 \geq 0.97$). Adsorption isotherm showed that systems with greater HSH concentration became more hygroscopic. Accelerated storage test (30°C, 84% RH) of modeled hard candy containing 10% HSH and pure isomalt formula was done. HSH enhanced water uptake and crystallization of polyols in hard candy during aging without packaging; however, those effects were lessen for the samples aged in polyethylene terephthalate/cast polypropylene (PET/CPP) pouches, and were negligible after the application of superior moisture barrier, oriented polypropylene/metalized cast polypropylene (OPP/MCPP) film. Although HSH adversely affected storage stability of sugarless hard candies, it could be add into the formulation together with the application of packaging having a good moisture barrier.

Keywords: glass transition, sorption isotherm, crystallization, polyol, hard candy

1. Introduction

Hard candies can be formulated with sugar-based ingredients, simply sucrose and glucose syrup, or made from polyols, creating sugar-free version. The latter formulation is usually based on either isomalt or lactitol due to their outstanding properties, especially those related with glass transition and hygroscopicity. For amorphous confections, such as hard candies, glass transition is in great concern. A product will be in a glassy state with enhanced storage stability if its T_g is higher than storage temperature. Selection of the ingredients with elevated T_g thus helps enhance the product stability. Moreover, if the ingredients are less hygroscopic, the resulting hard candies will not prone to absorb moisture during storage. Water plasticization leading to T_g reduction is not likely to occur. Isomalt and lactitol which are very low hygroscopic and have reasonably high glass transition temperature (T_g) (Mitchell, 2006) thus provide sugarless hard candies with enhanced storage stability

Another polyol recommended for sugarless hard candies is hydrogenated starch hydrolysate (HSH), which may serve as a doctoring agent; this is also the role of glucose syrup in sugar-based hard candies (Raudonus *et al.,* 2000). Good doctoring agent should help retard crystallization of ingredients (sugars or polyols) even when glassy hard candy transform to rubbery melt, causing dramatically increase in molecular mobility which is favorable to crystallization phenomena (Hartel *et al.,* 2011). The ability of HSH to retard crystallization in hard candy varies with its molecular weights (McFetridge *et al.,* 2004). However, this polyol may adversely affect storage stability of hard candies. In comparison with isomalt and lactitol, HSH is more hygroscopic and may have lower T_g, depending on its molecular weight (McFetridge *et al.,* 2004; Raudonus *et al.,* 2000). Studies regarding the

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influence of HSH on crystallization of isomalt-based or lactitol-based system are still limited and somewhat contradictable. Raudonus *et al.* (2000) found that addition of 10% HSH in lactitol-based hard candy could help delay the crystallization during storage under high humidity (80% relative humidity, RH; 25°C). However, they reported that both low and high molecular weight HSHs in a range of 10-50% enhanced crystallization of isomalt-based hard candies under the same storage condition. Nevertheless, McFetridge *et al.* (2004) reported that both low and high molecular weight HSH at 10% addition level retarded crystallization in isomalt-based system stored at 80% RH, 20°C. Low molecular weight HSH was more effective in this case. It is interesting to note that packaging materials were not used in those storage tests. Further studies regarding effects of HSHs on physical properties and storage stability of sugar-free hard candies are still required to help determine if HSHs should be recommended in the formulation.

This study aimed to evaluate influence of HSH on T_g, adsorption isotherm and crystallization of the isomalt-based mixtures. Due to its greater popularity, isomalt was selected as a representative polyol recommended for sugarless hard candies. Mathematical modeling of data regarding plasticization effect of water on T_g and sorption isotherm was performed. Accelerated storage test was conducted in modeled hard candies. Impact of packaging materials on storage stability of the hard candies was also considered. The latter part could enhance industrial application of this research.

2. Materials and Methods

2.1 Materials

Isomalt (Palatinit®) was purchased from BENEO-Palatinit GmbH, Mannheim, Germany. HSH syrup (MU-50) was obtained from Ueno Fine Chemicals Industry, Samut prakarn, Thailand. Its chemical composition was shown in Table 1. Two types of the laminated plastic films, oriented polypropylene/metalized cast polypropylene (OPP/MCPP) and polyethylene terephthalate/cast polypropylene (PET/CPP), were used as packaging for modeled hard candies. Total thickness of OPP/MCPP and PET/CPP films was 46 mm and 38 mm, respectively. In case of barrier properties, water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of the OPP/MCPP film were 0.73 $g \times m^{-2} \times day^{-1}$ and 120 $cm^3 \times m^{-2} \times day^{-1}$, respectively. While PET/CPP film had WVTR of 8.56 $g \times m^{-2} \times day^{-1}$ and OTR of 122 $cm^3 \times m^{-2} \times day^{-1}$.

2.2 Preparation of amorphous systems

Amorphous systems of isomalt, HSH and the polyol mixtures (10% and 20% HSH) with varied moisture content were prepared with the modified method of Raudonus *et al.* (2000). Solution containing 70% solids by weight, with desired proportion of polyols, was heated under atmospheric pressure until its temperature reached 105-160°C, and cooled down. Moisture content of the samples was measured by

Table 1. Chemical composition and glass transition temperature of the hydrogenated starch hydrolysates used in this study and previous studies.

Type	Chemical composition of dry matter	T_g of anhydrous material (°C)	Reference
MU-50 (69-71% solids)	≤7% sorbitol 43–53% maltitol 16–26% maltotriitol 20–30% larger oligomers	44.2	This study
Hystar 5875 (75% solids)	7% sorbitol 60% maltitol 33% larger oligomers	54.2	Allen and Watkins (2007); Mcfetridge *et al.* (2004)
Hystar 3375 (75% solids)	13% sorbitol 20% maltitol 11% maltotriitol 56% larger oligomers	54.6	Raudonus *et al.* (2000)
Hystar 6075 (75% solids)	12% sorbitol 8% maltitol 8% maltotriitol 72% larger oligomers	75.0	Raudonus *et al.* (2000)

Karl-Fischer volumetric titrator (795 KFT Titrino, Metrohm AG, Herisau, Switzerland). Various heating temperatures were used to allow different degrees of water evaporation, resulting in amorphous systems with final moisture content of 1-15%. T_g of all samples were determined. The samples with <2% moisture were used for constructing adsorption isotherm.

2.3 Differential scanning calorimetry

T_g of the amorphous mixtures were determined by differential scanning calorimetry (DSC) (Diamond, Perkin-Elmer Co., Norwalk, CT, USA), equipped with an Intracooler 2P (Perkin-Elmer) and nitrogen gas purge, using the method modified from Raudonus *et al.* (2000). Approximately 10 mg of the amorphous mixtures were weighed into an aluminum volatile sample pan and hermetically sealed. An empty DSC pan was used as a reference. The sample was heated from -40°C to 95°C at 10°C/min (first heating scan), cooled down to -40°C at 30°C/min, and rescanned to 95°C at 10°C/min (second heating scan). T_g was determined from the second heating scan using Pyris™ operation software version 8 (Perkin-Elmer). T_g midpoint, identified from the temperature corresponding to the midpoint of the change in heat capacity caused by glass transition, was recorded. Gordon Taylor equation was used to fit the T_g data at various solid content (Gordon and Taylor, 1952).

$$T_g = (w_1T_{g1} + kw_2T_{g2}) / (w_1 + kw_2) \quad (1)$$

where w_1 and w_2 are the weight fractions of dried solids and water, and T_{g1} and T_{g2} are the T_g of dried solids and pure water, respectively. According to Johari *et al.* (1987), T_{g2} was -134°C. The constant k represents the plasticization effect of water on T_g.

2.4 Adsorption isotherm

Adsorption isotherm of the polyol samples was determined with static gravimetric technique (Hadjikinova *et al.*, 2003). Samples of 0.5±0.1 g were equilibrated at 30±2°C under certain RH (11.3-92.3% RH) controlled by series of saturated salt solutions (Greenspan, 1977). The samples were equilibrated over saturated salt solutions in hygrostats up to two weeks to ensure the maximum water uptake. Equilibrium moisture content (EMC) was determined by hot air oven method at 110±5°C (AOAC, 1995). Moisture content determination was done in triplicate.

2.5 Preparation of modeled hard candies

Modeled hard candies consisting of polyols, flavoring agent, sucralose and caramel color were prepared. Food additives other than polyols were < 1% (dry basis) in the formula. Polyol solution (70% solids by weight) was heated under atmospheric pressure until its temperature reached 160°C. After removing the solution from the heat source, flavoring substance, sucralose and caramel color was then added and mixed well. The mixture (≥140 °C) was then poured onto a silicone mold and cooled down in a desiccator. Candy samples, each with 2.5 cm diameter, 0.5-0.7 cm thick and weighed 3.0-3.5 g, were obtained.

2.6 Crystallization of polyols in modeled hard candies during storage

Each hard candy piece was packed in PET/CPP or OPP/MCPP pouch (3×3 cm) and heat sealed. The packed samples, as well as the samples without packaging, were incubated at 30±2°C in hygrostats containing saturated KCl solution to create high humidity environment (84.0±0.2% RH) (Greenspan, 1977). The samples were periodically weighed during storage. Percentage of weight increase at a given storage time in comparison with the initial weight was calculated. Surface and cross section images of the candy pieces were taken by stereomicroscope (SMZ-1000, Nikon Corporation, Tokyo, Japan) equipped with 10× eyepiece lens, Plan Apo 1 WD-70 objective lens and digital camera (DXM1200F, Nikon Corporation, Tokyo, Japan). Intermediate magnification was set as 0.8×. Images were captured via Nikon ACT-1 software, version 2.6.3.0 (Nikon Corporation, Tokyo, Japan). Thickness of the crystalline layers on the surface of the candy pieces was measured from the cross section images using UTHSCSA ImageTool version 3.0 (Department of Dental Diagnostic Science, University of Texas Health Science Center, San Antonio, Texas). For each sample, thickness was obtained from 6 positions, right, middle and left positions of the upward and downward crystalline layers. The experiments were done in triplicate. Each sample piece was used only once for the measurement at a specific storage time.

3. Results and Discussion

3.1 Effects of HSH on glass transition temperature and adsorption isotherm of isomalt-based systems

Plasticization effect of water on T_g of the isomalt, HSH and isomalt-HSH mixtures were shown in Figure 1. All data were fitted well with Gordon Taylor equation ($R^2 \geq 0.97$) (Table 2). For anhydrous system, T_g of HSH used in this study was lower than that of the pure isomalt (Table 2) and those of HSHs reported in the previous studies (Table 1). In general, HSH with higher molecular weight had higher T_g (McFetridge *et al.*, 2004; Raudonus *et al.*, 2000). Based on its chemical composition and T_g as shown in Table 1, HSH used in this study could have lower molecular weight than those applied in the earlier research. Although proportion of sorbitol and maltitol in MU-50 and Hystar 5875 was comparable, their T_g were 10°C difference. This might be due to different processing techniques used resulting in varying types and proportions of the larger hydrogenated oligomers presented in those

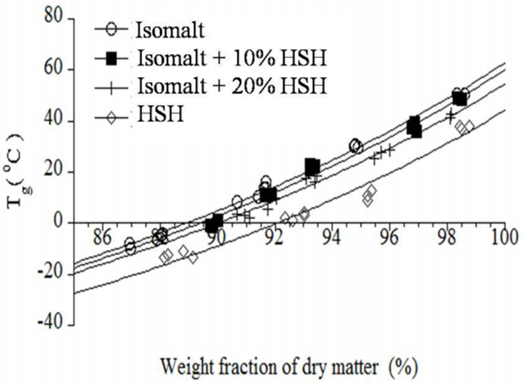

Figure 1 Glass transition temperature of the amorphous systems containing isomalt, HSH and their mixtures at different dry matter contents. Connecting line represents the data fitted with Gordon-Taylor equation.

HSH samples. For any given solid content, as HSH proportion increased, T_g of the systems decreased; however, T_g of the isomalt-HSH mixtures fell between that of the individual polyol (Figure 1), corresponding to the results reported by McFetridge *et al.* (2004). Since commercial hard candies could have 2-5% moisture content (Ergun *et al.,* 2010), calculated T_g of the 2% moisture systems could reflect the estimated T_g of the isomalt-based hard candies (Table 2). At this moisture content, T_g of the samples containing pure HSH approached ambient temperature of tropical countries (~30°C). This could thus affect stability of the hard candies marketed in those countries. As for Gordon Taylor constant k, all systems had relatively similar k values (Table 2), implying the similar extent of water plasticization of all isomalt-based systems.

Adsorption isotherms of the isomalt-based systems and HSH were depicted in Figure 2. HSH enhanced hygroscopicity of the polyol mixtures. At a given a_w, the system containing higher proportion of HSH tended to have greater EMC (Figure 2). Greater hygroscopicity of the HSH-formulated food systems, particularly hard candies, could reduce its storage stability, especially in tropical countries with elevated ambient temperature and RH.

Critical moisture content (CMC) at which glass transition could occur at a given storage temperature were determined from the plasticization (Gordon Taylor equation) behaviors of different isomalt-based systems (Fabra *et al.,* 2011; Roos, 1995). In this study, since all adsorption isotherms were evaluated at 30°C, CMC was calculated at this storage temperature. A system was in glassy state if its moisture content was lower than CMC. It was clearly seen that addition of HSH decreased CMC of the systems (Table 3). Control of ambient RH would be in greater concern for the samples containing HSH in order to avoid glass transition during storage. However, this problem could be alleviated by the selection of packaging material having good moisture barrier.

Data regarding plasticization effects of water on T_g, adsorption isotherm as well as CMC values of the system with 10% HSH were close to those of the pure isomalt, reflecting reasonable storage stability. Therefore, this HSH-isomalt mixture was applied to the modeled hard candy. Effect of polyol composition and packaging materials on stability of the hard candies during storage were evaluated in the next section.

3.2 Effects of HSH and packaging on water absorption and crystallization in modeled hard candies

Elevated temperature (30±2°C) and humidity (84.0± 0.2% RH) used in the storage test could be considered as

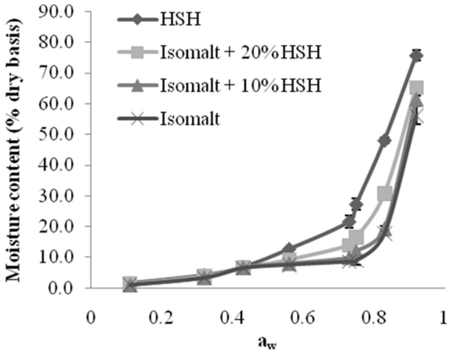

Figure 2. Adsorption isotherm of the systems containing isomalt, HSH and their mixtures at 30±2°C.

Table 2. Glass transition temperature and Gordon-Taylor constant k of the amorphous systems containing isomalt, HSH and their mixtures.

Systems	T_g (°C)^a		k	R^2
	Anhydrous	2% moisture		
Isomalt	62.8	48.5	3.8	0.99
Isomalt +10% HSH	60.1	46.1	3.8	0.98
Isomalt +20% HSH	54.4	41.2	3.7	0.99
HSH	44.2	31.4	3.8	0.97

^{a}T_g was calculated from Gordon-Taylor equation.

Table 3. Critical moisture content of the amorphous systems containing isomalt, HSH and their mixtures related to glass transition at 30°C.

Systems	Critical moisture content (% dry basis)
Isomalt	5.26
Isomalt +10% HSH	4.83
Isomalt +20% HSH	4.02
HSH	2.28

an accelerated condition. This severe condition could occur during summer season of tropical countries. Initial moisture content of the hard candy samples was below 3%, corresponding to low initial a_w (<0.3) (Figure 2). Therefore, water absorption and glass transition were expected in the candy samples during storage at the accelerated condition. Those changes initiated at the surface of the candy pieces. When moisture content on the surface exceeded CMC, glass transition occurred, causing an increase in molecular mobility of the polyol molecules. As the molecular mobility was sufficient for nuclei formation, crystallization could be initiated. Water molecules were able to migrate towards the core of the candy pieces. Hence, the crystallization proceeded into the center of the samples (Hartel *et al.,* 2011). An increase in thickness of crystalline layers was also anticipated during storage. Figure 3 depicted the polyol crystallization on the surface of modeled hard candies during storage. Crystal formation resulted in white, grainy surface (Figure 3c and 3e). After cutting the candy piece in halves, opaque white layers surrounding the candy pieces representing the crystalline layers could easily be detected (Figure 3d and 3f).

Moisture uptake and progress on crystallization of polyols in modeled hard candies during storage were shown in Figure 4. Without packaging material used, addition of 10% MU-50 HSH apparently enhanced the rate and extent of moisture absorption and crystallization (Figure 4a and 4c). Raudonus *et al.* (2000) also reported that the addition of Hystar 3375 and Hystar 6075 HSHs to isomalt-based hard candies accelerated moisture uptake and crystal formation. Although HSH could serve as a doctoring agent, they postulated that viscosity reduction resulting from moisture absorption overcame the viscosity enhancing effect of doctoring agent. This presumption was verified in our study. In comparison with Hystar 3375 and Hystar 6075, MU-50 with lower molecular weight might induce greater extent of moisture uptake, viscosity reduction, and thus further increase the crystallization rate on the surface of the hard candies. However, our results did not agree with those reported by McFetridge *et al.* (2004). In their study, addition of 10% HSH, Hystar 5875 or Hystar 6075, to amorphous isomalt systems increased induction time of the crystallization under high humidity environment (80% RH, 20°C). Surprisingly, Hystar 5875 with lower molecular weight was more effective to retard the crystallization. The disagreement might be due to different investigation techniques and different forms of sample used. McFetridge *et al.* (2004) visually observed the crystallization in ground freeze-dried amorphous samples. They defined the induction time as the time required for the first appearance of polyol crystals in the samples. Polyol crystallization in powdered samples might have different mechanisms and/or kinetics comparing to surface crystallization on hard candy samples, as determined in this study and in previous study by Raudonus *et al*. (2000). In the latter case, it might be concluded that low molecular weight HSH not only failed to be an acceptable doctoring agent, but also adversely affected storage stability of the isomalt-based hard candy due to its high hygroscopicity.

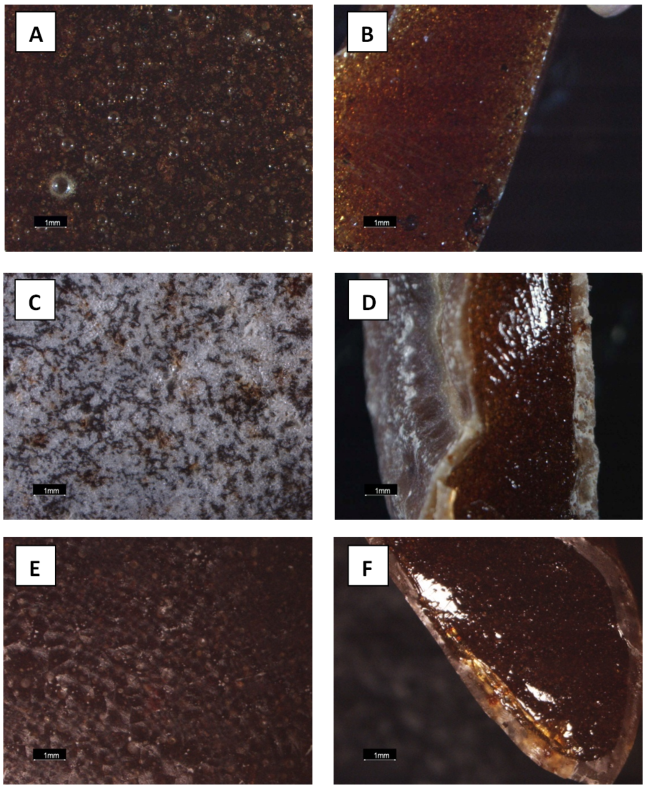

Figure 3. Stereomicroscopic images of modeled hard candy containing isomalt and 10% HSH during storage at 30°C, 84% relative humidity: A, C, E, surface images; B, D, F, cross section images; A, B, freshly prepared samples without crystalline layers; C, D, samples stored without packaging for two days; E, F, samples packed in PET/CPP pouches and stored for 30 days. All images were taken under the same magnification.

When packaging materials were applied, water absorption and crystallization in both formulated hard candies were obviously retarded (Figure 4b and 4d). PET/CPP and OPP/MCPP plastic films were commonly applied for commercial hard candies in Thailand. In case of the samples packed in PET/CPP pouches, extent of water absorption and crystal formation at the 90th day was still lower than those of the 12

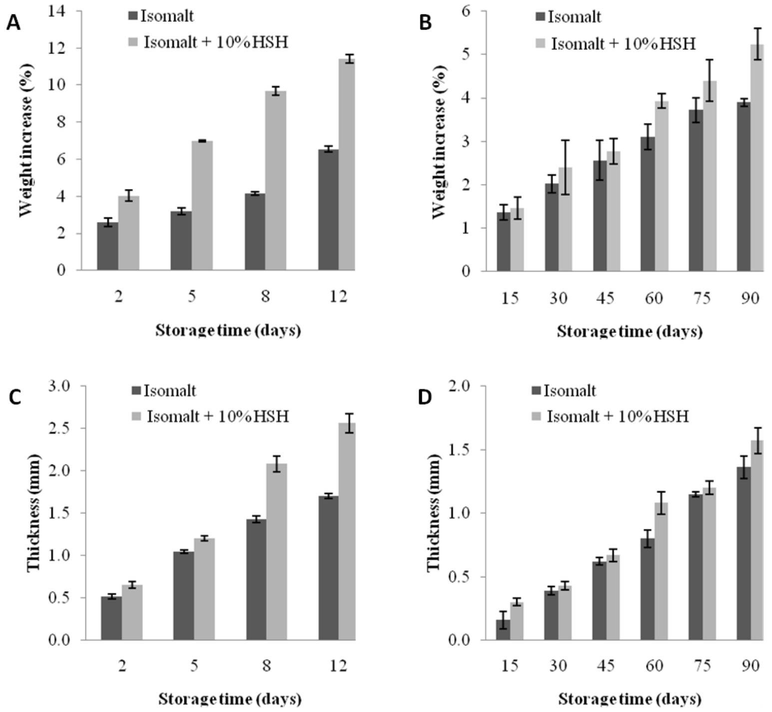

Figure 4. Percentage of weight increase due to moisture uptake and thickness of the crystalline layers at the surface of modeled hard candy during storage at 30°C, 84% relative humidity: A, C, samples stored without packaging; B, D, samples packed in PET/CPP pouches.

days old samples aged without packaging. Deteriorated effects of HSH were also reduced after the application of PET/CPP pouches. At the same storage time, there was only slight difference in the weight increase (<1.5%) and the thickness of crystalline layers (<0.3 mm) determined from the two hard candy formulas. For the application of OPP/MCPP pouches having excellent moisture barrier, both hard candy formulas had small weight increase (<0.3%) and did not have detectable crystalline layer during 90 days of storage. OPP/MCPP pouches thus greatly enhanced storage stability of the hard candy samples. In this study, initial moisture content of the candy samples was less than 2% (wb), which was below CMC of the corresponding polyol system (Table 3). Application of the OPP/MCPP film, having very low water vapor transmission rate, could effectively prevent moisture uptake during storage. Glass transition and the resulting crystallization did not occur as long as moisture content of the samples was lower than CMC. Adverse effects of HSH on storage stability of the isomalt-based hard candies could thus be neglected in this case. Higher level of HSH (>10%) could be added into the hard candies with the application of the packaging having superior water vapor barrier.

4. Conclusions

Overall results indicated that HSH with relatively low molecular weight used in this study negatively influenced storage stability of sugarless hard candy. Addition of low molecular weight HSH resulted in T_g reduction, greater hygroscopicity and enhanced crystallization of the isomalt-based hard candies. Those adverse effects were amplified when the products were stored under elevated temperature and/or relative humidity (e.g. 30°C, 84% RH), particularly in tropical countries. However, the effects could be minimized by the application of packaging materials with very limited water vapor transmission rate. The selected packaging could inhibit water uptake, helped maintain low moisture content and high T_g, and eventually enhanced shelf life of the hard candies. Hence, HSH could still be added to sugar-free hard candies, with cautious consideration on packaging selection, especially for the products marketed in tropical countries.

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