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Physical aging of glassy normal and waxy rice starches: Effect of crystallinity on glass transition and enthalpy relaxation

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Abstract

Effect of crystallinity on the relaxation behavior of normal and waxy rice starches was examined by differential scanning calorimetry (DSC). Starch samples with different crystallinities were prepared by heating granular rice starch (14% moisture) in DSC pans to different temperatures (170 and 200 °C), and an amorphous sample was prepared by dissolving the starch in dimethylsulfoxide and then recovering it in absolute ethanol. The heat capacity increment (ΔC_p) at the glass transition decreased with increasing sample crystallinity. The glass transition temperature (T_g) of native granular starch was higher than that of partially melted starches, but the starch heated to 200 °C displayed a higher T_g than did the starch heated to 170 °C, suggesting the occurrence of additional changes besides crystal melting during heating to 200 °C. Moreover, network structure formed between crystalline and amorphous regions could affect the amorphous transition. With regard to amorphous structural relaxation, the peak temperature of relaxation endotherm (T_p) increased linearly with log aging time (t_a), but the rate of the relaxation temperature increase ($dT_p/d\log t_a$) depended on residual crystallinity. The temperature of the relaxation endotherm positively correlated with glass transition. For partially melted starches, the extent of relaxation increased proportionally with the level of amorphous fraction, whereas the rate of relaxation decreased as the amorphous fraction increased.

Keywords: Physical aging; Glass transition; Enthalpy relaxation; Rice starch; Semicrystalline

1. Introduction

Granular starch in nature exists in a partially crystalline state. However, starch-based products for food and industrial uses are more often consumed in an amorphous or limited crystalline state, due to the preceding heat processing. The presence of crystallinity in starch influences the physical properties of heat-processed starch products. For example, the amorphous state transitions (glass transition and enthalpy relaxation) of starch are affected by the degree of residual crystallinity (Champion, Le Meste, & Simatos, 2000; Slade & Levine, 1987, 1988, 1991, 1995; Zeleznak & Hoseney, 1987).

When an amorphous polymer is cooled below its glass transition temperature (T_g), the polymer does not usually reach a state of true thermodynamic equilibrium. Thus, spontaneous changes toward equilibrium occur, with changes in many physical properties over time. This slow change toward equilibrium at a temperature below T_g is often referred to as a process of structural relaxation, known as physical aging. Physical aging is often observed at room temperature for low-moisture polymers with a T_g higher than room temperature. The property changes attributed to this relaxation process in an amorphous phase include reductions in enthalpy and free volume. These changes also result in increases in density, yield stress, and elastic modulus of a polymer matrix, whereas impact strength and creep rate decrease with increasing aging time (Struik, 1978).

The effect of residual crystallinity on amorphous relaxation has been reported for synthetic polymers, such as polypropylene, poly(ether-ether-ketone) (PEEK) and poly(ethylene terephthalate) (PET). Tant and Wilkes (1981) evaluated the aging of semicrystalline PET films, and reported that the extent and rate of aging decreased with increasing crystallinity because the crystalline phase acted as physical cross-links that retard amorphous relaxation. Mukherjee and Jabarin (1995) also studied the aging of PET, and found that the rate and extent of relaxation

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decreased with increasing crystallinity. Yield stress and density were also reduced by increasing the degree of crystallinity. Yoshida (1995), who studied PEEK of low or high crystallinities, observed that relaxation rate decreased slightly with increasing crystallinity.

Although many studies have been conducted on the physical aging of synthetic polymers, few studies on the physical aging of starch have been done (Borde, Bizot, Vigier, & Buleon, 2002; Chung & Lim, 2003). For the utilization of starch, crystalline regions are often transformed to varying extents to an amorphous state, in order to produce desired physical properties. Thus, the effect of residual crystallinity on the physical aging of starch is important to understand structural relaxation and to control the physical changes induced by aging.

In the present study, the effect of crystallinity on the physical aging behavior of starch was investigated for normal and waxy starches containing different degrees of crystallinity.

2. Materials and methods

Experiments were performed using a differential scanning calorimeter (Seiko Instruments, DSC 6100, Chiba, Japan) equipped with a liquid nitrogen cooling accessory. Temperature and enthalpy were calibrated with indium ($T_m = 156.6$ °C, $\Delta H_m = 28.590$ J/g) and mercury ($T_m = -39.0$ °C, $\Delta H_m = 11.472$ J/g), and heat capacity with sapphire. An empty pan was used as a reference.

Normal and waxy rice starches were isolated from corresponding rice flours (Japonica type), obtained from a local grocery (Seoul, Korea), by using a dilute NaOH solution (Lim, Lee, Shin, & Lim, 1999). Starch (10 ± 0.1 mg, dry solid basis) was placed in a silver DSC pan (70 μl), and hydrated excessively in a humidity chamber over distilled water. Excess moisture was allowed to evaporate on a balance until a desired moisture content (14%) was reached, and then the pan was hermetically sealed. The starch sample was then equilibrated at room temperature for 1 day prior to DSC analysis. To obtain different crystallinities, starch in a DSC pan (14% moisture) was heated to 170 or 200 °C in the DSC. In the melting endotherm of the starch, the midpoint in the melting temperature range was at about 170 °C. During DSC heating, complete melting of the starch was observed at around 240 °C, but thermal degradation could occur at this temperature. Thus, a starch sample, for which the crystalline regions were nearly removed, was obtained by heating to 200 °C. Completely amorphous normal and waxy starches were alternatively prepared by a chemical procedure using dimethylsulfoxide (DMSO) and ethanol (Jane & Chen, 1992). The moisture content of the amorphous starches was adjusted to 12%, because, at that moisture content, the T_g of the amorphous starch was similar to that of the native starch at 14% moisture.

Each starch sample was heated to above its T_g, at 10 °C/min, in order to eliminate thermal history, and then quenched at 20 °C/min to an aging temperature ($T_a = 50$ °C), which was approximately 25 °C below T_g ($T_g - 25$ °C). The starch samples were aged for different times (t_a) up to 240 h. Physically aged samples were cooled to 5 °C (T_0, starting temperature) at a cooling rate of 20 °C/min, and then the thermal transitions were immediately measured, by heating at 5 °C/min to $T_g + 60$ °C. For analysis of unaged samples, the DSC measurement was repeated with heated sample (thermal history eliminated). Measurements were made at least in triplicate.

3. Results and discussion

3.1. Glass transition temperature

The glass transition temperature and heat capacity increment (ΔC_p) at T_g for unaged samples, at different crystallinities, are shown in Table 1. It was expected that the starches heated to 200 °C (NCS and WCS) have greater amorphous content than would those heated to 170 °C (NMS and WMS). As expected, ΔC_p at T_g was higher for starches treated at higher temperature, due to their greater amorphous content (Table 1). In the native state waxy rice starch (WS) exhibited a ΔC_p value lower than that of normal rice starch (NS). It has been reported that NS melted with a lower enthalpy than did its waxy counterpart, because waxy starch is more crystalline (Biliaderis, Page, Maurice, & Juliano, 1986). Thus, WS contained a lower amorphous content than did NS, resulting in a lower ΔC_p value. The amorphous starches prepared in DMSO and ethanol had ΔC_p values of 0.230 and 0.213 J/g °C, for NAS and WAS, respectively, which were much greater than those for native starches.

In terms of glass transition of starch, it has been found that native rice starch, with inherent crystallinity, had a higher T_g than its gelatinized form (Chung, Lee, & Lim, 2002). For nylon 6, too, the presence of crystallites resulted in a higher T_g (Jin, Ellis, & Karasz, 1984). The interactions induced at

Table 1
Glass transition temperature (T_g) and heat capacity increment (ΔC_p) at T_g of unaged starch samples at 14% moisture content

Starches	T_g (°C)	ΔC_p (J/g °C)
NS	74.5 ± 0.5	0.101 ± 0.006
NMS	72.5 ± 1.5	0.129 ± 0.022
NCS	73.8 ± 1.3	0.180 ± 0.044
WS	76.3 ± 0.6	0.091 ± 0.007
WMS	73.8 ± 1.2	0.150 ± 0.024
WCS	74.9 ± 1.2	0.189 ± 0.029
NAS[a]	76.0 ± 1.2	0.230 ± 0.013
WAS[a]	73.6 ± 0.9	0.213 ± 0.008

[a] At 12% moisture content.

the amorphous–crystalline interface act as physical cross-links, and add rigidity to the amorphous regions (Jin et al., 1984; Slade & Levine, 1987, 1988, 1991, 1995). For the present data, T_g values for partially melted starches (NMS and WMS) were lower than those for native starches (NS and WS), in agreement with previous literature. According to the same theory, WS, which had higher crystallinity, exhibited higher T_g than did normal starch (NS). However, unexpectedly, starches heated to 200 °C (NCS and WCS) exhibited higher T_gs than did starches heated to 170 °C (NMS and WMS). In a study on semicrystalline PET, no correlation was found between extent of crystallinity and T_g (Dobbertin, Hensel, & Schick, 1996). Rather, ΔC_p at glass transition was correlated with the amorphous fraction. Based on present data and previous literature, unlike ΔC_p, T_g may not be affected solely by the quantity of amorphous fraction. Rather, the internal structure of amorphous regions, and the interface structure between crystalline and amorphous regions, may also affect T_g.

NMS and WMS, due to partial transformation of their amorphous regions, displayed the reduced T_g and increased ΔC_p, compared to the original unheated samples (NS and WS). However, the higher T_gs for NCS and WCS, compared to those for NMS and WMS, might suggest that there were additional changes beyond crystal melting, possibly in the interface structure between crystalline and amorphous regions. Such changes would result in increased rigidity of the amorphous regions.

3.2. Kinetic analysis of enthalpy relaxation

The structural relaxation process causes simultaneous decreases in free volume and segmental mobility, as a system approaches a metastable equilibrium state. The material continuously relaxes toward the enthalpy of the equilibrium state with aging time, and consequently, the relaxation enthalpy increases, as shown in Fig. 1. For all starch samples, the enthalpy increase proceeded rapidly at the beginning of aging, and reached a plateau as aging continued, due to decreased free volume and molecular mobility of chain segments (Montserrat, 1992, 1994). For an equal aging period, native starch exhibited lower relaxation enthalpy than did partially melted starch (Fig. 1). The relaxation enthalpy for fully amorphous starch was also much higher than that for partially melted starch. Only the amorphous regions in starch experience aging phenomena. Thus, like ΔC_p, the relaxation enthalpy appeared to be simply positively correlated with the proportion of amorphous fraction.

The kinetics of enthalpy relaxation can be analyzed using the following relationship, 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 a maximum equilibrium enthalpy, t_c is an average relaxation time, and β is the width of the relaxation time distribution. The three kinetic parameters, ΔH_∞, t_c, and β, calculated by non-linear curve fitting, describe the relaxation behavior. The maximum relaxation enthalpy (ΔH_∞) increased as crystallinity decreased (Table 2). The same trend was also observed for the average relaxation time, t_c, which was negatively correlated with relaxation rate. Thus, the retardation of relaxation resulted in increased ΔH_∞. The changes in ΔH_∞ and t_c with varying crystallinity showed the same trends for normal and waxy rice starches. Thus, a higher t_c value induced a

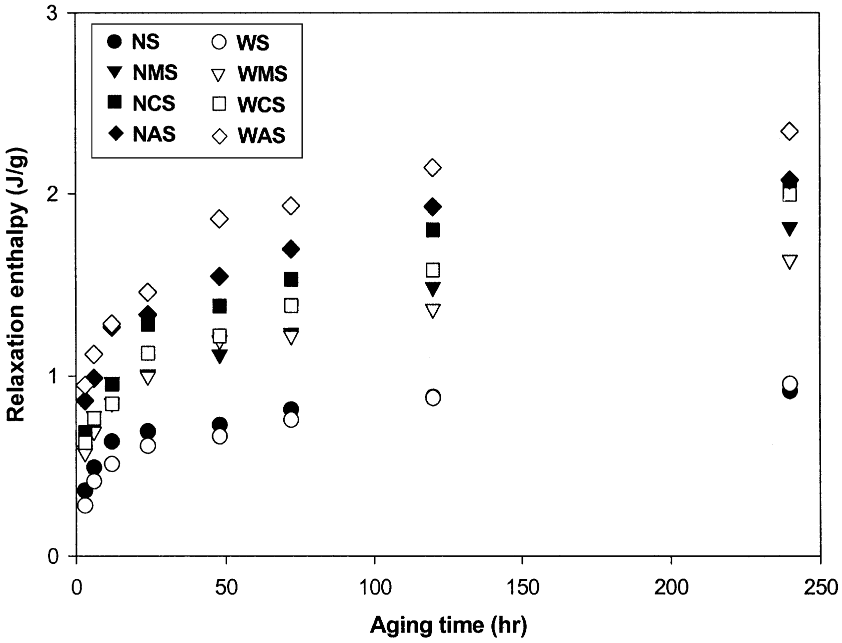

Fig. 1. Relaxation enthalpy vs. aging time for native, partially melted, and fully amorphous starches.

Table 2
Parameters for enthalpy relaxation kinetics in native and partially melted starches at 14% moisture content

Starches	ΔH_∞ (J/g)	t_c (h)	β
NS	0.9397	13	0.4210
NMS	3.1777	455	0.3126
NCS	4.0991	841	0.3604
WS	1.1475	55	0.3941
WMS	2.7650	406	0.2819
WCS	4.4492	1094	0.3276
NAS[a]	3.1921	183	0.2793
WAS[a]	2.9839	63	0.3289

[a] At 12% moisture content.

higher ΔH_∞, regardless of starch type or extent of crystallinity.

The t_c increase indicates that relaxation rate decreased as crystallinity decreases. However, several researchers have previously reported that relaxation rate decreases proportionally with increasing crystallinity. Mukherjee and Jabarin (1995), and Tant and Wilkes (1981) examined the aging of semicrystalline PET, and found that relaxation rate increased with decreasing crystallinity, because the crystalline phase acted as physical cross-links. Yoshida (1995) described relaxation parameters for both quenched and slow-cooled poly(aryl ether ether ketone) (PEEK) samples, which showed low and high extents of crystallinity, respectively. He reported that t_c for slow-cooled PEEK was slightly greater than that for quenched PEEK, due to a retardation effect of crystallites on enthalpy relaxation. In our experiment, an opposite trend for relaxation rate vs. crystallinity was found (Table 2). This might be due to differences in sample preparation methods. In the literature for synthetic polymers, crystallinity was increased by annealing amorphous samples at different temperatures and times. In the present experiment, however, the degree of crystallinity was changed by heating native starch to different temperatures. As suggested by our T_g results, heating to 200 °C might have induced the formation of a different structure in the amorphous regions, and possibly in the network matrix.

Among the native starches, NS showed a higher relaxation rate than that for WS. This might be explained by the difference in crystallinity, which was higher for waxy starch. But the difference in amylose content should also be considered. NS would include amylose chains in its amorphous regions, whereas waxy starch contains only amylopectin. Due to a lack of information on the morphology of amorphous regions in native starch, our understanding of the amorphous thermal transitions is very limited. But our transition results suggested that the amorphous structures formed by different starch chains are not identical.

The β values ranged from 0 to 1. A smaller β value indicates a broader relaxation time distribution. The native starches had higher β values than did the partially melted starches, indicating that the native starches had a narrower relaxation time distribution. This result suggests that the partially melted starches had increased structural heterogeneity. It should also be noted that the β values for NMS and WMS were lower than those for NCS and WCS. According to the same theory, the lower β values for NMS and WMS suggest that they contained more heterogeneous amorphous structures. Because the β value was not expected to be closely related to residual crystallinity, it was hypothesized that excessive heating (to 200 °C) resulted in increased homogeneity of amorphous structure. NS exhibited higher β than did WS, which suggested that the waxy starch was more heterogeneous for some unknown reason.

The relaxation parameters for native and fully amorphous starches were also compared, after $T_g - T_a$ was adjusted to be similar, by varying the moisture contents (14 vs. 12%, respectively, for native and amorphous starches). ΔH_∞ was greater for NAS than for WAS, as previously reported (Chung & Lim, 2003, 2004). The difference in ΔH_∞ between native and amorphous starches might be explained by the difference in ΔC_p, as shown in the following equation (Montserrat, 1992, 1994):

$$\Delta H_\infty = \Delta C_p (T_g - T_a) \tag{2}$$

Because $T_g - T_a$ was nearly equal for the starches tested, a linear relationship existed between ΔH_∞ and ΔC_p. The ΔC_p values for native normal and waxy starches (14% moisture) were 0.101 and 0.091, and 0.223 and 0.213 J/g °C for the corresponding amorphous samples (12% moisture) (Table 1). Thus, it appears that the extent of enthalpy relaxation clearly depends on the mobility of amorphous chains.

The t_c data showed that, in an amorphous state (NAS and WAS), the relaxation rate for normal starch was much lower than that for waxy starch. Similar results were obtained in our previous work (Chung & Lim, 2003, 2004), in which it was suggested that the compositional heterogeneity due to the presence of amylose in the matrix of normal starch accounted for a slower relaxation. It was presumed that amorphous starch, prepared using DMSO and ethanol, had more heterogeneity in its amorphous regions than did native starch. The smaller β for amorphous starch implies a broader distribution of times for the relaxation process, which also suggests a more heterogeneous structure.

From results for the kinetic parameters, we conclude that the relaxation of amorphous starch depends not only on the structural heterogeneity of the matrix (or amorphous regions), but on the relative proportion of amorphous regions.

3.3. Peak temperature of relaxation endotherm

The peak temperature of the relaxation endotherm (T_p) increased with aging time, regardless of crystallinity or starch type (Figs. 2 and 3). The curve shape for T_p vs. aging

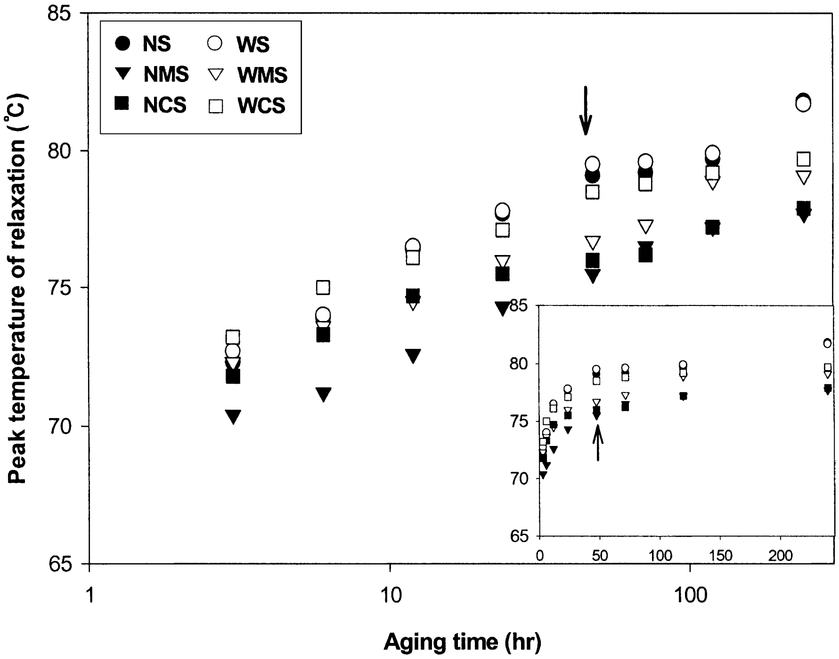

Fig. 2. Peak temperature of enthalpy relaxation vs. log aging time for native and partially melted starches.

time (small box in Fig. 2) was very similar to that for relaxation enthalpy vs. aging time. But the linearity of T_p with log t_a did not continue, as the matrix approached its equilibrium (marked by arrows). Montserrat (1994) reported a similar trend for an epoxy resin, i.e. the increase in T_p with log t_a deviated from linearity for an aging temperature lower than that where $T_g - T_a = 10$ °C.

The kinetic parameters for the changes in T_p with log t_a are shown in Table 3. The slopes before and after the points of deviation in Figs. 2 and 3 were defined as slope 1 and 2, respectively. The slope during the early stage of aging (slope 1) was greater than that during the late stage of aging (slope 2), similar to the trend for relaxation enthalpy (Fig. 1). The extent of relaxation decreases with increasing aging time, because segmental chain mobility in the system becomes restricted as free volume decreases, and consequently, the system densifies rapidly during the early stage of aging. This rapid densification of structure during the early stage of aging was indicated by the greater slope. However, as the system continues to approach a metastable

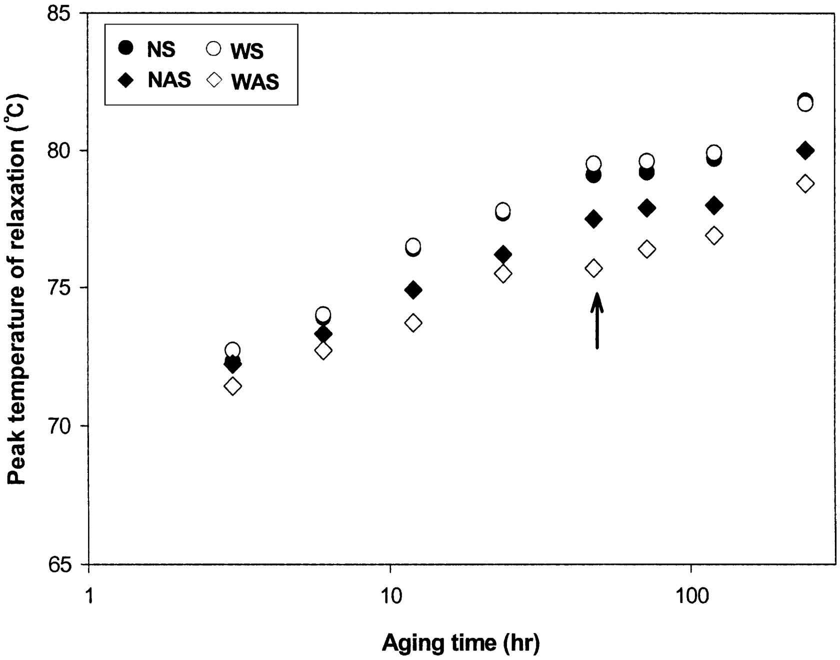

Fig. 3. Peak temperature of enthalpy relaxation vs. log aging time for native and fully amorphous starches.

Table 3
Kinetic parameters for peak temperature (T_p) of relaxation endotherm for native and partially melted starches at 14% moisture content

Starches	$dT_p/d \log t_a$			$T_p(t_a \approx 0)$
	Total slope	Slope 1	Slope 2	
NS	4.74	5.78	1.54	70.6
NMS	4.19	4.42	3.05	68.3
NCS	3.28	3.99	3.07	70.9
WS	4.66	5.78	1.02	70.9
WMS	3.70	3.99	3.10	70.6
WCS	3.27	3.86	2.98	72.2
NAS[a]	3.97	4.48	1.74	70.4
WAS[a]	3.62	3.79	2.26	69.8

[a] At 12% moisture content.

equilibrium state, the change caused by structural relaxation slows down, which results in a reduced slope (slope 2). It was not clear, however, why the slope change was so abrupt as to cause a discontinuity.

The proportion of amorphous regions appeared to affect the slope of the change in T_p. As amorphous content increased, slope 1 decreased, whereas slope 2 increased. This result might be explained by the kinetics of enthalpy relaxation in the presence of different amorphous structures, as discussed earlier. The rate of the relaxation process was greater for native starch than for partially melted starches heated to 170 or 200 °C. The fast relaxation process for native starch resulted in the largest slope 1 and the smallest slope 2 among the tested starches. However, an increased heterogeneity in partially melted starches could account for the smaller slope 1 and larger slope 2 than those for native starches. The difference in heating temperatures (170 or 200 °C) was more impactful for slope 1, for which NMS and WMS were larger than for NCS and WCS. This trend correlated well with the t_c data from the enthalpy relaxation kinetics. The peak temperature of the endotherm at t_a near 0, T_p ($t_a \approx 0$), displayed a trend similar to that for the T_g data in Table 1. This might indicate that the endothermic recovery of the relaxed matrix depends on T_g, i.e. higher T_g results in a higher T_p for the relaxation endotherm.

For native and fully amorphous starches, the kinetic parameters for T_p, which included total slope, slope 1 and slope 2, were well correlated with the relaxation kinetics, and the change in T_p ($t_a \approx 0$) was also consistent with that for T_g.

Thus, the experimental data suggest that the peak temperature for the relaxation endotherm has similar kinetics as the relaxation enthalpy.

4. Conclusions

The ΔC_p showed a linear relationship with amorphous content, as expected theoretically. But T_g was affected not only by melting behavior, but also by other structural changes induced by heating. The relaxation enthalpy, as reflected by the endotherm obtained after physical aging, increased with decreasing crystallinity. The rate of relaxation, however, was reduced by increasing the amorphous content in the starch matrix, a result that differed from previous findings for thermally recrystallized synthetic polymers. The heterogeneity of a system may play an important role in determining relaxation kinetics. The lower values for the kinetic parameter β for partially melted starches than that for native starches suggested that partially melted starches have greater heterogeneity, which consequently results in slower relaxation. The peak temperature of the relaxation endotherm showed a positive linear relationship with log aging time, and this trend was highly correlated with relaxation enthalpy and rate. The relaxation process for the amorphous regions in a starch system is a complex one, governed not only by residual crystallinity, but also by structure and networking of both amorphous and crystalline regions.

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