



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Carbohydrate Polymers 53 (2003) 289–296

Carbohydrate
Polymerswww.elsevier.com/locate/carbpol

Kinetic process of enthalpy relaxation of glassy starch and effect of physical aging upon its water vapor permeability property

Yu Jin Kim, Tomoaki Hagiwara*, Kiyoshi Kawai, Toru Suzuki, Rikuo Takai

Department of Food Science and Technology, Tokyo University of Fisheries, 4-5-7 Konan, Minato-ku, Tokyo 108-8477, Japan

Received 26 July 2002; revised 30 January 2003; accepted 7 February 2003

Abstract

The enthalpy relaxation during aging below T_g of an amorphous starch was examined via the Kohlrausch–Williams–Watts (KWW) relation in order to describe its kinetic process quantitatively. The experimental data were fitted satisfactorily by the KWW equation of stretched exponential form. Comparison to the results reported in previous studies reveals that both the values of the mean relaxation time τ and the relaxation time distribution $\beta(0.23–0.34)$ obtained through the fitting process were reasonable. Furthermore, the effect of physical aging below T_g on the water vapor permeability (WVP) of starch film was investigated. The WVP was reduced by aging below T_g , which agreed with the results reported previously for several synthetic polymer systems. Consequently, in the present study, the reduction of moisture transfer during aging can also be interpreted as a result of decreasing free volume, which occurs simultaneously with enthalpy relaxation.

© 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Glassy starch; Enthalpy relaxation; Physical aging; Kohlrausch–Williams–Watts; Permeability

1. Introduction

Recently, enthalpy relaxation phenomenon has been observed in amorphous starch or starch-based products. Chung, Lee, and Lim (2002) reported the enthalpy relaxation of native and gelatinized rice starch, including the effects of moisture content. Their results showed that enthalpy relaxation appeared only when the moisture of gelatinized starch was under 20% (dry basis). Borde, Bizot, Vigier, and Buleon (2002) investigated the enthalpy relaxation of various gelatinized starches at different aging temperatures using DSC. They found that physical aging was dependent on the storage temperature and the cooling rate. In addition, several studies have reported that the sub- T_g endotherm, which has often been observed in the DSC curve of native starch at low moisture content (Kalichevsky, Jaroszkiwicz, Ablett, Blanshard, & Lillford, 1992; Thiewes & Steeneken, 1997), is referred to as recovery from the enthalpy relaxation (Hodge, 1994; Shogren, 1992; Thiewes & Steeneken, 1997). We have reported that the ball-milling process enhances the enthalpy relaxation of

potato starch (Kim, Suzuki, Hagiwara, Yamaji, & Takai, 2001a). In general, the enthalpy relaxation of amorphous materials is accompanied by a change in macroscopic properties, such as density, mechanical strength, and transport properties. In the field of synthetic polymer, the enthalpy relaxation is recognized to be an important factor related to change in the physical properties of polymer, because the rate of enthalpy relaxation is estimated as molecular motion at temperature below T_g (Yoshida, 1988). Since enthalpy relaxation can be conveniently followed by differential scanning calorimetry (DSC), the kinetics of enthalpy relaxation in glassy polymers have been investigated extensively, which has led to the prediction of how their macroscopic properties change (Cernokova, Cernosek, Holubova, & Frumar, 2001; Drozdov, 2001; Komatsu, Noguchi, & Benino, 1997; Matsuoka, 1992; Robertson & Wikes, 2000; Robertson, Santangelo, & Roland, 2000; Sinko, Yee & Amidon, 1991; Sun, Yang, & Shen, 1999; Tsitsilianis, 1989; Yoshida, 1995). Being analogous to a synthetic polymer system, the enthalpy relaxation may be an important phenomenon that is related to the physical properties of amorphous starch and starch based products. In fact, our previous study indicated that the water sorption ability of glassy starch induced by ball-milling decreased

* Corresponding author. Tel.: 81-3-5463-0402; fax: 81-3-5463-0585.
E-mail address: tomoaki@tokyo-u-fish.ac.jp (T. Hagiwara).

simultaneously with enthalpy relaxation (Kim, Suzuki, Matsui, Pradistsuwanna, & Takai, 2001b). However, enthalpy relaxation in glassy starch itself has not been investigated thoroughly. Above all, little information has been reported concerning kinetic data of the enthalpy relaxation process, which may be a useful tool for predicting changes in physical properties during storage.

An approach using the Kohlrausch–Williams–Watts (KWW) equation is one method by which to describe the kinetic process of enthalpy relaxation quantitatively (Williams & Watts, 1970). The KWW equation is a relaxation function of stretched exponential form (Eq. (1)) that describes the approach to a fully relaxed state,

$$\phi(t) = \exp[-(t/\tau)^\beta] \quad (1)$$

where τ is a mean relaxation time constant and β is a relaxation time distribution parameter. Typically, the enthalpy relaxation in amorphous substances is non-exponential, in which case β takes values between 0 and 1. The KWW equation is applicable for a wide range of glassy materials, such as synthetic polymers (Cameron, Cowie, Ferguson, & McEwan, 2000; Yoshida, 1995), pharmaceutical products (Duddu, Zhang, & Dal Monte, 1997; Hancock, Shamblin, & Zografis, 1995), and small saccharides (Hancock et al., 1995). However, such an analysis has not been performed for glassy starch.

In the present study, we attempt to describe the enthalpy relaxation process in amorphous starch using the KWW equation. In addition, the effects of aging below T_g on the physical properties of glassy starch are also assessed. As one of the physical properties, herein we focus on the water vapor permeability (WVP), which can be obtained via a permeation experiment using a shaped film sample. For several glassy synthetic polymers, it has been reported that vapor permeability decreases by aging below T_g (McCaig & Paul, 1999; Nagai & Nakagawa, 1995; Tiemblo, Guzman, Riande, Mijangos, & Reinecke, 2001). This is explained by a reduction of ‘free volume’ (Benczédi, 1999; Odani, 1995) as the enthalpy relaxation progresses (Kim et al., 2001b). We examined whether the decrease in the vapor permeability by aging below T_g would be also observed in glassy starch. The obtained experimental results were examined in relation to the enthalpy relaxation process.

2. Experiments and methods

2.1. Enthalpy relaxation experiment

2.1.1. Sample preparation of gelatinized amorphous starch

We examined potato starch (Wako chemical Ind.Ltd, Osaka, Japan) which had a moisture content of approximately 16% (dry basis), as indicated by an oven drying (Yamato DV 61, YAMATO SCIENTIFIC, Ind. Ltd, Japan). In order to obtain gelatinized amorphous starch, native

starch was heated using a Differential Scanning Calorimeter (Shimadzu DSC-50, Shimadzu Ind. Ltd, Japan). The DSC apparatus was calibrated for temperature and enthalpy measurement using indium and pure water as standards. Approximately 27 mg of sample were placed in an aluminum pressure pan and hermetically sealed in order to prevent water loss due to evaporation. α -Alumina powder was used as the reference material. The samples were scanned from -20 to 200 °C at a heating rate of 5 °C/min and were cooled from 200 to -20 °C at a cooling rate of 20 °C/min. This scanning was repeated twice. Preliminary DSC experiment revealed the glass transition temperature of unaged sample to be 59 °C from the midpoint of the DSC baseline shift.

2.1.2. Aging process

After undergoing the repeated scanning described in Section 2.1, the samples sealed in the aluminum pans were stored at 25 , 33 , 42 and 50 °C, respectively, in a thermostatic chamber. Each sample was aged from 2 to 197 h.

2.1.3. Enthalpy relaxation measurements

The enthalpy relaxation during aging, ΔH , was determined by calculating the area difference between the DSC curve of the aged sample and that of the unaged samples.

2.2. Water vapor permeability (WVP) experiment

2.2.1. Preparation of films

For this experiment, the starch described in Section 2.1 was used. A 20% starch solution in a beaker was heated during stirring at 95 °C for 50 min. During stirring, the beaker was covered with a thin vinyl film to prevent water evaporation. Next, a volume of 25 ml of the solution was spread onto a petri dish (diameter: 9 cm) that was coated with SIGMACOTE (USA). After deaeration, the sample was then dried in an oven at 45 °C. After 30 h, the film was cut into the shape of a circle (diameter: 2.8 cm).

The thickness of the film was measured at 10 different positions using a hand-held micrometer (Model No. 293-421-20, Mitutoyo Inc. Ltd, Japan) and contact faces. The average of these 10 measurements was used as the thickness in the present investigation.

2.2.2. Aging processes of films

The hermetically sealed films were stored for 1 h at 140 °C in order to eliminate the effect of prior thermal history and were then aged for 10 days at 42 °C in a thermostatic chamber. In addition, in order to investigate the effect of isothermal aging, samples were aged for 2, 10 and 20 days at 42 °C.

2.2.3. Water vapor permeability (WVP)

WVP measurements were performed as described below, and several similar methods have been reported (Arvanityannis, Nakayama, & Aiba, 1998; Chang, Cheah, & Seow,

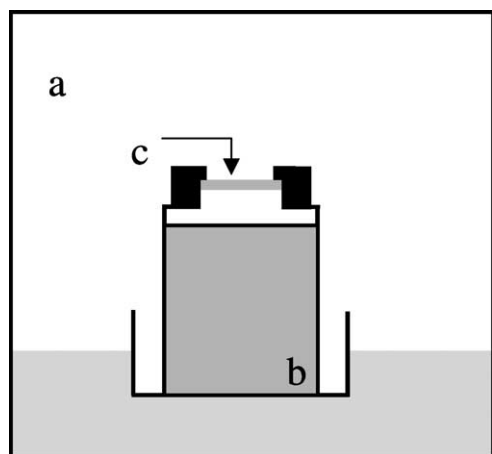


Fig. 1. Schematic diagram of the apparatuses used in the permeability experiment.

2000; Mangata, Bauduin, Boutevin, & Gontard, 2001; Yildirim & Hettiarachchy, 1998). A schematic diagram of the apparatus used in this experiment is shown in Fig. 1. The film (c) was set between the bottle containing silicagel (b) and its cap, and then hermetically sealed in a glass cell containing MgCl_2 (RH = 33%) saturated solution (a).

The water vapor transfer through the exposed film area was measured from the weight increment value as a function of time at 25 °C. The permeability of films was calculated from the following equation (Tsujida, 1995):

$$P = \Delta q / A(p_1 - p_2)\Delta t \quad (2)$$

where P is permeability coefficient ($\text{gm}^{-1} \text{s}^{-1} \text{Pa}^{-1}$), Δq is the increment weight of the transmitted amount, l is the film thickness, A is the area of exposed film, p_1 is the RH above the MgCl_2 saturated solution, p_2 is the RH above the silicagel, which is negligible, and Δt is the exposure time.

3. Results and discussion

3.1. Enthalpy relaxation

The DSC curves of samples stored at 25, 33, 42 and, 50 °C in a thermostatic chamber, are shown in Fig. 2 (a)–(d), respectively. The DSC curve of the unaged sample (0 h in Fig. 2 (a)) shows only baseline shift in the endothermic direction that is characteristic of the glass to rubber transition. For the samples stored at 33 and 42 °C, the endothermic peak overlap with glass transition was observed at approximately T_g as a result of the recovery of enthalpy relaxation. These endothermic peaks developed with increasing aging time. The peak position of the sample stored at 25 °C appeared at a slight distance from T_g and did not overlap the base line shift. This behavior, referred to as ‘sub- T_g endotherm’, was also observed in previous studies (Kalichevsky et al., 1992; Shogren, 1992; Thiewes & Steeneken, 1997). The endothermic peak

tended to develop more rapidly with increasing aging temperature. However, the peak was not clear at 50 °C, as shown in Fig. 2 (d). Therefore, the enthalpy relaxation process for the sample aged at 50 °C was impossible to examine. From the DSC curves of the samples stored at 50 °C, the change in the baseline shift upon glass transition tended to decrease with increasing aging time, suggesting that some components having low T_g s, such as the low molecular weight fraction in starch, underwent glass to rubber transition during aging and so the enthalpy relaxation process was not so clear.

Fig. 3 shows the amount of the enthalpy relaxation (ΔH) as a function of aging time about different aging temperatures for 10 days. The value of ΔH increased with aging time. Using these data, we verified the applicability of the KWW relation for describing the enthalpy relaxation process of the starch. In the KWW equation, ϕ (Eq. (2)) is related to the amount of enthalpy relaxation ΔH as follows (Hancock et al., 1995)

$$\phi(t) = 1 - (\Delta H / \Delta H_\infty) \quad (3)$$

where ΔH_∞ is a maximal value of the enthalpy relaxation, which is given by

$$\Delta H_\infty = \Delta C_p(T_g - T_a) \quad (4)$$

where T_g is the glass transition temperature and T_a is the aging temperature, and ΔC_p is the specific heat capacity change at T_g (Hancock et al., 1995; Yoshida, 1986; Yoshida, 1988). Fig. 4 shows the plot of ϕ as a function of aging time for different aging temperatures. Solid lines in the plot are the results obtained by fitting Eq. (1) to experimental data. The fitting was done using the computer software Kaleida Graph (Synergy Software, USA) on Windows platform. For all of three aging temperatures, the data fitting was satisfactory ($R > 0.99$). This suggested that the long-term enthalpy relaxation process could be predicted from the short-term data.

The values of τ and β in the present study were compared with those of other substances reported previously (Hancock et al., 1995). Furthermore, by confirming that the result obtained in the present study does not contradict those obtained in previous studies, the validity of the experimental and analytical methods used in the present study were approved. Here, we used primarily data of τ and β for sucrose (Hancock et al., 1995), which has a chemical structure similar to that of starch. The values of β are summarized in Table 1. For all aging temperatures, the β values were significantly different from 1, which indicates a distribution of the relaxation time rather than a single relaxation time. The β values for starch in the present study were smaller than the β values calculated for sucrose (0.4–0.8; Hancock et al., 1995). This is in agreement with the results reported by Hancock et al. (1995), in which small molecules were generally reported to have higher β values than polymers. The aging temperature dependence was unclear in the present study. As for the effect of aging

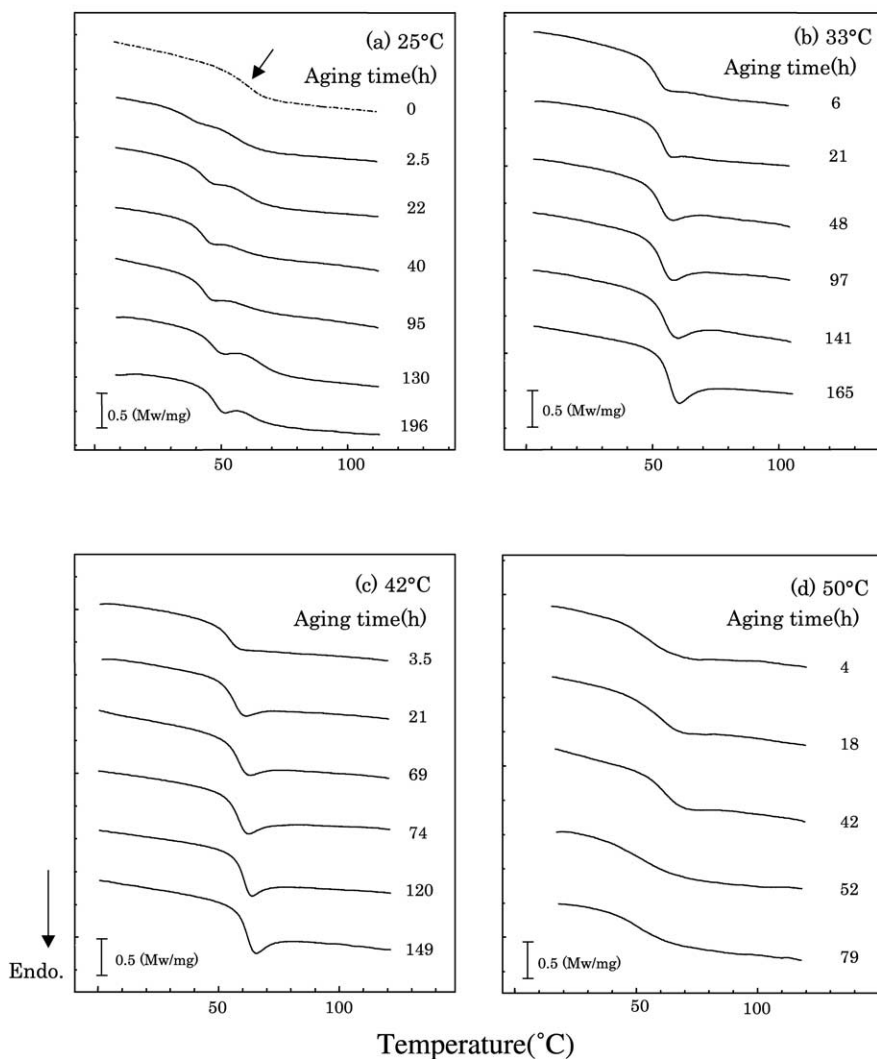


Fig. 2. DSC curves of glassy starch aged in a thermostatic chamber: (a) at 25 °C, (b) at 33 °C, (c) at 42 °C, and (d) at 50 °C.

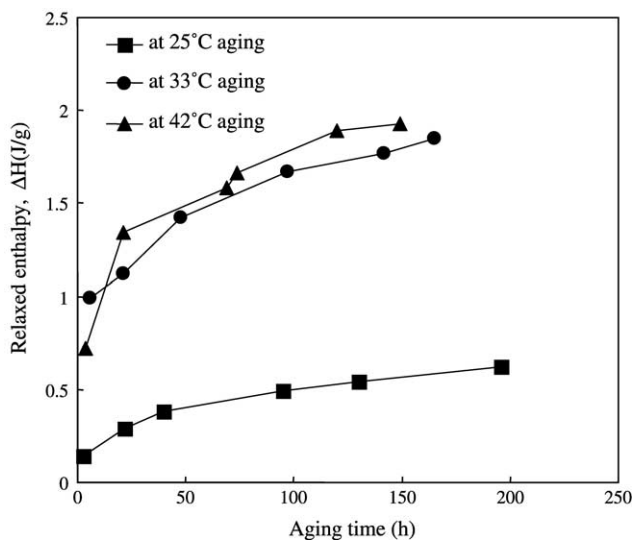


Fig. 3. Dependence of enthalpy relaxation on aging time measured after isothermal aging at different temperatures below the glass transition temperature.

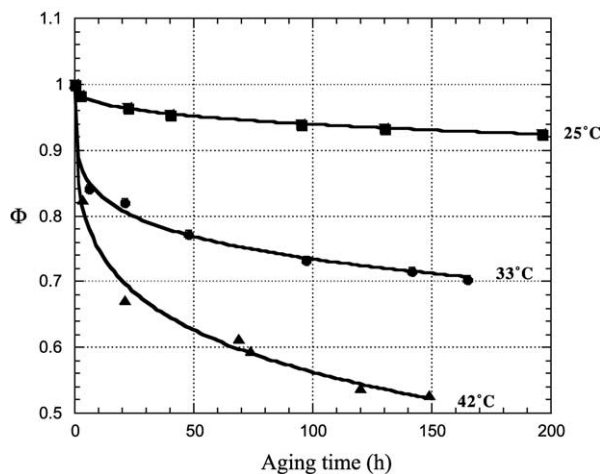


Fig. 4. Plot of the relaxation function (ϕ) of glassy starch at 25, 33 and 42 °C.

Table 1
Relaxation time distribution parameter β of the KWW equation

T_a (°C)	β (-)	τ (h)
25	0.34	$3.12 \pm 0.66 \times 10^{+5}$
33	0.23	$1.51 \pm 0.58 \times 10^{+4}$
42	0.30	$6.37 \pm 1.17 \times 10^{+2}$

temperature on β , previous reports have been inconsistent. For example, Van den Mooter et al. (1999) reported that the β value decreased when the aging temperature decreased for amorphous benzodiazepines, whereas in the case of certain synthetic polymer systems, the dependence of aging temperature was not clear (Cameron et al., 2000). Therefore, in the present study, we do not discuss the effect of aging temperature on β in detail. Fig. 5 shows a plot for logarithmic of τ as a function of the scaled temperature ($T_g - T_a$), in the manner presented by Hancock et al. (1995). The τ data for sucrose obtained by Hancock et al. (1995) is also shown in the same plot. This parameter provides an idea of the kinetics of the process. A higher value implies a slower relaxation process (Cameron et al., 2000). The values of τ for starch increased, with decreasing aging temperature, in the same manner as those for sucrose, indicating that the aging process is slower at the low T_a . This is because the motion of relaxation elements is more restricted with increasing distance from T_g . Compared to the data for sucrose, the τ value of starch was slightly larger, which suggests that the starch is more stable than sucrose at the same temperature range. This may be due to its higher molecular weight and structure complexity such as branching. Entanglement effect of polymers may also contribute the slower aging process.

In order to obtain a rough estimate of the susceptibility of the relaxation process to the aging temperature increment, we calculated the apparent Arrhenius activation energy (E_A)

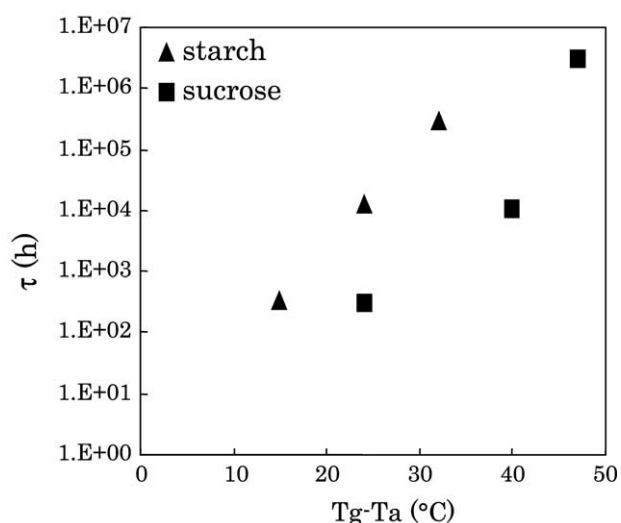


Fig. 5. Semi logarithmic plot of mean relaxation time τ as a function of the scaled temperature ($T_g - T_a$). ▲ : starch, ■ : sucrose.

of starch by using the value of τ in Fig. 5. The activation energy of starch is 284 kJ/mole. For sucrose, Hancock et al. (1995) reported that $E_A = 360$ kJ/mole. Since these values do not differ greatly, the susceptibility of starch is similar to that of sucrose over the scaled temperature range in Fig. 5.

As other models for analyzing enthalpy relaxation process, the Defect Diffusion model and the multi-parameter phenomenological (MP) (e.g. the TMN (Tool, Moynihan and Narayanaswamy) model (Tool, 1946; Narayanaswamy, 1971; Moynihan, Eastale, Wilder, & Tucker 1974; Moynihan et al., 1976), Scherer-Hodge (Scherer, 1984; Hodge, 1987) and Kovacs-Akloins-Hutchinson-Romos (KAHR) model (Kovacs et al., 1979)) are also Known. While the KWW equation method used in this study is rather pragmatic or empirical, the Defect Diffusion model correlates a microscopic structural change during aging with enthalpy relaxation process; it assumes that the supercooled liquid has fluctuation in enthalpy (i.e. in entropy and density), called 'defects' which can be either positive or negative. The physical aging is considered as an annihilation process of the defects. The defect concentration is related with macroscopic enthalpy by the usual argument of statistical thermodynamics. Perez (1988) reported that good agreement was obtained between the prediction by the Defect Diffusion model and experimental enthalpy recovery as well as volumes for poly (vinyl acetate). However, in order to use the Defect Diffusion model, it is necessary to know preliminarily many values of parameters (e.g. thermal expansion coefficient of sample, enthalpy of formation of defects, entropy of formation of formation of defects). To the contrary, the approach in this study does not need such the values. Therefore, from the point of easiness to follow enthalpy relaxation process, it has an advantage over the Defect Diffusion model, although the physical interpretation of result may be limited since it is rather than phenomenological approach. The MP models look at an enthalpy relaxation as a relaxation process with non-linearity as well as non-exponentiality. Cameron et al. (2000) compared the MP models and the KWW equation approach. They stated that one of the shortcomings of the MP models is that they fail to predict the enthalpy lost on aging, though they have succeeded in predicting the shape of C_p curve (i.e. DSC curve) in some case. They emphasized that each type of model describes a different aspect of aging. That is to say, while the MP models trace the structural changes produced by a given thermal history, the KWW equation method follows the enthalpy changes during annealing only and tries to determine the quality of enthalpy lost on reaching equilibrium. As they pointed out, it is believed that enthalpy changes in materials are sometimes more significant technologically than the ability to accurately predict its C_p (Cameron et al., 2000).

3.2. Water vapor permeability

Fig. 6 shows the amount of water vapor transferring through starch films aged for various durations as

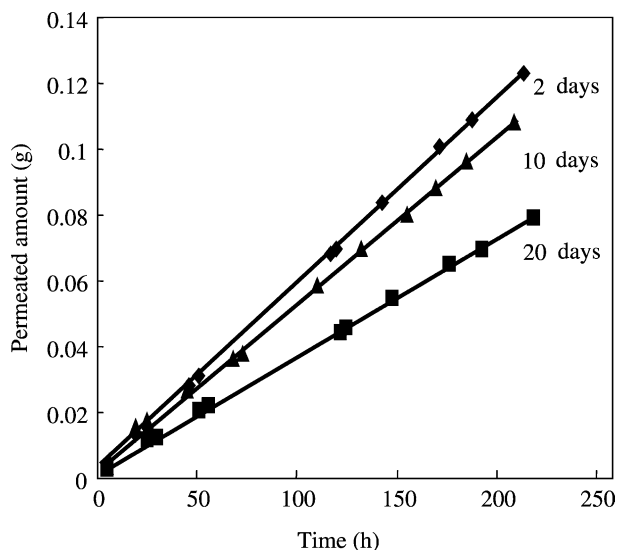


Fig. 6. Time course of permeated amount of moisture through the aged films at 42 °C.

a function of time. After approximately 19 h, the plots were approximated to be straight lines ($R > 0.99$). The water content of the film was 1.26% (dry basis) before the WVP experiment. After permeation experiment, all films examined had almost same water content 8.2% (dry basis). Since both data of water content were smaller than that of DSC sample in Section 2.1.1 (16%, $T_g = 59$ °C), the film most likely remained in glassy state during both aging and the permeability experiment. Furthermore, from the fact that there was no difference in water content after permeation experiment, it was suggested that after reaching a steady state (after 19 h; corresponding to a linear range in the plot of Fig. 7), all films had same T_g values.

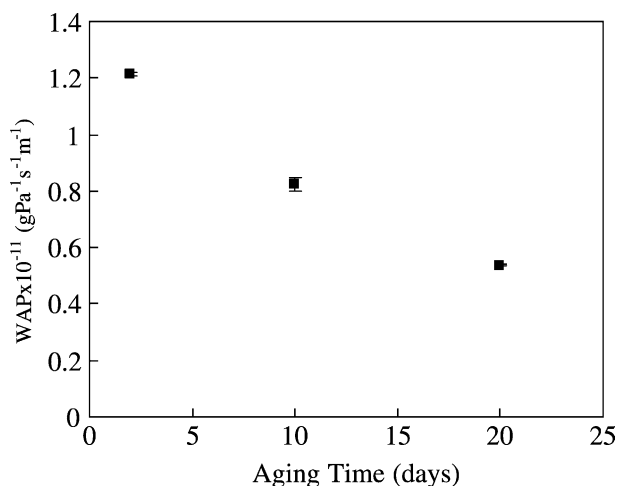


Fig. 7. Plot of the permeability coefficient as a function of aging time.

The WVP was evaluated according to Eq. (2), and Fig. 7 shows the plots of WVP for various aging times. As aging time increased, the WVP tended to decrease. The same behavior was observed in several glassy synthetic polymers, such as polyvinyl chloride (Tiembló et al., 2001), polyacrylate (McCaig & Paul, 1999, 2000; McCaig, Paul, & Barlow, 2000), poly (1-trimethylsilyl-1-propyne) (Nagai & Nakagawa, 1995). The mechanism causing the reduction of the permeability was explained by using the concept of ‘free volume’ as follows. The free volume is defined as the vacant space, that is, not occupied by the microstructure of the polymer molecule (Benczédi, 1999; Odani, 1995). Based on the concept of free volume, the transport rate through polymeric material is reduced by diminishing the free volume. In general, glassy polymers are not in the thermodynamic equilibrium state, and the free volume is above that corresponding to equilibrium state. Therefore, as in the case of enthalpy, the free volume relaxes with aging time towards its equilibrium state. Consequently, aging reduces the permeability rate. Until now, knowledge regarding physical properties and free volume of glassy starch has not yet been well reported. However, our previous study suggested that the water sorption ability of glassy starch, which is obtained by ball-milling, decreases due to reduction in free volume as the enthalpy relaxation progress. (Kim et al., 2001b). Considering the above explanation, the reduction of permeability in the present study during aging can also be interpreted as a result of decreasing free volume, which occurs simultaneously with enthalpy relaxation. The glass transition temperature has been identified as one of the factors that are important to the stability of the physical properties of starch or starch-based products. However, the result of the WVP experiment indicated that even when stored below T_g , the change in the physical properties of a glassy starch could not be prevented as the enthalpy relaxation proceeded. When considering the stability of the physical properties, the concept of enthalpy relaxation is also important.

4. Conclusion

The enthalpy relaxation process of amorphous starch was well described using the KWW relaxation function of stretched-exponential form. Through fitting, reasonable values of τ and β were obtained. Compared to the data for sucrose, the τ value of starch was slightly larger, which suggests that the starch is more stable than sucrose at the same temperature range. This may be due to its higher molecular weight and structure complexity such as branching.

The WVP decreased due to aging below T_g . This behavior is interpreted as being a result of reduction of

free volume, which occurs simultaneously upon enthalpy relaxation.

From the result in the present study, it is suggested that the long-term enthalpy relaxation process could be predicted from the short-term data and that following enthalpy relaxation should allow a more systematic understanding of stability of physical properties of starch or starch-based products.

References

- Arvanitoyannis, I. S., Nakayama, A., & Aiba, S. (1998). Chitosan and gelatin based edible films: state diagrams, mechanical and permeation properties. *Carbohydrate Polymers*, *37*, 371–382.
- Benczédi, D. (1999). Estimation of the free volume of starch–water barriers. *Trends in Food Science & Technology*, *10*, 21–24.
- Borde, B., Bizot, H., Vigier, G., & Buleon, A. (2002). Calorimetric analysis of the structural relaxation in partially hydrated amorphous polysaccharides II. Phenomenological study of physical ageing. *Carbohydrate Polymers*, *48*, 111–123.
- Cameron, N. R., Cowie, J. M. G., Ferguson, R., & McEwan, I. (2000). Enthalpy relaxation of styrene-maleic anhydride (SMA) copolymers. Part 1. Single-component systems. *Polymer*, *41*, 7255–7262.
- Cernoskova, E., Cernosek, Z., Holubova, J., & Frumar, M. (2001). Structure relaxation near the glass transition temperature. *Journal of Non-Crystalline Solid*, *284*, 73–78.
- Chang, H. P., Cheah, P. B., & Seow, C. C. (2000). Plasticizing–Antiplasticizing effect of water on physical properties of tapioca starch films in the glassy state. *Journal of Food Science*, *65*, 445–451.
- Chung, H. J., Lee, E. J., & Lim, S. T. (2002). Comparison in glass transition and enthalpy relaxation between native and gelatinized starches. *Carbohydrate Polymers*, *48*, 287–298.
- Drozdov, A. D. (2001). Physical aging and nonlinear viscoelasticity of amorphous glassy polymers. *Computational Materials Science*, *21*, 197–213.
- Duddu, S. P., Zhang, G., & Dal Monte, P. R. (1997). The relationship between protein aggregation and molecular mobility below the glass transition temperature of lyophilized formulations containing a monoclonal antibody. *Pharmaceutical Research*, *14*, 596–600.
- Hancock, B. C., Shamblin, S. L., & Zografi, G. (1995). Molecular mobility of amorphous pharmaceutical solids below their glass transition temperatures. *Pharmaceutical Research*, *12*, 799–806.
- Hodge, I. M. (1987). Effect of annealing and prior history on enthalpy relaxation in glassy polymers. 6. Adam–Gibbs Formulation of non-linearity. *Macromolecules*, *20*, 2897–2908.
- Hodge, I. M. (1994). Enthalpy relaxation and recovery in amorphous materials. *Journal of Non-Crystalline Solid*, *169*, 211–266.
- Kalichevsky, E. M., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M. V., & Lillford, P. J. (1992). The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydrate Polymers*, *18*, 77–88.
- Kim, Y. J., Suzuki, T., Hagiwara, T., Yamaji, I., & Takai, R. (2001a). Enthalpy relaxation and glass–rubber transition of amorphous potato starch formed by ball-milling. *Carbohydrate Polymers*, *46*, 1–6.
- Kim, Y. J., Suzuki, T., Matsui, Y., Pradistsuwanna, C., & Takai, R. (2001b). Water sorption for amorphous starch and structural relaxation. *Japan Journal of Food Engineering*, *3*(1), 121–125.
- Komatsu, T., Noguchi, T., & Benino, Y. (1997). Heat capacity changes and structural relaxation at glass transition in mixed-alkali tellurite glasses. *Journal of Non-Crystalline Solid*, *222*, 206–211.
- Kovacs, A. J., Aklonis, J. J., Hutchinson, J. M., & Ramos, A. R. (1979). Isobaric volume and enthalpy recovery of glass. II. A transparent multiparameter theory. *Journal of Polymer Science, Physics Edition*, *17*, 1097–1162.
- Mangata, J. I., Bauduin, G., Boutevin, B., & Gontard, N. (2001). New plasticizers for wheat gluten films. *European Polymer Journal*, *37*, 1533–1541.
- Matsuoka, S. (1992). *Relaxation phenomena in polymer*. Munich: Carl Hanser Verlag, pp. 80–142.
- McCaig, M. S., & Paul, D. R. (1999). Effect of UV crosslinking and physical aging on the gas permeability of thin glassy polyarylate films. *Polymer*, *40*, 7209–7225.
- McCaig, M. S., & Paul, D. R. (2000). Effect of film thickness on the change in gas permeability of a glassy polyarylate due to physical aging. Part 1. Experimental observations. *Polymer*, *41*, 629–637.
- McCaig, M. S., Paul, D. R., & Barlow, J. W. (2000). Effect of film thickness on the change in gas permeability of a glassy polyarylate due to physical aging. Part 2. Mathematical model. *Polymer*, *41*, 639–648.
- Moynihan, C. T., Easteal, A. J., Wilder, J. A., & Tucker, J. (1974). Dependence of glass transition temperature on heating and cooling rate. *Journal of Physical Chemistry*, *78*, 2673–2677.
- Moynihan, C. T., Macedo, P. B., Montrose, C. J., Gupta, P. K., DeBolt, M. A., Dill, J. F., Dom, B. E., Drake, P. W., Easteal, A. J., Elterman, P. B., Moeller, R. P., Sasabe, H., & Wilder, J. A. (1976). Structural relaxation in vitreous materials. *Annals New York Academy of Sciences*, *279*, 15–35.
- Nagai, K., & Nakagawa, T. (1995). Effect of aging on the gas permeability and solubility in poly(1-trimethylsilyl-1-propyne) membranes synthesized with various catalysts. *Journal of Membrane Science*, *105*, 261–272.
- Narayanaswamy, O. S. (1971). A model of structural relaxation in glass. *Journal of American Ceramic Society*, *54*, 491–498.
- Odani, H. (1995). *Syuchaku. Koubinsi-to-mizu*. Tokyo, Japan: Kyoritsu Shuppan, pp. 1–23, The Society of Polymer Science, Japan.
- Perez, J. (1988). Defect diffusion model for volume and enthalpy recovery in amorphous polymers. *Polymer*, *29*, 483–489.
- Robertson, C. G., & Wikes, G. L. (2000). Physical aging behavior of miscible blends containing atactic polystyrene and poly(2,6-dimethyl-1,4-phenylene oxide). *Polymer*, *41*, 9191–9204.
- Robertson, C. G., Santangelo, P. G., & Roland, C. M. (2000). Comparison of glass formation kinetics and segmental relaxation in polymers. *Journal of Non-Crystalline Solid*, *275*, 153–159.
- Scherer, G. W. (1984). Use of an Adam–Gibbs Equation in the analysis of structural relaxation. *Journal of the American Ceramic Society*, *67*, 504–511.
- Shogren, R. L. (1992). Effect of moisture content on the melting and subsequent physical aging of cornstarch. *Carbohydrate Polymers*, *19*, 83–90.
- Sinko, C. M., Yee, A. F., & Amidon, G. L. (1991). Prediction of physical aging in controlled-release coatings: The application of the relaxation coupling model to glassy cellulose Acetate. *Pharmaceutical Research*, *8*(6), 698–705.
- Sun, N., Yang, J., & Shen, D. (1999). The effect of water absorption on the physical aging of amorphous poly(ethylene terephthalate) film. *Polymer*, *40*, 6619–6622.
- Thiewes, H. J., & Steeneken, P. A. M. (1997). The glass transition and the sub-T_g endotherm of amorphous and native potato starch at low moisture content. *Carbohydrate Polymers*, *32*, 123–130.
- Tiembo, P., Guzman, J., Riande, E., Mijangos, C., & Reinecke, H. (2001). Effect of physical aging on the gas transport properties of PVC and PVC modified with pyridine groups. *Polymer*, *42*, 4817–4823.
- Tool, A. Q. (1946). Relation between inelastic deformability and thermal expansion of glass in its annealing range. *Journal of American Ceramic Society*, *29*, 240–253.
- Tsitsilianis, C. (1989). Effect physical ageing in sorption properties of polymer. *Polymer Communications*, *30*(November), 331–333.

- Tsujida, Y. (1995). *Touka. Koubinsi-to-mizu*, Tokyo, Japan: Kyoritsu Shuppan, pp. 51–73, The Society of Polymer Science, Japan.
- Van den Mooter, G., Augustijns, P., & Kinget, R. (1999). Stability prediction of amorphous benzodiazepines by calculation of the mean relaxation time constant using the Williams–Watts decay function. *European Journal of Pharmaceutics and Biopharmaceutics*, *48*, 43–48.
- Williams, G., & Watts, D. C. (1970). Non-symmetrical dielectric relaxation behaviour arising from a simple empirical decay function. *Transactions of the Faraday Society*, *66*, 80–85.
- Yildirim, M., & Hettiarachchy, N. S. (1998). Properties of films produced by cross-linking whey proteins and 11S globulin using transglutaminase. *Journal of Food Science*, *63*, 248–252.
- Yoshida, H. (1986). Enthalpy relaxation of polymeric glasses. *Netsu Sokutei*, *13*(4), 191–199. in Japanese.
- Yoshida, H. (1988). Enthalpy relaxation of engineering plastics. *Netsu Sokutei*, *15*(2), 65–69. in Japanese.
- Yoshida, H. (1995). Relaxation between enthalpy relaxation and dynamic mechanical relaxation of engineering plastics. *Thermochimica Acta*, *266*, 119–127.