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Phase transition phenomena and the corresponding relaxation process of wheat starch–water polymer matrix studied by dielectric spectroscopic method

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Abstract

The excess amount of water molecule in wheat starch is able to unravel the helix structure. The relaxation process are associated with a collective helical motion is largely affected with the variation of water concentration. Depending on the concentration of water molecules in the system, several kinds of phase could be identified with the variation of temperature. Inter-crystalline and liquid crystalline phases appear in our study depending on the concentration of water molecules. The shape and the intensity of several relaxation processes were largely affected with the variation of water concentration in wheat starch. The total activation energy of all existed relaxation was increased with the increase of water concentration. Two α-relaxations and two γ-relaxations were observed that are going to be reported at first time.

Keywords: Wheat starch; Dielectric relaxation; Gelatinization

1. Introduction

Wheat starch, a long chain molecular system contained high polar molecular structures linked by anhydro glucose unit (AGU) show interesting and scientifically significant dielectric properties that implies us to find whether dipole–dipole interaction or any other non-polar interactions for creating gelatinization. The change occurred in structure and morphology of the granules of polysaccharide molecular system depends on temperature as well as water concentration in the system (Waigh, Gidley, Komanshek, & Donald, 2000). Since the dielectric relaxation spectroscopy (DRS) is an efficient technique to find the electronic behaviour changed drastically with the variation of water content and to investigate the changes within the molecular dynamics of wheat starch influenced by interaction of wheat starch with water molecules (Butler & Cameron, 2000; Cameron & Donald, 1993; Einfeldt, Meißner, & Kwasniewski, 2000, 2003; Einfeldt, Meißner, Kwasniewski, & Einfeldt, 2001; Hatakeyama & Hatakeyama, 1998; Majumder, Meißner, & Schick, 2004; Marcus, 1995; van den Berg, 1981), we are informing the cause and effect of appearance of several relaxation phenomena by DRS.

We are reporting the importance of spin–orbit, spin–lattice and dipole–dipole interaction in creating gelatinization of wheat starch. With the variation of water content in wheat starch the gelatinization process could be assessed, those may largely affect the relaxation phenomena qualitatively and quantitatively. In this work, we are going to study the assigned distinct relaxations, such as α-, δ-, β-, and γ- relaxations based on the variation of strength and other cooperative parameters under several experimental conditions. This work will provide us to think about microscopic cause in creating gelatinization. Finally, the effect of relaxation phenomena observed by introducing water molecules in wheat starch with the increase of its concentration.

2. Experimental procedure

The wheat starch sample was used without additional purification for three different water concentration ca. 23, 37 and 46% (w/w) and then compared with earlier reported results (Majumder et al., 2004) contained dried sample and wet sample

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(13%). The sample was collected from Prof. W. Flamme, Institut für Stressphysiologie und Rohstoffqualität Groß Lüsewitz, Germany and was blocked from electrodes by thin Teflon sheets of approximately 0.03 mm thick. The sample thickness was approximately 0.42 mm measured by a measuring screw (Majumder et al., 2004). The complex dielectric constant was measured in the frequency range from 10 mHz to 10 MHz by using the NOVOCONTROL Broadband Dielectric Spectrometer System BDS 4000 with the active cell BDC-S with the application of $1V_{pp}$ ac measuring field. The concentration was constant throughout the experiment, for each concentration, and it was checked by measuring mass of the prepared cell before the experiment and after the experiment. The dielectric strength, relaxation time, relaxation frequency, and their cooperative parameters including the contribution came from dc conductivity were estimated by using the following Equation (Havriliak & Negami, 1966)

$$\varepsilon^*(T) = \sum_{i=1}^{n} \frac{\Delta\varepsilon_i}{[1+(i\omega\tau_i)^{\alpha_i}]^{\beta_i}} + \mathrm{i}\frac{S}{\omega^N} \tag{1}$$

where α_i is the width of relaxation process and β_i is the asymmetry of this process. τ_i is the relaxation time, $\Delta\varepsilon_i$ corresponds to the dielectric strength. All the above parameters were function of temperature T.

3. Results and discussion

We estimated all fitting parameters (S, N, τ_i, $\Delta\varepsilon_i$, α_i and β_i) of α-, δ-, β- and δ- relaxations and dc conductivity (S, N) by using HN- fitting functions.

The temperature variation of relaxation time (τ) of 37% water content (Fig. 1, Table 1) and 46% water content (Fig. 3, Table 2) indicate that six relaxation phenomena could be assessed. Two relaxations phenomena designated as α-relaxation (α_1 and α_2) could be observed for both concentrations at high temperature region only due to the breaking of double helical structure and each relaxation simply arose due to spin–orbit and spin–lattice coupling as according to mode coupling theory (Johari, 2002; Johari et al., 2002; Roland & Ngai, 1992). Urakawa, Fuse, Hori, Tran-Cong, and Yano (2001) identified two α-relaxations as the segmental motion of two polymer components with a large difference in glass transition temperatures. They indicated that both α-relaxations arose due to only intrinsic phenomena. From the mode coupling theory we can assume both α_1 and α_2 relaxations arising in this occasions due to spin–orbit and spin–lattice coupling, having higher relaxation frequencies compared to other relaxations. Both α_1 and α_2 relaxations have same frequency region and temperature region in both concentrations. But, dielectric strength of both α_1 and α_2 relaxations is little bit higher in 46% than 37%. It simply indicates that presence of higher concentration of water molecules enhancing the strength of α-relaxation. That implies the presence of higher concentration of water molecules enhancing the possibility for creating glass transition and its gelatinization. It can be noticed that the spin of water molecules due to its intrinsic rotational motion at higher temperature interacts with the orbital motion of AGUs unit and lattice formation by joining AGUs unit.

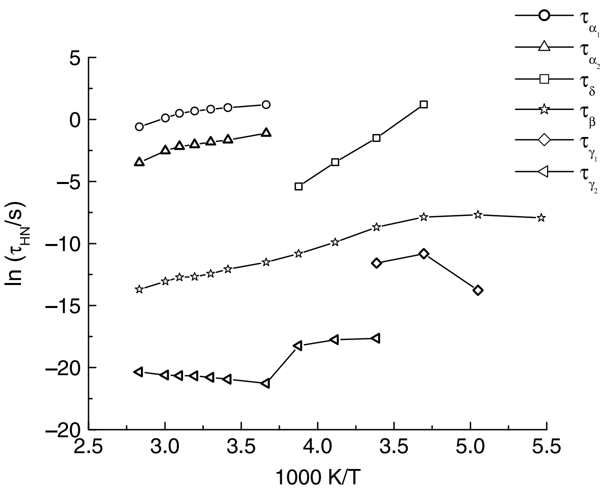

Fig. 1. Variation of relaxation times (τ) for all relaxation processess found in 37% water content (w/w) wheat starch with temperature.

Since, the mode coupling theory suggests us spin–lattice interaction energy will be higher than that of spin–orbit interaction energy which implies relaxation time due to spin–lattice coupling will be lower than spin–orbit coupling. Due to such reasons, we can assign α_1-relaxation as a higher relaxation time phenomena compared to α_2-relaxation.

Zetsche, Kremer, Jung, and Schulze (1990) mentioned the α-relaxation of poly (vinyl methyl) ether with polystyrene could be measured in the one- and two-phase region. In this paper two α-relaxations could be assumed at lower relaxation time compared to β-relaxation, as suggested their relaxation times (Figs. 1 and 3; Tables 1 and 2) or relaxation frequencies and its dielectric strength (Figs. 2 and 4; Tables 1 and 2) (Ngai, 1998a, b) for both concentrations (37 and 46%). The third relaxation designated as δ-relaxation, appeared in the medium region of temperature for both concentrations is the pre-transitional relaxation of double strand structure. δ-relaxation is generally arising due to reorientation of bound water molecules in the sample (McBriety, Keely, Coyle, Huan, & Vij, 1996). In both concentrations, δ-relaxation has same relaxation time and appears in same temperature region. It shows simply an Arrhenius behaviour. Dielectric strength of δ-relaxation for both concentrations is approximately constant with temperature and having same value. It indicates δ-relaxation arises due to the presence of water molecules itself. β-relaxation is generally arising due to local chain motion (Butler & Cameron, 2000). The fourth relaxation designated as β-relaxation appeared throughout the temperature region. Relaxation time of β-relaxation in both concentrations having equal value and appears throughout the temperature region. It indicates that experimental water concentration (37 and 46%) does not make any influence to change the segmental motion of AGUs unit. So it may be assumed that β-relaxation arose due to free rotational motion of AGUs unit.

Table 1
Relaxation frequencies (τ) in s and dielectric strengths ($\Delta\varepsilon$) for 37% water content wheat starch–water polymer matrix

Temperature (°C)	α_1-relaxation		α_2-relaxation		δ-relaxation		β-relaxation		γ_1-relaxation		γ_2-relaxation	
	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$
−90							3.60×10^{-4}	14.24				
$^{-}75$							4.60×10^{-4}	14.96	1.05×10^{-6}	0.89		
$^{-}60$					3.33	25.11	3.80×10^{-4}	12.63	2.00×10^{-5}	1.06		
−45					0.22	34.56	1.70×10^{-4}	9.00	9.37×10^{-6}	1.37	2.19×10^{-8}	10.45
$^{-}30$					0.03	43.34	5.00×10^{-5}	8.59			1.94×10^{-8}	6.91
$^{-}15$					0.00	52.73	2.00×10^{-5}	5.96			1.19×10^{-8}	7.18
0	3.30	54289.54	0.33	3917.70			1.00×10^{-5}	54.30			5.76×10^{-10}	45.76
20	2.59	103187.03	0.19	6855.89			5.71×10^{-6}	64.95			8.05×10^{-10}	26.04
30	2.28	155193.25	0.16	13737.01			3.99×10^{-6}	74.24			9.35×10^{-10}	28.63
40	1.96	214569.43	0.13	19651.97			3.12×10^{-6}	91.37			1.06×10^{-9}	32.40
50	1.63	257981.26	0.11	27453.09			2.98×10^{-6}	110.74			1.07×10^{-9}	32.63
60	1.13	281236.22	0.08	26079.86			2.14×10^{-6}	125.60			1.13×10^{-9}	33.40
80	0.55	328939.93	0.03	15942.09			1.12×10^{-6}	131.49			1.44×10^{-9}	17.64

Table 2
Relaxation frequencies (τ) in s and dielectric strengths ($\Delta\varepsilon$) for 46% water content wheat starch–water polymer matrix

Temperature (°C)	α_1-relaxation		α_2-relaxation		δ-relaxation		β-relaxation		γ_1-relaxation		γ_2-relaxation	
	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$	τ	$\Delta\varepsilon$
−90							3.50×10^{-4}	23.90	3.88×10^{-6}	1.82	2.71×10^{-9}	0.24
−75							2.30×10^{-4}	24.11	6.99×10^{-7}	2.96	1.54×10^{-9}	0.17
−60					0.99	44.08	1.40×10^{-4}	23.17	1.49×10^{-7}	6.95	2.00×10^{-9}	0.30
−45					0.09	53.38	4.00×10^{-5}	23.41	1.14×10^{-7}	12.08	4.10×10^{-9}	1.18
−30					0.01	65.87	3.00×10^{-5}	24.82	1.26×10^{-7}	9.65	3.98×10^{-9}	1.79
−15					0.00	67.81	1.00×10^{-5}	21.41	1.10×10^{-7}	7.39	3.97×10^{-9}	1.94
0	1.16	3.14×10^{6}	0.06	250995.32			2.20×10^{-6}	36.77			1.71×10^{-9}	19.90
20	0.65	4.66×10^{6}	0.03	263677.83			9.26×10^{-7}	43.54			1.53×10^{-9}	15.13
40	0.68	8.23×10^{6}	0.02	279160.04			6.03×10^{-7}	64.63			5.41×10^{-9}	10.03
60	0.86	8.23×10^{6}	0.03	359596.64			5.27×10^{-7}	94.37			3.80×10^{-9}	3.87
80	0.87	7.96×10^{6}	0.03	400058.71			3.26×10^{-7}	115.68			1.00×10^{-15}	1.00×10^{-6}
90	0.66	5.07×10^{6}	0.02	242172.14			1.99×10^{-7}	125.71				

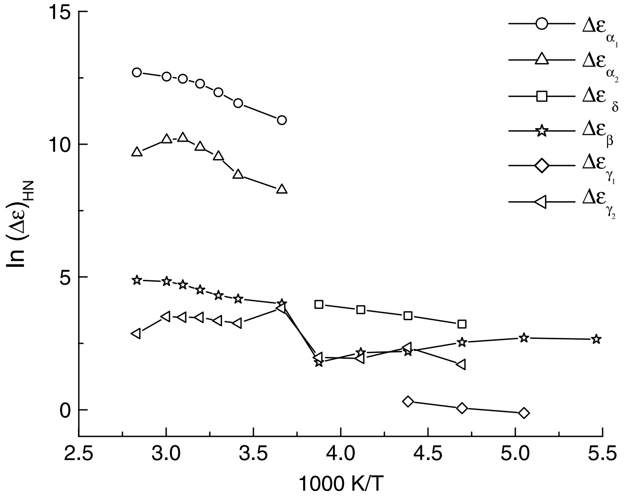

Fig. 2. Variation of dielectric strength ($\Delta\varepsilon$) with temperature for 37% water content (w/w) wheat starch with temperature.

γ-relaxation a boat-chain inter-conversion of the pyranose ring, which can be associated with the acetyle-side group motion in the position C6 at the AGU (Einfeldt et al., 2001). The fifth and sixth relaxations designated as γ-relaxation (γ_1 and γ_2) are associated with the interactions of hydrogen bonds with AGUs unit. Actually, γ-relaxation can be arisen due to the fluctuation in the system or the fluctuation of orientation of the sample may be created by dipole–dipole interaction. Since, both amylopectin and amylose constituents in starch are dipolar, so dipole–dipole interaction between amylose and hydrogen bond creates the fluctuation of the orientational motion in the sample. Therefore, the fifth relaxation (γ_1) that observed in lower temperature region may be arising due to the interaction of hydrogen bond with amylose unit and the sixth relaxation (γ_2) observed throughout the temperature region, may be arising due to the interaction of hydrogen bond with amylopectin unit. Both γ-relaxations may be arisen due to dipole–dipole interaction.

The activation energy of β- process were 41.34 (dried sample) (Majumder et al., 2004), 61.38 (wet sample, 13% water content) (Majumder et al., 2004), 27.26 (23% water content), 47.54 (37% water content) and 44.82 kJ/mol (46% water content). The pre-exponential factor τ_0 are 3.58701×10^{-10} (dried sample) (Majumder et al., 2004), 6.67474×10^{-15} (wet sample, 13% water content; Majumder et al., 2004), 7.38×10^{-29} (23% water content), 1.90×10^{-31} (37% water content), and 1.17×10^{-29} (46% water content) seconds, respectively.

The total activation energy ($E_a=E_\alpha+E_\beta+E_\delta+E_\gamma$) of observed dielectric relaxation process was increased largely with the increase of concentration of water molecules, but the equivalent pre-exponential factor ($1/\tau_{eq.}=1/\tau_\alpha+1/\tau_\beta+1/\tau_\delta+1/\tau_\gamma$) was decreased largely with the increase of concentration of water molecules. In case of linear (Arrhenius law) behaviour, the activation energy and pre-exponential factor was calculated using Arrhenius law (Majumder et al., 2004). In case of non-linear and transition the activation energy ($E_a\approx H_a+S_a\ T_g$) and pre-exponential factor was calculated using the combined Eyring's rate theory and VFT (Vogel Fulcher Tamman) method as per the following equation

$$\tau\left(\frac{T}{T_0}\right)^{\alpha}=\tau_D\exp\{-S_a/R\}\exp\left\{\frac{H_a}{R(T-T_g)}\right\} \tag{2}$$

where activation energy is defined by, $E_a=H_a+S_aT_g$; H_a stands for activation enthalpy, S_a stands for activation entropy and T_g stands for the transition point in each occasion.

The activation energy of α1-mode are 80.10 and 80.17 kJ/mol for 37 and 46%, respectively, and pre-exponential factor are 3.13×10^{-44} and 2.11×10^{-42} s for 37 and 46%, respectively. For 46%, the interaction is greater for α1-mode compared to 37%, although in both cases α1-mode may be arose due to weak spin–orbit coupling interaction (Figs. 1 and 3) as according to mode-coupling theory. The activation

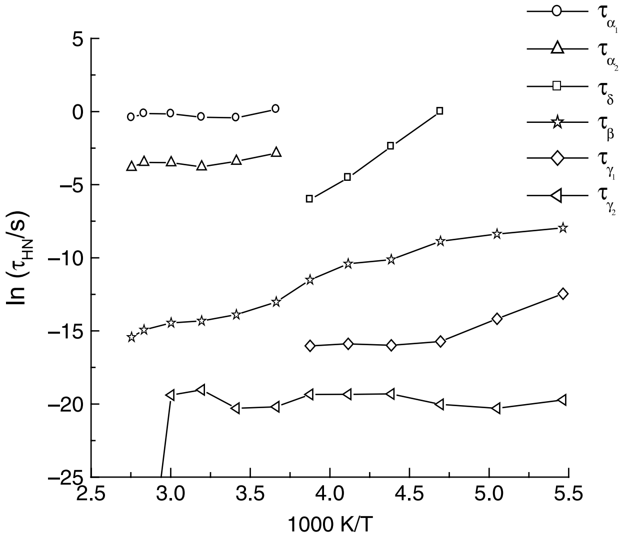

Fig. 3. Variation of relaxation time (τ) for all dielectric relaxation processess found in 46% water content (w/w) wheat starch with temperature.

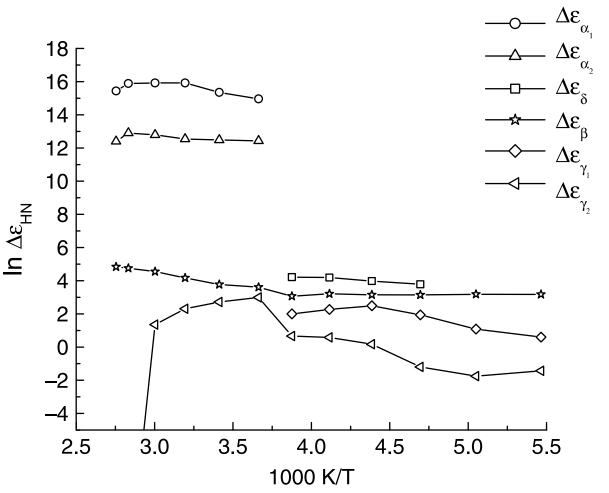

Fig. 4. Variation of dielectric strength ($\Delta\varepsilon$) with temperature for 46% water content (w/w) wheat starch with temperature.

energy for α2-mode are 75.96 and 70.83 kJ/mol for 37 and 46%, respectively, and pre-exponential factor are 7.35×10^{-42} and 5.20×10^{-39} s for 37 and 46%, respectively. For 37%, the interaction is greater for α2-mode compared to 46%, although in both cases α2-mode may be arising due to weak spin–lattice coupling interaction (Figs. 1 and 3) as according to mode-coupling theory.

The activation energy of γ1-mode is 36.63 and 27.37 kJ/mol and the pre-exponential factors are 3.82×10^{-34} and 5.12×10^{-27} s for 37 and 46%, respectively. The activation energy of γ2-mode is 21.24 and 23.51 and the pre-exponential factors are 1.23×10^{-21} and 1.49×10^{-22} s for 37 and 46%, respectively.

In excess water, amorphous growth rings suck in water and rapidly expand in size. Retrogated starches gelatinized in excess water depending on the composition of amylose and amylopectin. Thus, means that amylose–amylopectin ratio in the system may play an important role. At the lower temperatures, there is a partial loss of crystallinity as double helices are stripped off the sides of the crystallites, but they remain intact as double helices and if the temperature is dropped again the remaining crystal acts as a template on which the helices will partially relocate.

Transition occurs at 39–48, 0, −60 °C for 37% water content wheat starch (Fig. 1). The A-type structure (wheat starch) is characterized by a denser type arrangement with staggered monoclinic packing of double helices with an open channel in the center filled with water molecules. The helix–coil transition occurs belong to a range of temperature. It is very difficult to find out the exact helix–coil transition point. Transition occurs at 60, 38, 0 and -30^{0}C for 46% water content wheat starch (Fig. 3). For 46%, a point of gelatinization (glassy nematic state to gel transformation) occurs at 60 °C. For 37%, the point of gelatinization appears higher than 60 °C and at ca. 80 °C. At such higher temperature, the molecular order losses are large and consequently a helix–coil transition occurs, because wheat starch (A-type starch) has shorter double helices length and has less stability and then has a little resistant power to prevent the dissociation. So the system will loss 3D crystallinity and also the order associated with the double helix structure gradually. This would imply the existence of several phases depending on the concentration.

Figs. 2 and 4 show dielectric strength behaviour of both concentrations for several relaxation phenomena. It also observed from the dielectric strength behaviour (Figs. 2 and 4) that dielectric strength in all occasions obeys non-exponential variation and also indicates several transition points as similar to Figs. 1 and 3.

The duality of α-relaxations for both 37% and 46% indicates that the co-existence of both glassy nematic and gel for a range of temperature. It also indicates that the bifurcation of double helices started at 38–40 °C. This is the creation of single strand. Those phases could be expected as liquid crystalline phases (Majumder, Mitra, & Roy, 1994; Majumder, Roy, & Roy, 1996; Waigh et al., 2000).

4. Conclusion

Two α-relaxations could be observed in wheat starch and higher concentration water system. Both α-relaxations has correlation with mode-coupling theory. So, we can assume that α1-relaxation may arise due to spin–orbit interaction and α2-relaxation may arise due to spin–lattice interaction. γ1-relaxation arose due to dipole–dipole interaction between hydrogen bond and amylose unit and γ2-relaxation arose due to dipole–dipole interaction between hydrogen bond and amylopectin unit. All those relaxation were largely depending on the water concentration. From the experimental observations, we find a few intermediate transition point, those may be liquid crystalline phases. It is suggested that the total activation energy of all existed relaxations is increased with the increase of concentration of water molecules in the starch–water system.

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