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Physical aging of glassy normal and waxy rice starches: thermal and mechanical characterization

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Abstract

Physical aging of glassy amorphous rice (normal and waxy) starches (14.5% moisture) was characterized in terms of thermal and mechanical properties, using a differential scanning calorimeter (DSC), dynamic thermal analyzer (DMTA), and Instron texturometer. The starch samples were prepared by compressing under heat (100 °C, 2000 psi), and subsequently aged at 25 °C for up to 29 days. Relaxation enthalpy, as measured by DSC, increased gradually with aging time, reaching a structural equilibrium. The peak temperature of the relaxation endotherm in DSC thermogram linearly increased with the logarithm of aging time. Relaxation kinetics revealed that relaxation rate was much slower for normal rice starch than for waxy rice starch. DMTA showed that storage modulus increased by aging, but the tan δ peak height reduced, indicating that the chain mobility of glassy starch was reduced by aging. Dual glass transitions were observed in both DSC and DMTA thermograms for normal rice starch samples, whereas a single transition was observed for waxy rice starch samples. It suggests that the amorphous regions in normal starch samples are heterogeneous. Breaking strength, measured using an Instron texturometer, increased gradually with aging time, in accordance with the change in relaxation enthalpy. The relaxation kinetics of glassy starch aging could be explained by thermal transition enthalpy and by mechanical properties such as storage modulus and breaking strength.

Keywords: Physical aging; Glass transition; Rice starch; Thermal property; Mechanical property

1. Introduction

Starch is a major component in cereal-based food products. These products are often consumed after being processed to the glassy state. One of the critical parameters determining consumer acceptance is texture, which includes crispness and crunchiness. Moreover, these textural attributes may change during storage. In polymer theory, this storage-induced change refers to physical aging, mainly related to amorphous fractions of polymers. Studies on the physical aging of glassy starch, especially at a low moisture content, are applicable to industries related to starch, such as food, pharmaceutics, paper, etc. (Blanshard & Lillford, 1993).

When a polymer matrix in a rubbery state is transformed into its glassy state by cooling through glass transition temperature (T_g), it often exists in a nonequilibrium state, where its physical values such as volume, and enthalpy, are greater than those in an equilibrium state. Thus, kinetic-controlled molecular rearrangements occur spontaneously and progress toward an equilibrium. This process for glassy polymers is generally referred to as structural relaxation or physical aging. The physical aging induced by structural relaxation is of significance for various glassy products, since it directly affects physical attributes.

Physical aging is experimentally characterized, by relaxation enthalpy measurement (Borde, Bizot, Vigier, & Buleon, 2002a,b; Chung, Lee, & Lim, 2002; Chung & Lim, 2003a,b), because thermal analysis is convenient and provides reproducible data. It has been also studied through the changes in mechanical properties, like viscoelasticity, (Barral Cano, Lopez, Lopez-Bueno, Nogueira, Abad, & Ramirez, 1999, 2000; Lourdin, Colonna, Brownsey, Noel, & Ring, 2002) and yield stress (Cook, Mehrabi, & Edward, 1999). However, the characterization of structural relaxation by mechanical analysis has been performed mainly for synthetic polymers, and rarely for starch.

Recently, Lourdin et al. (2002) observed the structural relaxation of amorphous maltose and starch, using various analysis techniques, and found that the amorphous glassy

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solids became less compliant with the mechanical relaxation as aging time increased, resulting in a slow densification.

In the present study, physical aging of amorphous rice starches, in normal and waxy types, was characterized by both thermal and mechanical analyses, using a differential scanning calorimeter (DSC), dynamic mechanical thermal analyser (DMTA), and Instron texturometer. Changes in the thermal and mechanical characteristics caused by physical aging were compared.

2. Materials and methods

2.1. Sample preparation

Normal and waxy rice starches were isolated from rice flour (Japonica type) purchased at a local grocery (Seoul, Korea), using a dilute NaOH solution (Lim, Lee, Shin, & Lim, 1999). Amorphous rice starch samples were prepared by heating starch/water dispersions (10% solids) in a boiling-water bath (30 min). The starch paste was poured onto petri-dishes as a thin layer, and subsequently dehydrated overnight into a film in a convection oven (50 °C). The film was then ground, and the powders were sieved (100 mesh).

To prepare specimens for mechanical tests, the starch powders were rehydrated to 20–25% (w/w) moisture in a humidity chamber, and then compressed using a compression molding machine (Dongjin Co., Korea) at 2,000 psi and 100 °C for 10 min into rectangular specimens (20 mm × 50 mm × 3 mm). The molded specimens were subsequently aged over a saturated salt solution (NaCl) at 25 °C for up to 29 days. The exact moisture content of the specimens was determined by drying at 105 °C until the weight became constant.

2.2. DSC measurement

Differential scanning calorimetric analysis was performed using a Seiko DSC 6100 (Chiba, Japan). Specimens that had been aged for different aging periods were broken into small pieces and a portion (~50 mg) was transferred into a silver DSC pan. After sealing, the sample was analyzed by heating to 140 °C at a heating rate of 5 °C/min. The sample pan was immediately cooled (20 °C/min) to 10 °C, and then reheated (5 °C/min) to 140 °C to determine the transition characteristics of the unaged sample. The DSC instrument was calibrated using indium and mercury, and an empty pan was used as a reference.

2.3. DMTA measurement

A dynamic mechanical thermal analyzer (DMTA, Seiko DMA6000, Chiba, Japan) was used to measure storage modulus (E'), loss modulus (E''), and tan δ of the compressed specimens aged for different periods (up to 29 days).

The measurements were carried out in a three-point bending mode at a frequency of 1 Hz. The heating rate was 2 °C/min, from 20 to 150 °C. In order to avoid water loss during heating, specimens were coated with silicon oil.

2.4. Instron texturometer measurement

The breaking strength of the compressed specimens were determined by a three-point bending test using an Instron texturometer (Instron 4465, Canton, MA), at a crosshead speed of 10 mm per minute. All the measurements for thermal and mechanical tests were done more than three times.

3. Results and discussion

3.1. Calorimetric behavior

Moisture content of the compressed starch sample quickly reached 14.5 ± 0.1% in the aging chamber equilibrated with NaCl, and then remained at a near constant level throughout the aging period (29 days) at 25 °C.

The DSC thermograms of the unaged starch specimens, in which the thermal history has been erased by heating (up to 140 °C), are shown in Fig. 1. For Normal rice starch (NRS), dual glass transitions were observed whereas a single glass transition was found for WRS. In the first derivative thermograms (dC_p/dT) (small box in Fig. 1), the dual glass transitions were evident at temperatures of 56.7 and 71.4 °C. The upper T_g was similar to the T_g of Waxy rice starch (WRS) (70.7 °C). The dual glass transitions could indicate that the NRS sample contained two different amorphous regions. Diego, Canadas, Mudarra and Belana (1999) reported double T_g values for partially crystallized poly(ethylene terephthalate), and suggested the presence of different amorphous regions, i.e. less restricted and more restricted. Similar results have also been reported for semicrystalline PET by Montserrat and Cortes (1995) and

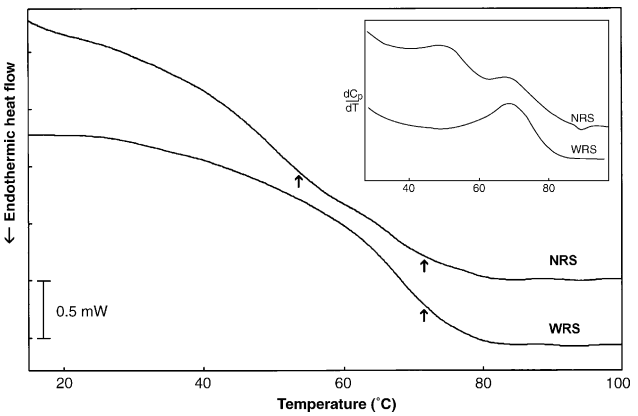

Fig. 1. DSC thermogram of unaged NRS and WRS.

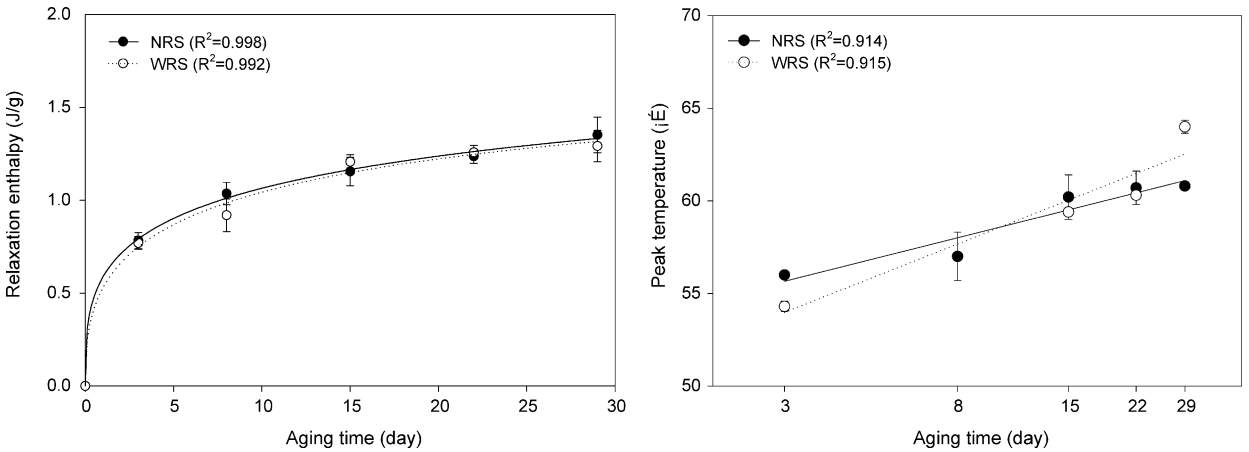

Fig. 2. Enthalpy and peak temperature changes of relaxation at different aging times up to 29 days for NRS and WRS.

Zhao, Wang, Li and Fan (2002). Several researchers (Diego et al., 1999; Montserrat & Cortes, 1995; Zhao et al., 2002) claimed that double glass transitions could appear when a moderate crystallinity was present. Starch recrystallization was induced during the drying of the starch paste. Accordingly we assume that the crystals in the NRS sample may induce the dual glass transitions, whereas the crystallinity in WRS sample is too low and insignificant to give dual transitions.

The heat capacity change (ΔC_p) at T_g was different for the two starches. The ΔC_p of NRS (0.328 J/g°C) was greater than that of WRS (0.215 J/g°C). In the case of the powdery starch used in our previous study (Chung & Lim, 2003a), the ΔC_p for NRS was slightly greater than that for WRS. The heterogeneity of starch components in NRS might have induced this ΔC_p difference.

The relaxation enthalpy measured by DSC at different aging periods (t_a), was increased by aging (Fig. 2). The relaxation rate ($d\Delta H/dt_a$), however, was gradually decreased by aging, in accordance with the result of our previous study (Chung & Lim, 2003a). At the beginning of aging, the relaxation is rapid because starch chains have sufficient mobility, but the rate decreases as the starch chains become less mobile on approaching equilibrium. The peak temperature of relaxation endotherm in the DSC thermogram linearly increased with logarithmic aging time. A linear relation between the peak temperature and the log aging time was observed for both starches (Fig. 2).

The kinetics for the enthalpy relaxation can be expressed using the following equation, proposed by Cowie and Ferguson (1986):

$$\Delta H(t_a, T_a) = \Delta H_\infty(T_a)[1 - \exp\{-(t_a/t_c)^\beta\}], \quad (1)$$

where ΔH_∞ represents the maximum equilibrium enthalpy, t_c the average relaxation time, and β the width of the relaxation time distribution.

These three kinetic parameters describing the relaxation of normal and waxy rice starches, (NRS and WRS, respectively), were calculated by a non-linear curve fit from the above equation, and are shown in Table 1. The maximum relaxation enthalpy (ΔH_∞) was greater for NRS (2.064 J/g) than for WRS (1.764 J/g) (Table 1). In our previous study (Chung & Lim, 2003a), ΔH_∞ values for amorphous normal and waxy rice starches at 15% moisture content were 2.692 and 2.480 J/g, respectively. In both previous and present studies, the presence of amylose resulted in an increase in ΔH_∞. However, the ΔH_∞ values in this experiment were substantially low. This might be from the difference in T_g. The T_g in the present study was about 70 °C but 55 °C in the previous study, whereas T_a was identical (25 °C). When the T_g is higher as in the present study, the molecular mobility is reduced and thus result in smaller relaxation enthalpy. The T_g difference was induced by the minor difference (0.5%) of moisture content, emphasizing the substantial effect of moisture in low-moistured system. The presence of starch crystals in the tested molded specimens may be another possible cause of T_g difference. During the starch paste drying period (~24 h at 50 °C), a partial recrystallization of starch could occur. This was proved in the DSC thermogram, which exhibited melting endotherms starting at about 150 °C for both NRS and WRS samples, with 2.21 and 0.35 J/g, respectively (Fig. 3). The enthalpy values indicated that the recrystallization was more favored by the NRS samples than the WRS samples. In contrast, no crystals were formed in the starch samples prepared in our previous study (Chung & Lim, 2003a), because the starch was isolated as a precipitate in ethanol after being dissolved in dimethylsulfoxide (DMSO). It has been also reported that the extent of physical aging

Table 1
Kinetic parameters for enthalpy relaxation of glassy normal (NRS) and waxy (WRS) rice starches

Samples	ΔH_∞ (J/g)	t_c (day)	β
NRS	2.064	26.0	0.336
WRS	1.764	13.2	0.401

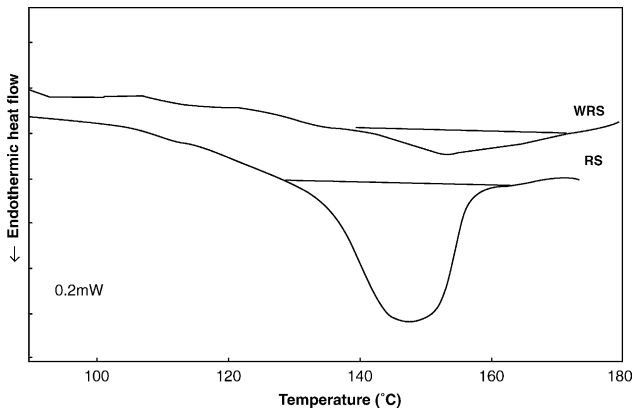

Fig. 3. DSC thermograms of NRS and WRS showing melting of recrystallized starch.

(relaxation) is inversely related to residual crystallinity (Diego et al., 1999; Mukherjee & Jabarin, 1995; Zhao et al., 2001). Additionally, morphological difference might affect the relaxation. The sample aged in our previous study were powders, whereas, in this study, the sample consisted of much bigger particles that were obtained from a compressed specimen. The relaxation enthalpy of the compressed specimen, under the same aging time and temperature, might be more restricted because of the compact nature of the matrix, which might result in a lower ΔH_∞.

The t_c values (average relaxation time) of NRS and WRS were 26.0 and 13.2 days, respectively. This difference indicates that relaxation occurs much faster in WRS than in NRS. In our previous study, the t_c values of NRS and WRS at a moisture content of 15% were 198 and 80 h, respectively (Chung & Lim, 2003a). Again, the substantially higher t_c found in the present study was due to the difference in $T_g - T_a$ and sample matrix structure, as discussed for ΔH_∞. In both studies, the t_c data revealed that the relaxation rate was much slower for NRS than for WRS. It was hypothesized that the heterogeneity caused by the presence of amylose in NRS retarded the relaxation rate.

β in Eq. (1) represents the relaxation time distribution, which depends on the aging conditions and the nature of the material. For NRS and WRS β was 0.336 and 0.401, respectively, which were similar to those found in our previous study (Chung & Lim, 2003a), despite the difference in the sample matrix. A smaller β indicates a broader distribution of the relaxation time and a slower approach to equilibrium (Montserrat, 1994). As shown by the t_c and ΔH_∞ data, a smaller β value for NRS suggests that the heterogeneity caused by the presence of amylose retards the relaxation process.

3.2. Viscoelastic behavior

The viscoelastic behaviors of the compression-molded NRS and WRS specimens were examined using a dynamic mechanical thermal analyzer (DMTA), while heating from 20 to 150 °C at a rate of 2 °C/min. The dynamic storage modulus (E') and loss factor (tan δ) were measured as a function of aging time. They are shown in Figs. 4 and 5, respectively.

The storage modulus (E') for NRS and WRS increased with aging time (3–29 days), an indication of chain stiffening by aging (Fig. 4). Similar trends have been reported for epoxy resin and starch by other researches (Barral et al., 1999, 2000; Lourdin et al., 2002). The E' values of the NRS and WRS samples were similar up to 15 days of storage, but thereafter, WRS displayed a greater E' than NRS.

The NRS and WRS samples exhibited different loss factors (tan δ) in the thermograms and both starch samples showed multiple peaks (marked by arrows in Fig. 5). The tan δ peaks observed between 60 and 100 °C were the results of glass transitions. As in DSC thermograms, NRS showed two small peaks, indicating dual glass transitions, whereas WRS showed one intense peak. The intensity of these tan δ peaks decreased with aging regardless of the starch type, indicating chain stiffening by aging. A minor peak also appeared at approximately 120 °C, which, we

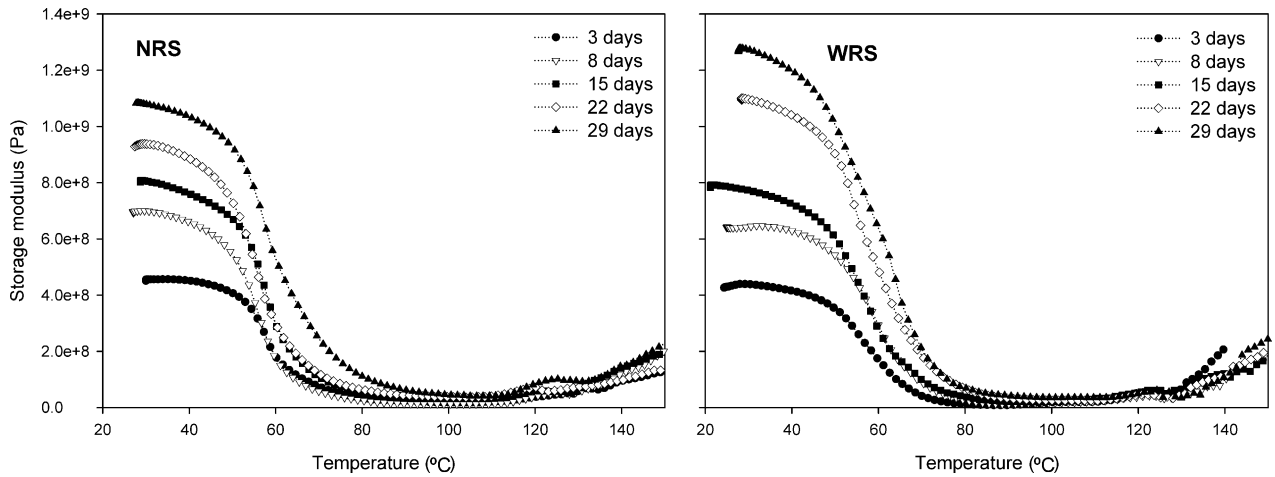

Fig. 4. Storage modulus (E') changes at different aging times up to 29 days for NRS and WRS.

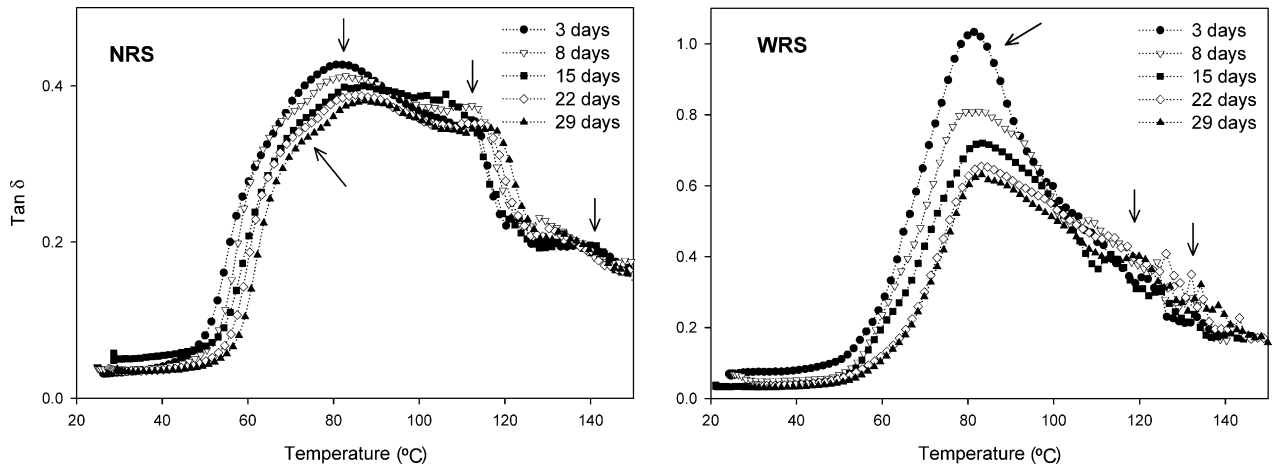

Fig. 5. Tan δ changes at different aging times up to 29 days for NRS and WRS.

assumed, corresponded to the evaporation of residual water. The E' increase at 120 °C (Fig. 4) also suggested the same assumption. Although the starch samples were coated with silicon oil, water loss could have occurred upon heating. The tan δ at 130–140 °C was possibly due to crystal melting, as was observed by DSC (melting at about 150 °C).

In Figs. 6 and 7, the changes in E' and tan δ peak intensity by aging are shown for both NRS and WRS samples. The tan δ peak intensity decreased with aging time, but the peak temperature increased, indicating that the glass transition shifted slightly to a higher temperature by aging (Fig. 7). Comparing both starches, NRS resulted in more increase in tan δ peak temperature, but less reduction in peak intensity. The tan δ peak intensity (Fig. 7) was substantially different for the two starch samples whereas E' difference was relatively small (Fig. 6). Because tan δ was calculated as the ratio of E'' and E', the significantly greater tan δ values of WRS suggested that the E'' for WRS was higher than that for NRS. The modulus difference between NRS and WRS samples was attributed to the inherently different natures of amylose and amylopectin.

Based on E' and tan δ result (Figs. 6 and 7), WRS displayed more changes in E' and tan δ peak intensity during aging than NRS. The faster relaxation rate shown by the WRS sample might also be related to this phenomenon. The linearity of amylose chains may favor chain–chain associations, and often its matrices are very compact and dense. The ease of amylose chain association is usually observed when under conditions allowing greater chain mobility, such as, when the water content is high. The experimental conditions for aging in this study included limited moisture and long-term kinetics. Possibly the structure of amorphous regions and physical nature in waxy starch are expected homogeneous due to the single constituent of amylopectin. Thus in the restricted conditions, the structural relaxation could be highly dependent on long-range structural arrangement and on composition. However, more study is required to obtain a clear understanding of the relaxation behavior of the two different starch molecules.

Yoshida (1995) studied the relationship between the enthalpy relaxation and the dynamic mechanical relaxation of amorphous poly(ether imide) and poly(aryl ether ether ketone). They found that the enthalpy relaxation process correlated well with the dynamic modulus relaxation process in amorphous polymers, but that the two systems

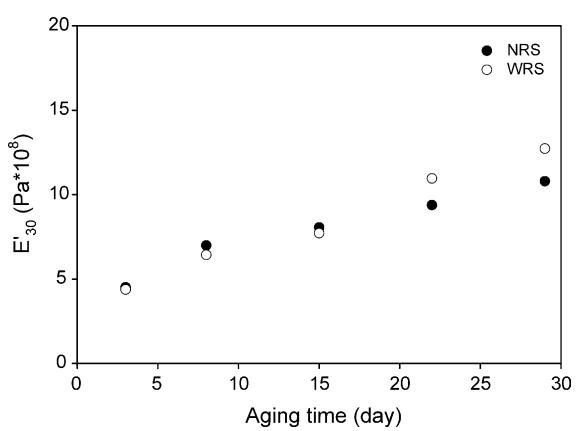

Fig. 6. Storage modulus at 30 °C (E'_{30}) at different aging times up to 29 days for NRS and WRS.

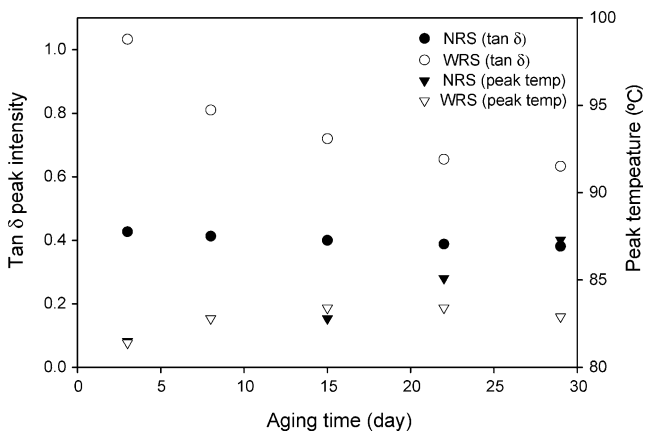

Fig. 7. Tan δ peak temperature and intensity at different aging times up to 29 days for NRS and WRS.

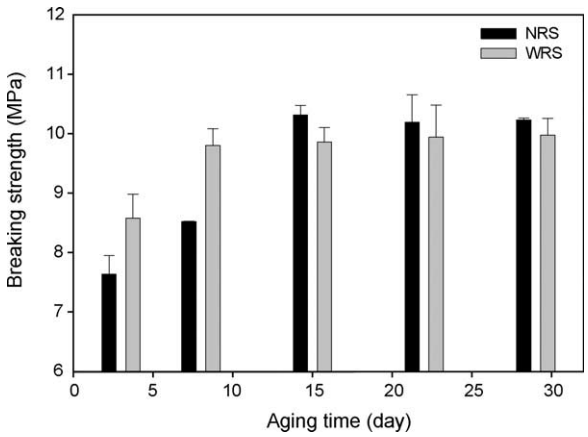

Fig. 8. Breaking strength changes at different aging times up to 29 days for NRS and WRS.

reached an equilibrium state in different times. A comparison between the relaxation enthalpy and dynamic modulus (E') data in this study showed that the relaxation increase by physical aging followed a similar trend, but the aging rates measured from the two methods were different. For example, the starch samples nearly reached enthalpy equilibrium after 13–26 days according to DSC analysis (Fig. 2), whereas the dynamic moduli data showed that the relaxation continued over this period (Fig. 6).

3.3. Mechanical behavior

The mechanical behavior of the NRS and WRS samples, at different aging times, was examined by a three-point bending test. The breaking strength increased with aging time, and approached a plateau before 15 days (Fig. 8). This trend was consistent with that found for an epoxy resin (Lourdin et al., 2002). In agreement with the relaxation enthalpy measured by DSC, the breaking strength was higher for WRS during the early stage of aging, whereas it became similar for both starches in the late stage of aging. Also, the time taken to reach the equilibrium state was shorter for WRS than for NRS. As discussed earlier, this implies that relaxation toward the equilibrium state was slower for NRS, due to the heterogeneity caused by the presence of amylose.

It has been reported that the kinetics of yield stress change and of relaxation enthalpy are similar (Cook, Mehrabi, & Edward, 1999). In this study the time required for reaching the equilibrium state as determined by breaking strength, differed from that determined by relaxation enthalpy measurement (Fig. 2 vs Fig. 8). Moreover, the time from breaking strength was much faster than that from the dynamic mechanical test. One possible explanation is that the small-range relaxation detected only by DMTA continues without significant change in enthalpy and large-deformation property. But in all cases of relaxation testing, WRS exhibited a faster relaxation than NRS. Based on these observations we conclude that in the absence of amylose and limited moisture, starch molecules in the amorphous state rapidly transform to form a matrix in thermodynamic equilibrium. Possibly spontaneous chain rearrangements and associations occur while approaching the equilibrium. These progressive changes could be measured by DSC, DMTA or by texture analysis, although the aging kinetics of starch could vary according to properties measured.

4. Conclusions

The physical aging of glassy starches from normal and waxy rices can be characterized by thermal or mechanical testing (DSC, DMTA, and Instron). Relaxation enthalpy, dynamic moduli, and breaking strength gradually increase with aging time. The storage modulus increased and tan δ peak height decreased continually with aging over the test period (29 days). These progressive changes indicate that starch chains become less mobile and the matrix is densified during aging. The relaxation rate was faster for waxy rice starch than for normal rice starch, possibly indicating that the heterogeneous matrix composition by amylose presence retarded the relaxation of amorphous regions toward equilibrium state. Changes in mechanical properties of low-moisture glassy starch products upon storage could be explained by this physical aging phenomena.

Acknowledgements

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