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Dielectric spectroscopic analysis of wet and well dried starches in comparison with other polysaccharides

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Abstract

The polymer dynamics of wet and well dried starches are investigated using the dielectric spectroscopy. In all starches three relaxation connected with the polymer dynamics have been observed: The β-relaxation is associated with the local chain motion, the δ-relaxation with an unknown molecular origin and the β_{wet}-relaxation with motions of a water polymer mixing phase. The mixing of wet starches with vacuum grease not effect the polymeric dynamics observed. The biological origin and the type of the starches products have also no great influence on the polymeric dynamics and starches show a similar dynamic behaviour like other pure polysaccharides. The main point for the characterization of the segmental motion is the type of the glucosidic linkage and not its position and orientation at the repeating unit. In various acetyl-starches the β-process can also be observed with low variations of the dynamic parameters. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric spectroscopy; Polysaccharides; Water effects

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1. Introduction

In recent years many papers have dealt with the polymeric dynamics of polysaccharides in the solid state by using dielectric spectroscopy [1–3]. Concerning the association of the relaxation processes found in the dielectric relaxation spectroscopy (DRS) to molecular reorientation motions the following opinion has recently been accepted: The main relaxation measured in the low temperature range (−120–0°C) is associated with the local backbone or segmental motion of the chain. This process will be called β-relaxation in comparison with the motion of the side groups at the repeating unit named γ-relaxation and the β_{wet}-relaxation measured in all wet or by solvent swollen systems (see also Refs. [1,5,24]).

Applications of the DRS on pure starches (Butler–Cameron [6]) and acetyl-starches (Einfeldt et al. [7]) were also published in this journal in the last year. In these two papers and in the review article by Parker–Ring [8] can be found a good survey of the literature focused on starches and its structural and dynamical investigations.

In the wet state, it is the general opinion [9–11], the great internal surface of both polysaccharides starch and cellulose is masked by water molecules and holes and capillaries are filled with water. The action of water in starch are intensively discussed by van den Berg [12], too, and in Refs. [13,14]. In this article we will restrict our investigations to water contents lower than 15%w/w. That means gelantinization and irreversible swelling can be ruled out in the discussions (see Refs. [6,15]).

In wet samples the water dipoles produce an additional dielectric effect, and modify the dipolar moments and the motion characteristics of the polymer chain and its side groups.

The dielectric function is complex $\epsilon^*(f,T)$ can be split off into the dielectric store coefficient $\epsilon'(f,T)$ (real part of $\epsilon^*(f,T)$) and in the dielectric loss coefficient $\epsilon''(f,T)$ (imaginary part of $\epsilon^*(f,T)$) (see Ref. [16]). Both experimental magnitudes available by capacity measurement of a condenser filled with sample contain the same information expressed by the Kramer–Kronig rule [17]. But the advantage of the simultaneous measuring of both spectra is that, on the one hand, it increases the statistical safety and, on the other hand, the influence of the dc-conductivity of the sample and its correction in the loss coefficient can be proved in this way.

In this paper we will present our results found for wet and dry starches and focus our presentation on (i) the method firstly used by Butler and Cameron [6] to measure a mixing

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of wet starch and vacuum grease to suppress conductivity effects by high water contents, (ii) the comparison of wet and well dried amylo-maize-starch by its dynamic properties, (iii) the influence of the starch type on the dielectric spectra at low temperatures, (iv) the dynamic properties of starch in comparison with other polysaccharides and (v) the variation of local chain motion by acetylation of starch.

2. Experimental

2.1. Materials and sample preparation

All starch samples are commercial chemicals. The amylo-maize starch (AMS: Hylon VII with amylose content of 71%) and the waxy-maize.starch (WMS: Amioca powder with amylose content of <1.5%) used were a gift from the National Starch and Chemical KG.

The Merck-starch is a product partially degraded in the molecular weight. Its degradation is preferentially made in the side chains of the starch. The Serva-starch is a commercial product containing 95% amylose.

All these chemicals were used without further purification. The 'well dried' samples were dried at 110°C in a vacuum preparation chamber for 20 h. The 'wet' starches were stored in a sealed box for two weeks at room temperature, which contains a water saturated atmosphere. The final water contents were determined by the weight loss after an intensive drying (24 h at 130°C under vacuum).

As proposed by Butler and Cameron, a few samples of the amylo-maize-starch were mixed with a low amount of vacuum grease (Dow Corning) [6], which does not show a marked dielectric effect in the frequency range measured and is thermally stable in the temperature range investigated.

The 2-*O*-acetyl amylo-maize-starch and the per-acetyl starches have been synthesized and analysed in the same manner as described in detail in our previous paper [7].

2.2. Dielectric spectroscopy

The complex dielectric function

$$\epsilon^*(f,T) = \epsilon'(f,T) - j\epsilon''(f,T) \tag{1}$$

(j is the imaginary unit: $j^2 = -1$) was measured in the extended frequency range of 10^{-2} c/s to $5 \times 10^{+6}$ c/s and in the temperature range of -135 to 120°C (or in any cases to 180°C) using the Novocontrol Alpha Analyser and the Quadro Temperature Controller.

The material was pressed under vacuum with a pressure of 1900 bar into thin sheets with a diameter of $D = 30$ mm and a thickness d of 0.07 to 0.13 mm. The thickness d of each sample was measured with a micrometer screw.

The measuring error of the temperature was ±0.1°C and the overall error of the dielectric coefficients is ±10–15% (pure error of the spectrometer 1.0–1.5%) resulting from the uncertainty in the determination of the sample thickness. But this error has no influence on the dynamic properties (relaxation time and shape parameter of the relaxation) of the material under test and only affects the intensity of the dielectric response measured.

2.3. Evaluation of dielectric spectra

In the case of high temperatures and for wet samples the dc-conductivity of the materials produces a marked dielectric loss of the sample under test which masks the pure dielectric losses at low frequencies

$$\epsilon''_{\mathrm{exp}} = \epsilon'' + \sigma_0(f)/\epsilon_0\omega, \qquad (\omega = 2\pi f) \tag{2}$$

using the commune statement for the frequency dependence of the dc-conductivity of amorphous ionic conductors [18]

$$\sigma_0(f) = \sigma_{1\mathrm{Hz}} f^a. \tag{3}$$

The dielectric store coefficient is not affected by the dc-conductivity of the sample.

From the basic theory of Mcdonald [19] and the explicit calculations from Schütt [20] the effective conductivity of a system with ideal polarizible electrodes can be expressed as Debye-like relaxation process (electrode polarisation):

Recalculation of the effective conductivity of the total system leads to the borderline case for low frequencies $2\pi f \ll 1/\tau_{el}$:

$$\sigma_{0,\mathrm{cell}}(f) \approx \mathrm{const} \times f^2 \tag{4a}$$

and the effective conductivity disappears if the frequency is zero (dc case)

For frequencies with $2\pi f \gg 1/\tau_{el}$ the effective conductivity is

$$\sigma_{0,\mathrm{cell}}(f) \approx \sigma_0(f) - \mathrm{const}/f^2 \tag{4b}$$

and approaches the dc-value ($\sigma_0(f)$ for sufficient high frequencies.

As an example, Fig. 1 shows the conductivity spectra measured for a wet amylo-maize-starch with 14.5%w/w water content. The pure dc-conductivity produce a straight line with a low gradient ($a < 0.2$) in this double logarithmic graph (see low frequency part of the 0°C curve and the middle part of curves for 40 and +80°C). The different dielectric relaxation processes lead to steps smoothed in the $\sigma(f)$-curve.

The dielectric spectra (dc-corrected) are evaluated with the help of the sum of the Havriliak–Negami-relaxation functions (HN-functions)

$$\epsilon^*(f) = \sum_i \{\Delta\epsilon_i/[1 + (\omega\tau_i)^\alpha]^\beta\}. \tag{5}$$

This model function is generally accepted in the literature [21,22] and shows good results for polysaccharides in the solid state [23,24]. For each relaxation process separated the HN-evaluation provides four characteristic parameters: The relaxation time (τ_i determines the position of the process in the time- or frequency- scale, the relaxation strength (or intensity) $\Delta\epsilon_i$ corresponds to the product of

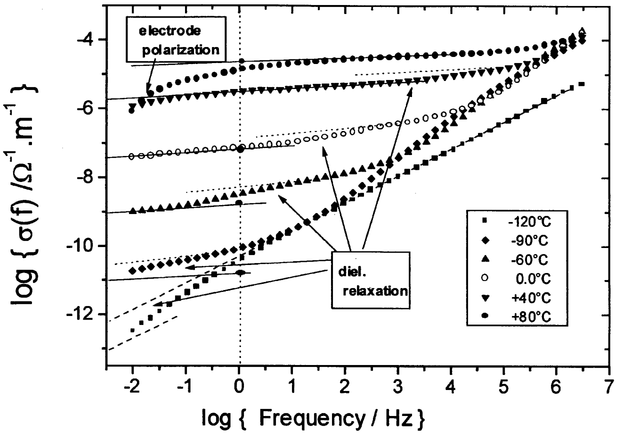

Fig. 1. Conductivity spectra of wet amylo-maize-starch (Hylon VII) with 14.5% w/w water at different temperatures showing the dc-conductivity (full lines — Eq. (3); $\alpha_{1\text{Hz}}$ marked by full dots), dielectric relaxations (smooth step at middle temperatures) and the electrode process (step at low frequencies and high temperatures).

the number of dipoles of reorientated units with its mean dipolar moment and α_i and β_i are shape parameters of the relaxation process, which present the distribution of the relaxation times with the meanings: α_i is the width of the relaxation process (width of the distribution of relaxation times) and β_i the asymmetry of this process. All these parameters are functions of the temperature T. For the thermally activated relaxation processes observed in our experiments the Arrhenius equation holds true

$$\tau_i(T) = \tau_0 \exp\{E_a/RT\} \tag{6}$$

with the molar activation energy E_a and the pre-exponential factor τ_0, which is associated with the entropic effect S_a of the reorientation dynamics [25]

$$-R\log\{\tau_0/\tau_D\} \approx S_a \tag{7}$$

if $\tau_D = 2\pi h/kT_0 = 1.7 \times 10^{-13}$ s (h — Planck constant, k — Boltzmann constant, $T_0 = 273.15$ K).

3. Results

3.1. The influence of the mixing with grease on the dielectric spectra

For extended temperature range Fig. 2 shows the dc-conductivity (exactly $\sigma_{1\text{Hz}}$) evaluated from σ-spectra as in Fig. 1 of amylo-maize starch with 14.5% w/w water content, on the one hand, in the pure state and, on the other hand, mixed with vacuum grease.

In the sample without grease the conductivity shows an Arrhenius behaviour at low temperatures with an activation energy $E_\sigma(\text{wet}) = (72.2 \pm 1.6)$ J/mol. The conductivity decreases with an increase of the temperature in the range 80–140°C by water losses of the sample by evaporating. It results in a drying of the starch and above 140°C the conductivity of well dried starch can be measured. Low temperature measurements of an annealed starch at 180°C (well dried product) continue the Arrhenius line of high temperature points. In this well dried starch the dc-conductivity is characterized by a higher activation energy $E_\sigma(\text{dry}) = (90.5 \pm 0.6)$ kJ/mol.

For wet amylo-maize starch with the same water content of 14.5% w/w but mixed with grease the conductivity curves show a reduced conductivity and are located between the wet and the dry curve of unmixed starch. The annealing of the wet starch mixed with grease has a little effect on the

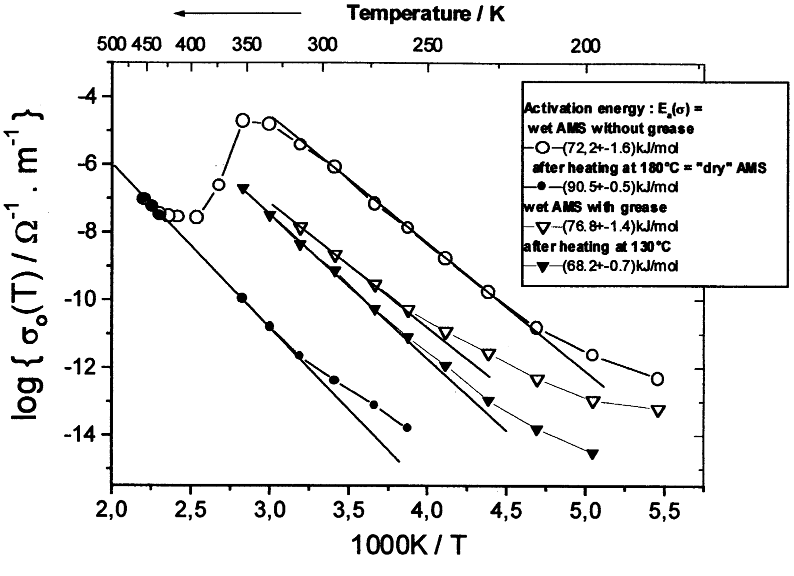

Fig. 2. Activation plots of the dc-conductivity for wet amylo-maize starch (14.5% w/w water) mixed with and without vacuum grease before and after annealing, respectively.

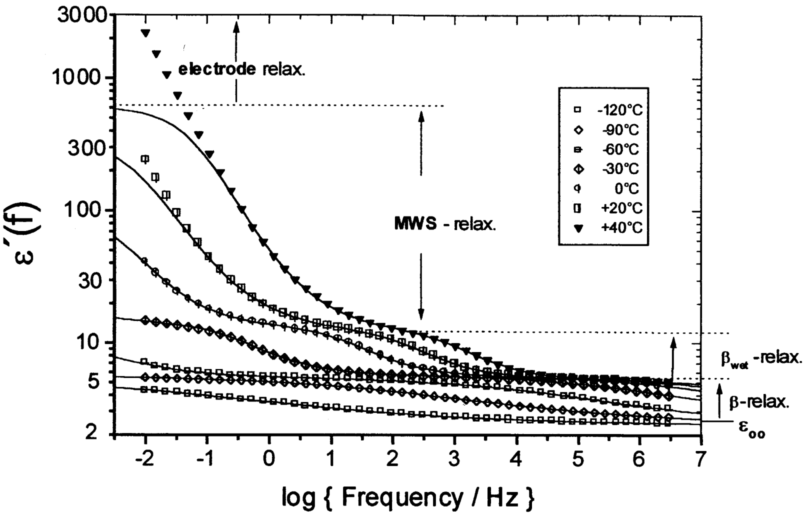

Fig. 3. Dielectric store spectra $\epsilon'(f,T)$ of wet amylo-maize starch with 14.5% w/w water content mixed with vacuum grease; symbols are experimental points, lines are HN-fitting curves — Two dielectric processes are shown: the β- and the β_{wet}-relaxation and additionally, the Maxwell–Wagner–Sillars relaxation.

conductivity measured. It means that the starch retains nearly its water content at the level in the heating process by covering with grease. The activation energies lies at (76.8 ± 1.4) and (68.2 ± 0.7) kJ/mol for the wet sample with grease before and after the annealing, respectively.

Figs. 3 and 4 show, as an example selected, the dielectric store spectra and loss spectra dc-corrected for wet amylo-maize-starch mixed with vacuum grease with 14.5% w/w water content, respectively.

For the same pure wet sample not mixed with vacuum grease the store and loss coefficients are similar. Fig. 5 compares the loss spectra for this wet and by annealing dried starch in the pure state and mixed with grease at the temperature of −90°C presenting the β-relaxation.

By thermoanalytic spectra showed in Fig. 6 the effect of mixing with vacuum grease can be also see. All dielectric spectra were fitted with three HN-functions and the HN-fit curves obtained are presented by lines in the figures. In all cases, the store and the loss spectra are represented by the same values of the HN-parameter. The accuracy in the presentation by HN-functions (<1%) lies in the order of magnitude of the experimental error for the dielectric spectrometer. The fit-parameters selected are summarized in Table 1.

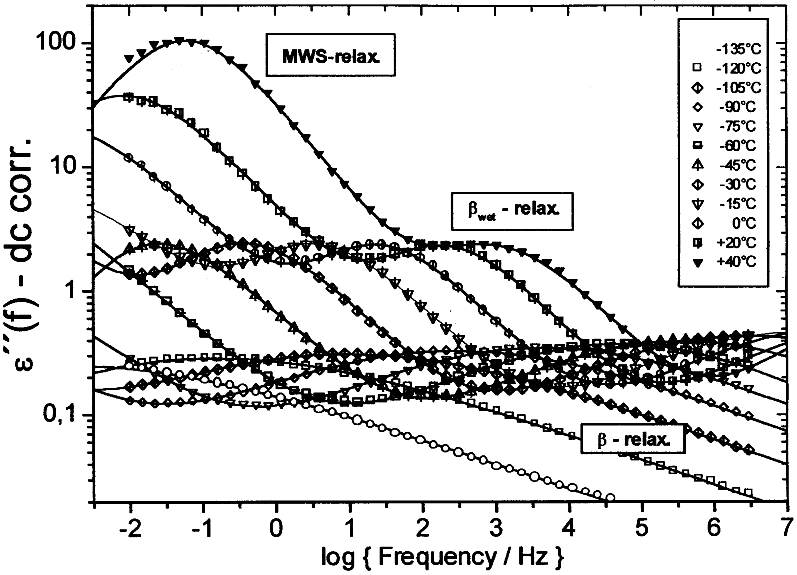

Fig. 4. Dielectric loss spectra $\epsilon''(f,T)$ of wet amylo-maize starch with 14.5% w/w water content mixed with vacuum grease; symbols are experimental points, lines are HN-fitting curves — Two dielectric processes are separated: the β- and the β_{wet}-relaxation and additionally, the Maxwell–Wagner–Sillars relaxation.

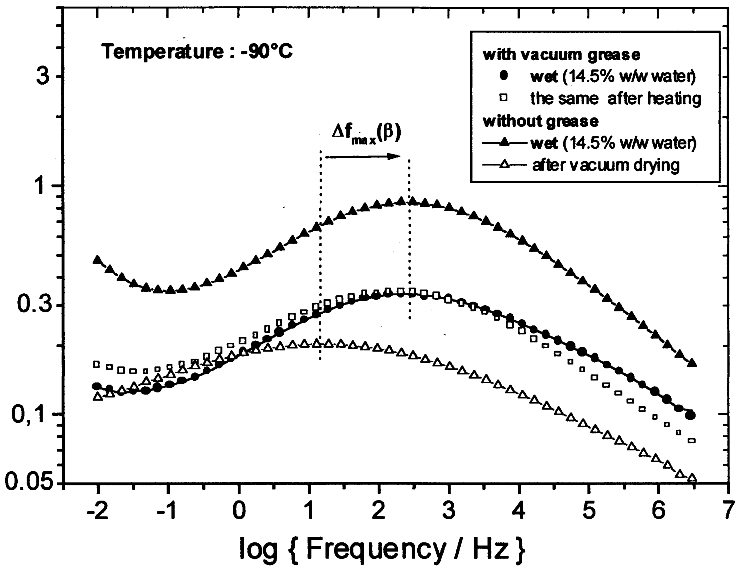

Fig. 5. Dielectric loss spectra $\epsilon''(f,T)$ of wet amylo-maize starch pure and 1:1 mixed with vacuum grease with 14.5% w/w water content at −90°C (β-relaxation) before and after annealing at 180°C (symbols are experimental points, lines are HN-fitting curves).

3.2. Dielectric spectra for wet and well dried amylo-maize-starch

Fig. 7 presents the dielectric loss spectrum of pure amylo-maize-starch (Hylon VII) dried over 20 h at 110°C under vacuum conditions and the same substance after additional annealing at 180°C in the upper window, in comparison, if the intensity is reduced for the sample annealed.

The full lines are the total HN-fit function and the dotted lines present two individual relaxation processes: the β-relaxation as dominant process and in its low frequency side the broad δ-relaxation with a low intensity. All amylo-maize-samples show qualitatively very similar spectra after different drying processes. The intensity of the β-relaxation is only increased by water content and by annealing, too. The relaxation intensity in the low frequency side of the β-process by annealing.

3.3. Comparison of different starch types

For a study of morphologic effects in the dielectric spectra of starches we have compared well dried samples

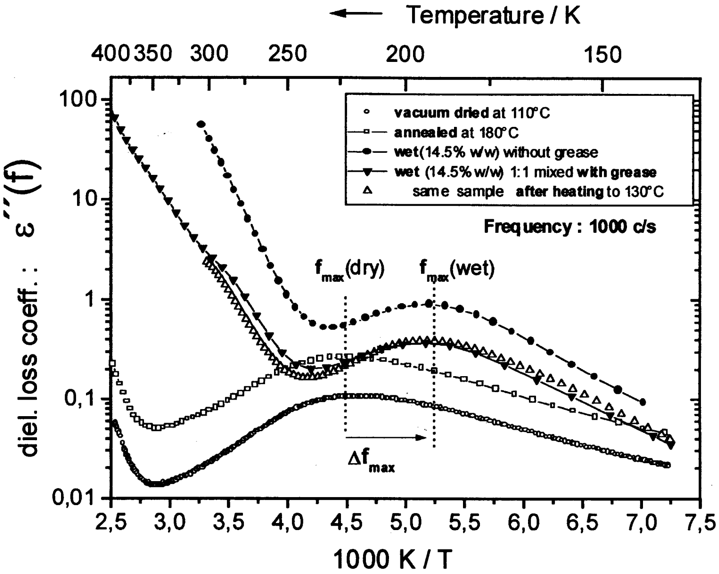

Fig. 6. Comparison of the thermoanalytic curve of the dielectric loss coefficient for the β-process at 1000 c/s of well dried amylo-maize-starch with wet starch mixed with vacuum grease before and after annealing at 130°C. In the left part of the figure the dc-conductivity contribution to the dielectric losses intensively masks the β_{wet}- and the MWS-relaxation.

Table 1
HN-Parameter of the β-relaxation and the δ-relaxation at −60°C of all well dried starches in comparison

	HN-param.	Amylo-maize-starch		Vacuum dried 110°C		
		Vacuum dried 110°C	Vacuum dried 60°C	Waxy-maize-starch	Merck-starch	Serva-starch
β-relax.	$\Delta\epsilon$	0.98 ± 0.15	2.36 ± 0.3	0.89 ± 0.15	1.17 ± 0.18	0.95 ± 0.15
	τ (s)	$(0.91 \pm 0.2) \times 10^{-4}$	$(1.73 \pm 0.2) \times 10^{-4}$	$(1.80 \pm 0.2) \times 10^{-4}$	$(1.68 \pm 0.2) \cdot 10^{-4}$	$(3.82 \pm 0.2) \times 10^{-4}$
	α	2.29 ± 0.02	2.28 ± 0.02	0.32 ± 0.02	0.30 ± 0.02	0.32 ± 0.02
	β	0.86 ± 0.03	0.86 ± 0.03	0.68 ± 0.04	0.72 ± 0.03	0.70 ± 0.03
δ-relax	$\Delta\epsilon$	0.058 ± 0.005	0.216 ± 0.026	0.19 ± 0.03	0.18 ± 0.04	0.096 ± 0.016
	τ (s)	9.42 ± 0.10	18.7 ± 1.5	60.2 ± 5.0	62.5 ± 5.2	34.7 ± 3.5
	α	0.65 ± 0.03	0.56 ± 0.05	0.53 ± 0.03	0.49 ± 0.03	0.54 ± 0.03
	β	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
Fit-variance	$(\sigma^2$	7×10^{-7}	3×10^{-7}	9×10^{-7}	11×10^{-7}	20×10^{-7}
	σ (10^{-3})	0.9	0.6	1.0	1.1	1.4

of Serva-starch (95% amylose), amylo-maize-starch (70% amylose), waxy-maize-starch (1% amylose/99% amylopectine) and the Merck-starch by its molecular weight reduced.

Fig. 8 presents the loss spectra at −60°C for all starches investigated with intensities partially reduced. It is apparent that the β-relaxation in all types of starches is very similar, the relaxation times and the shape of the relaxation peaks are only slightly shifted (see Table 2).

3.4. Dynamic properties of starches in comparison with other polysaccharides

The quantitative similarity of the dielectric response of all well dried starches investigated and thus the similarity of the molecular dynamics underlying the relaxation processes observed leads to the conclusion that the same α(1–4)-glucosidic linkage in the polymer chains of amylose and amylopectine is responsible for this similar behaviour of starches. We also compared the β- and the β_{wet}-relaxation found in starches, celluloses, dextran and other pure polysaccharides.

Fig. 9 shows the β-process at −90°C for well dried samples of amylo-maize-starch, cellulose (powder from CarboMer, granule size 100 μm), dextran (CarboMer-product with a $M = 1,00,000$), curdlan and pullulan, in comparison.

The β-process (segmental motion) in all these polysaccharides is similar, only the local chain motion in the

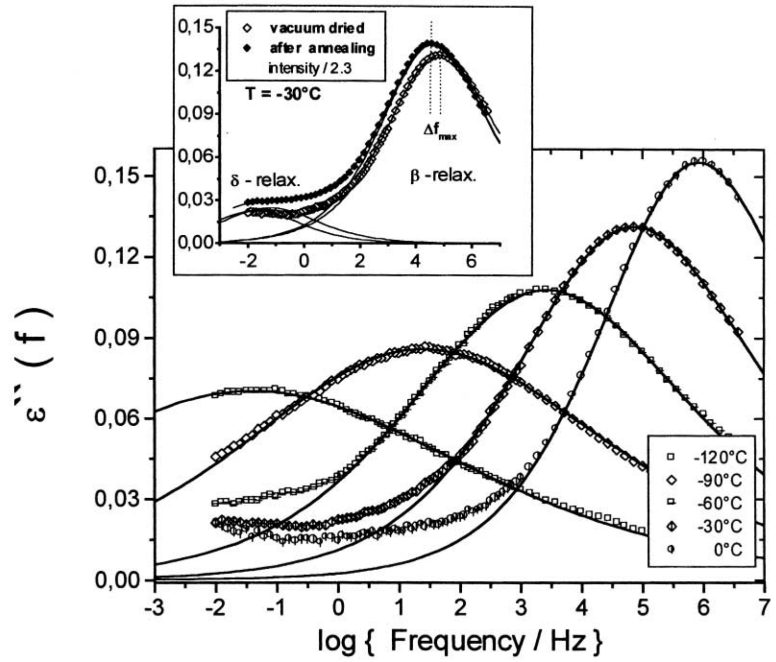

Fig. 7. Dielectric loss spectra of well dried (20 h at 110°C under vacuum) amylo-maize-starch window: comparison of loss spectra of this dry AMS at −30°C before and after annealing at 180°C (intensity reduced for sample annealed) The individual processes are shown by lines.

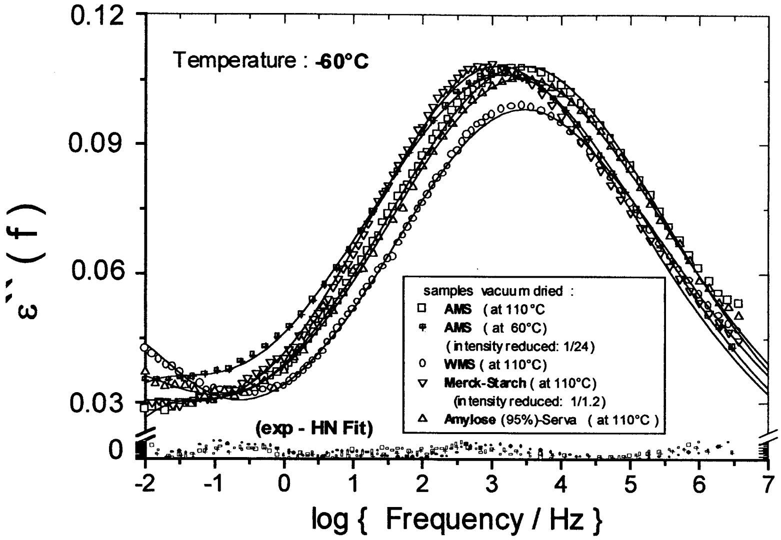

Fig. 8. Comparison of dielectric loss spectra at −60°C (β-relaxation) for various well dried types of starches: Amylo-maize -starch vacuum dried at +110°C, the same starch vacuum dried at 60°C and also at 110°C vacuum dried samples of waxy-maize-starch, Merck-starch and Serva-starch. The intensities of some spectra are reduced for a better comparison of the dynamical properties.

α(1–6) linked dextran is markedly shifted to higher frequencies. This means that the –CH$_2$–O– linkage between the pyranose rings is more flexible than the simple –O– bridge for (1–4)- and (1–3)-like connections.

A comparison of the β_{wet}-relaxation in wet amylo-maize-starch (Hylon VII), wet-cellulose powder and wet-dextran are shown in Fig. 10. This relaxation disappears completely after drying the same sample as shown by the upper curves for annealed samples. (In the resolution of this graph the points for the dry samples are not distinguishable.) In general, the loss spectra of the β_{wet}-relaxation is masked by the conductivity contribution (see Eq. (2)) and the intensive MWS-relaxation complicating the evaluation of this process. In many cases the β_{wet}-relaxation is only visible as shoulder of the MWS-process in the dc-corrected loss spectra. But in all polysaccharides containing water (investigated only samples with water content lower than 15–20%) or other swelling solvents this relaxation process can be observed and characterized in a sufficient way.

3.5. Chain dynamics in acetyl-starches

The β-process can also be observed in derivatives of starch-like acetates. In this case the β-relaxation is superimposed on the orientational motion of the acetyl-side groups. In our previous paper [7] we presented results for

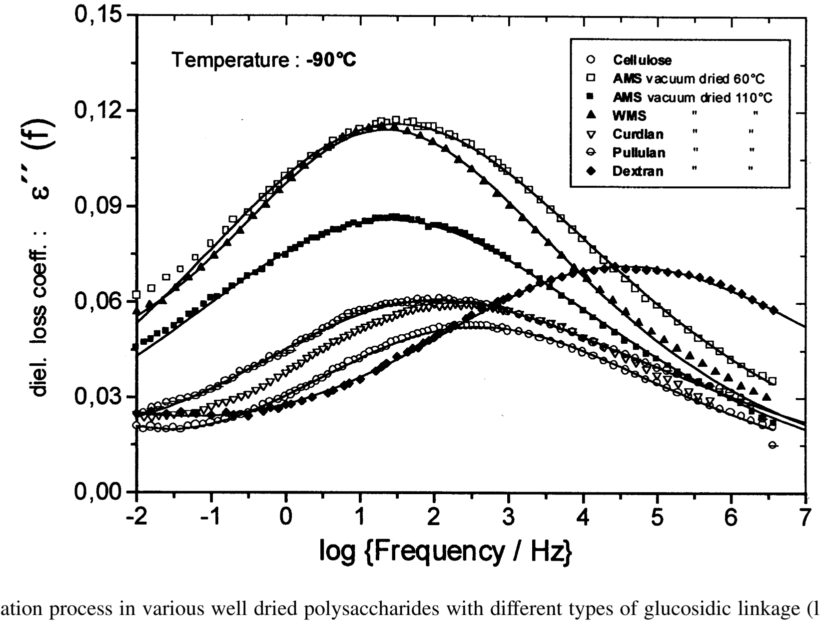

Fig. 9. The β-relaxation process in various well dried polysaccharides with different types of glucosidic linkage (lines: HN-fit results).

Table 2
Parameter of all relaxation processes measured by dielectric spectroscopy in wet and well dried starches

No	Type of starch	β-relaxation				β_{wet}-relaxation				δ-relaxation			
		E_a (kJ/mol)	τ_0 (s)	($\Delta\epsilon$ (−60°C)	α (−60°C)	E_a (kJ/mol)	τ_o (s)	$\Delta\epsilon$ (0°C)	α (0°C)	E_a (kJ/mol)	τ_0 (s)	$\Delta\epsilon$ (0°C)	α (0°C)
1	AMS-vacuum dried 110°C	51.5 ± 0.5	3.1×10^{-16}	1.0 ± 0.15	0.29 ± 0.02	–	–	–	–	??	??	??	??
2	AMS-vacuum dried 60°C	53.8 ± 1.3	6.4×10^{-18}	1.4 ± 0.15	0.27 ± 0.02	–	–	–	–	63.3 ± 3.4	5.8×10^{-14}	0.2 ± 0.1	0.32 ± 0.02
3	AMS-annealed at 180°C	53.5 ± 0.6	1.5×10^{-16}	2.3 ± 0.15	0.31 ± 0.02	–	–	–	–	49.5 ± 1.9	3.5×10^{-11}	0.38 ± 0.07	0.32 ± 0.02
4	Wet AMS- (11 ± 2)% w/w	58.3 ± 1.4	1.1×10^{-19}	3.0 ± 0.3	0.31 ± 0.02	59.0 ± 2.0	6.0×10^{-16}	0.5 ± 0.5	0.80 ± 0.1	??	??	??	??
5	Wet AMS- (14.5 ± 2)% w/w	55.1 ± 1.2	1.2×10^{-19}	7.3 ± 0.3	0.36 ± 0.02	58.1 ± 1.0	7.3×10^{-14}	15.0 ± 2.0	0.82 ± 0.02	??	??	??	??
6	Wet AMS- (14.5 ± 2)% w/w and 1:1 mixed with grease	58.6 ± 1.0	3.1×10^{-20}	6.0 ± 1.5	0.33 ± 0.02	77.5 ± 2.0	1.7×10^{-17}	7.5 ± 0.5	0.69 ± 0.03	??	??	??	??
7	WMS-vacuum dried 110°C (<2% Amylose)	51.5 ± 1.5	0.7×10^{-16}	0.9 ± 0.2	0.36 ± 0.02	–	–	–	–	61.4 ± 4.2	3.3×10^{-14}	0.19 ± 0.10	0.31 ± 0.02
8	Amylose-Serva (85%Amyl.)-vacuum dried 110°C	53.2 ± 1.5	0.8×10^{-16}	0.97 ± 0.2	0.35 ± 0.02	–	–	–	–	??	??	??	??
9	Merck-starch (partially decomponed)	45.8 ± 2.0	6.6×10^{-16}	0.2 ± 0.15	0.30 ± 0.02	–	–	–	–	??	??	??	??
10	Cellulose-vacuum dried 110°C	45.9 ± 1.5	4.0×10^{-16}	0.7 ± 0.15	0.33 ± 0.02	–	–	–	–	68.9 ± 2.0	5.5×10^{-16}	0.13 ± 0.05	0.30 ± 0.02
11	Dextran-vacuum dried 110°C	38.6 ± 0.7	4.7×10^{-16}	0.38 ± 0.08	0.28 ± 0.15	–	–	–	–	??	??	??	??
12	Curdlan-vacuum dried 110°C	52.3 ± 0.9	0.2×10^{-16}	0.74 ± 0.12	0.32 ± 0.15	–	–	–	–	??	??	??	??

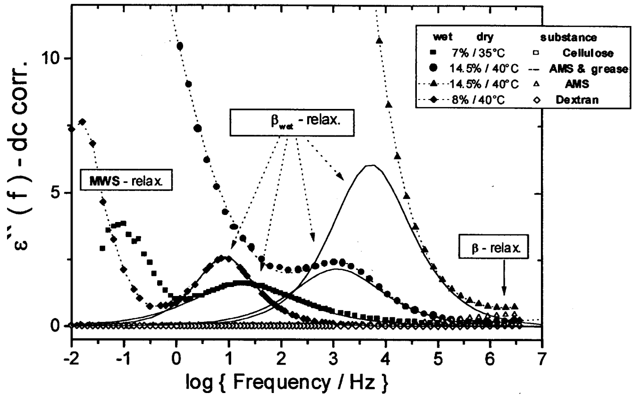

Fig. 10. The β_{wet}-relaxation process (lines) in various wet polysaccharides (full symbols: experimental points) with different types of glucosidic linkage: Starch with α(1–4) linkage, cellulose with β(1–4) linkage and dextran α(1–6) linkage. After annealing these samples at 170°C the water content is reduced to a value (<0.2% and this β_{wet}-relaxation is not visible in the spectra (open symbols).

2-*O*-regioselctive acetyl-starches with different degrees of substitution. We have extended these investigations to a DS-value of 0.6 and to triacetates of amylo-maize-starch and waxy-maize-starch.

Fig. 11 shows the dielectric loss spectrum of 2-*O*-acetyl-amylo-maize starch with a degree of substitution $DS_{Ac} = 0.6$ for −45°C. Two relaxation processes can be clearly distinguished: the β-relaxation at higher frequencies and the γ-relaxation at lower frequencies, which can be associated with the acetyl-side group motion in the position C6 at the AGU (called γ(2-*O*-Ac)). In the tri-acetyl-AMS and tri-acetyl-WMS three relaxation processes are detectable. In addition to the last two processes there is a process connected with the side group motion of the acetyl group in position C6 at the AGU (also a γ-type relaxation) shown in Fig. 12.

The intensity of the dielectric β-response is strongly

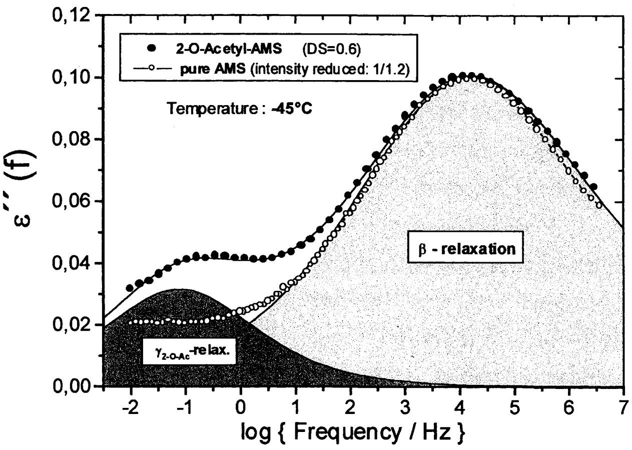

Fig. 11. Dielectric loss spectrum of 2-*O*-acetyl-amylo-maize-starch at −45°C with two separated relaxation processes: the β-relaxation and the γ(2-*O*-Ac)- side group relaxation.

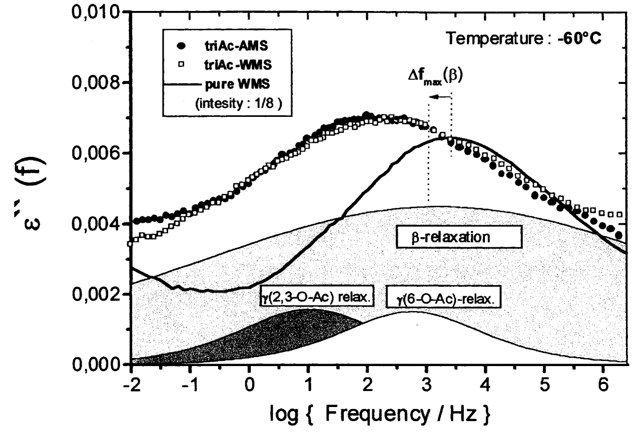

Fig. 12. Dielectric loss spectrum of tri-acetyl-amylo-maize-starch at −60°C with three separated relaxation processes: the β-relaxation, the γ(2,3-*O*-Ac)- and the γ(6-*O*-Ac)-side group relaxation (γ(2-*O*-Ac)- and γ(3-*O*-Ac)-relaxation are indistinguishable).

reduced by acetylation and the local chain motion is more extended than in pure starch. Both γ-processes are more Debye-like than the chain dynamics. It is very interesting that the per-substituted amylo-maize- and waxy-maize starch show nearly identical dynamic spectra. On the other hand, in both derivatives per-substituted, in which does not exist a methylol-side group, the β-process is well detectable. This experimental fact is one evidence more that the β-relaxation must be associated with the local chain motion of the polymer. Considering this, we must also correct the assignment of the main relaxation in the low temperature range in starch acetates presented in our first paper [7]. The variation of intensity with increase of the degree of derivatization between $\mathrm{DS}_{\mathrm{Ac}} = 0$ and 3 are presented in Fig. 13 for the partial relaxations in all acetyl-amylo-maize starches investigated.

At low degrees of substitution the side group relaxation in position C2 at the AGU increases with an increase of DS, but the intensity of the β-relaxation decreases. Further increase of DS reduces more the relaxation strength of the β-process and thus the total relaxation strength: $\Delta\epsilon_{\mathrm{tot}} = \Delta\epsilon_{\beta} + \Delta\epsilon_{\gamma}$. By the cross-correlation between the different modes of polymer motion the side group dynamics (γ-relaxation) is also reduced at high values of DS.

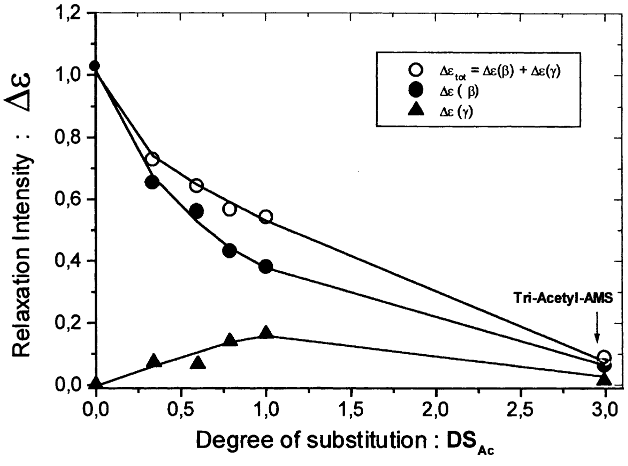

Fig. 13. Influence of the degree of substitution on the intensity of the dielectric relaxation processes in acetyl-amylo-maize-starches.

4. Discussions

4.1. The influence of the mixing with grease on the dielectric spectra

Butler–Cameron [6] proposed to mix wet starch with vacuum grease, which is thermally stable to higher temperatures and shows a negligible dielectric relaxation, with two aims: firstly, to ensure that the starch retains its water content at the level it possessed prior to the spectral measuring run, and secondly, that the conductivity effects in the experimental loss factor are reduced. The results presented in Fig. 3 confirm the first aspect: Heating of the wet starch at +130°C decreases the dc- conductivity of wet starch without protecting it by grease by seven orders of magnitude, whereas this effect is reduced to a factor less ten in the mixture with grease. The inherent problem of this processing method is that mixing with grease increases the number of components of our system and affects the distribution of water in the sample by the water-repelling properties of the vacuum grease.

Fig. 6 compares the β-relaxation by its loss coefficient at a fixed frequency as a function temperature (dielectric thermo-analytic diagram) meaning the local chain dynamics of the starch polymer in wet samples mixed and not mixed with grease. The sequential motion is not affected by grease in its dynamic parameter (relaxation time and shape parameter). Relaxation in wet or dry state is only shifted in its frequency position and the intensity of the dielectric response is strongly dependent on the water content. Annealing of wet starch mixed with grease has a low effect on intensity of the dielectric response caused by the conservation of the water in the sample. These results conform to our findings in celluloses [5].

In general, the β_{wet}-relaxation spectra are more sensitive to the water content and the morphologic structure of starches, too. The spectra for the loss coefficient presented in Fig. 14 for well dried and wet starches with and without mixing with grease, respectively, show similar results for the β-relaxation. In the well dried sample the β_{wet}-process is absent. This relaxation is slightly shifted in the wet sample with grease but masked in such a way that only a careful HN-fit of the spectra can separate these processes.

In Fig. 15 the results of the HN-fit of all starch samples investigated are summarized in the form of an activation plot (Arrhenius plot) for the relaxation time. This presentation shows more details than the original spectra: There are three groups of straight lines, one for the β-relaxation, one

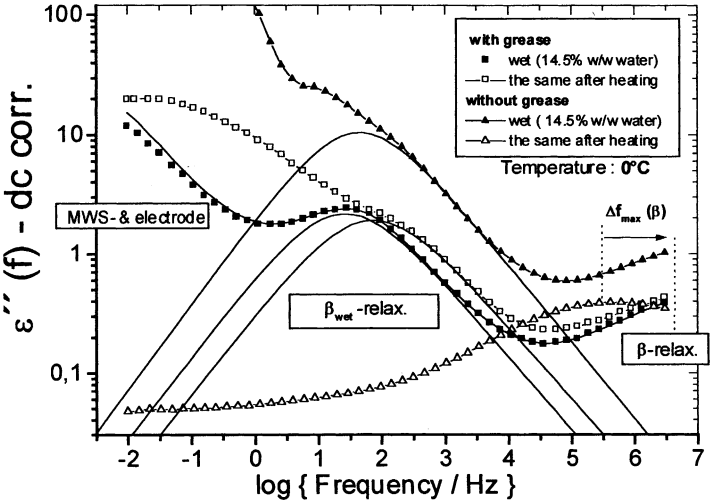

Fig. 14. Comparison of the dielectric loss coefficient for the β_{wet}-process at 0°C of well dried amylo-maize-starch with wet starch mixed with vacuum grease before and after annealing at 130°C (well dried).

for the β_{wet}-relaxation and another one for the δ-relaxation separated only in dry samples. The group for the β-relaxation separates in subgroups for dry and wet starches. Wet starches show a higher value for the activation energy E_a and a lower value for the pre-exponential factor τ_0 (Eq. (6)). We can interpret this fact in such a way that the respective motion is more cooperative (Eq. (7)) and presents a connected group of molecular units. The grease effect is also low in this presentation. The group of straight lines for the β_{wet}-relaxation is markedly separated into lines depending on the water content. With increase of the water content the lines are shifted to higher relaxation times indicating the process is faster. It is a fact that the β_{wet}-relaxation in starch mixed with grease lies higher than for pure starch. It can be interpreted in such a way that effective concentration of water in the space filled with starch material is higher caused by the hydrophobic properties of the vacuum grease, which presses water from the holes and capillaries of the starch system into the granules. The HN-fit parameters for all starches are summarized in Table 2 quantifying our findings. We can also summarize that the mixing with grease does not directly affect the polymer dynamics in the starches, but influences the distribution of water in the sample (Fig. 16).

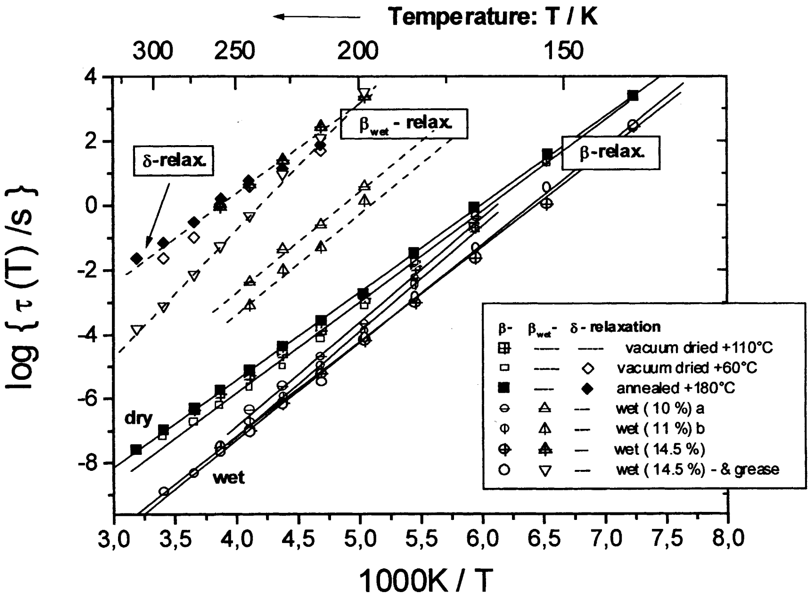

Fig. 15. Comparison relaxation times for all dielectric relaxation processes found in well dried amylo-maize-starch and in wet starches mixed with and without vacuum grease before and after annealing at 130°C (well dried) in the form of activation plots. (Results from the $\epsilon''(f)$- and the $\epsilon'(f)$ fits are the same in the resolution of the graph).

The shape parameters of the relaxation process $\alpha(T)$ presenting the width of the relaxation processes are shown for all starches investigated in Fig. 15. Water content increases the relaxation width of the β-process, but mixing with grease weakly reduces this effect. This can be a hint that the internal surface of the granular starch system influences the dielectric response. The β_{wet}-process is smaller than the β-process. Unfortunately the α-values for the β_{wet}-relaxation are very scattered caused by the problem to separate in the evaluation the β_{wet}-process from the parasitic effects of the MWS- and the conductivity contributions. Independent of this it is evident that the relaxation width of the β_{wet}-process depends on the water content and is affected by the mixing with grease. Whereas in activation plots of the relaxation times the β_{wet}-relaxation and the δ-process coincide for the highest water content and give a hint that both processes have the same origin. In the high temperature range (−30°C to 40°C) of the $\alpha(T)$-diagram can be clearly separate both processes and in this temperature range the separation of the two different processes is well possible. Annealing of the sample always reduces the relaxation strength in the δ-region and increases the intensity in the real β-peak region. The relation between these two processes is not clear up to now and it is open, which influence have residues of water (or other swelling solvents) on this process or does it represent a pure dry polymer property?

Water content in the starch sample increases the activation energy for the segmental motion and decreases the pre-exponential factor τ_0 for this dynamic process (see Table 2 and Fig. 15). This finding is similar to the behaviour of celluloses and should be explained by the adsorption of water molecules that form water bridges between the repeating units of the same chain and to other adjacent chains. This network-forming by water molecules is also the base of the cooperativity for the β-process found by the great entropic effect of this motion (Eq. (7)).

The network formed from starch and water is also the basis of the β_{wet}-process presenting a motion of a mixing phase. It is evident from spectral results not explicitly presented in this paper that the internal interface relaxation (MWS-relaxation) and also the electrode relaxation increase with an increase of the water content caused by the higher dc-conductivity of the wet samples.

The finding that annealing of starch at a high temperature increases the intensity of the β-process corresponds to results for cellulose pulps published in Ref. [26] can be interpreted as producing more order in the orientation of the polymeric chains by high temperatures (compare window in Fig. 7). This increase of dielectric intensity in the specific frequency range of the β-peak is accompanied by a relative expense of intensity in the range of the δ-relaxation (or unstructured underground) in many cases. Details of this molecular process are unknown at present.

4.2. Comparison of different starch types

The differences in the mixing relation of amylose and amylopectine and in the granular structure of starches with a different biological origin does not have a marked influence on the local chain motion detected with the help of the β-relaxation as is shown in Fig. 8. This result conforms to the results presented by Buttler–Cameron [6] for various types of starches and with findings for various cellulosic products in the dry state as (native celluloses, different types of cellulose pulps, regenerative celluloses and cellulose fibres (regular Viscose-, Modal- or Lyocell- fibres) (see Refs. [5,23,24] and results prepared for publication). These

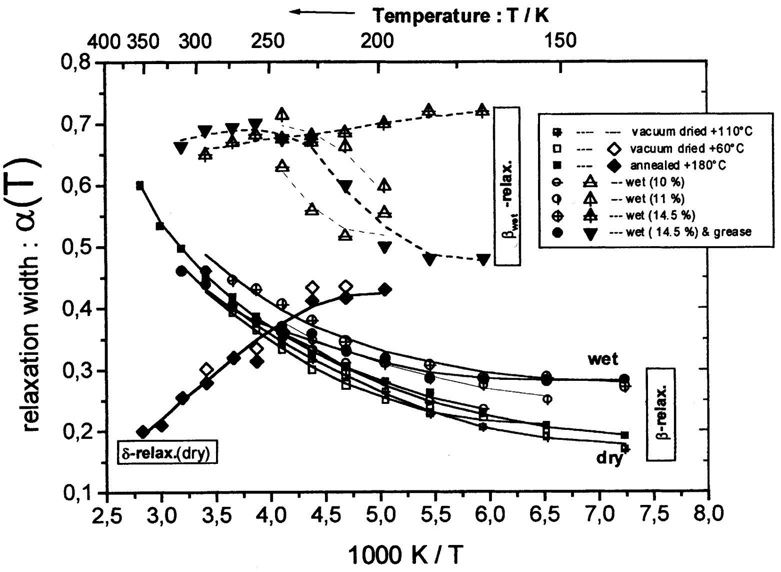

Fig. 16. α–HN parameter for all relaxation processes observed in wet and well dried starches mixed with and without vacuum grease for the same samples as in Fig. 15.

results should be interpreted in such a way that the local or segmental motion observed in the β-process gives information about a little spatial range of any repeating units and in these dimensions a uniformity exists an in all starches determined by the α(1–4) linkage between the AGUs. Marked changes of the segmental motion are observed for particular decomposed starch like Merk-starch (see Table 1). Its activation energy is reduced in comparison with the other starches. This decomposition preferably takes place in the side chains, and this should reduce the forming of ordered structures, which hinder the orientational motion of chain segments.

From investigations on cellulosic materials we know that sub-molecular structural effects or morphologic differences can only be detected, if we compare the dielectric response for wet and dry samples. For starches a similar result should be expected. Unfortunately, an extended set of systematic dielectric measurements of various types of starches well characterized morphologically in the wet and dry state with a quantitative comparison of its dynamic parameters is unavailable at present.

4.3. Dynamic properties of starches in comparison with other polysaccharides

The comparison of the dynamic properties of the local main chain motion with the help of the β-relaxation for different well dried polysaccharides is shown in Fig. 9 presenting the dielectric loss spectra at −90°C. Only the α(1–6)-linked dextran shows a marked shift of the β-peak to higher frequencies. The differences of its dynamic parameters between the α(1–4)- and the β(1–4) (like cellulose or also chitosan) or the β(1–3)-linkage (like curdlan) are low (see also Table 2). Apparently, for the mobility of the polymer the orientation of the linkage relative to the pyranose rings chain is not important but the form of the glucosidic bond: In the case of dextran the AGUs are connected via an $-O-CH_2-$ bridge, whereas in the other cases a simple –O– bridge exists. The $-O-CH_2-$ bridge is apparently more flexible than the $-O-CH_2-$ bridge producing a faster reorientation motion in the chain. The pullulan with an alternation of three cellulose like β(1–4)- and one dextran like α(1–6)- linkage in the chain behaves similar to starch or cellulose. The intensity of the dielectric response of starches is bigger than the intensity measured for all other pure polysaccharides in the dry state. That should be a mean orientation effect of the repeating units in the specific sub-molecular structures, because the intensity of the dielectric response must be calculated by a vector sum over all molecular dipolar units, which is determined by the mean orientations of the dipoles in the real spatial structure of the whole sample volume.

The dynamic shape parameter of the β-relaxation and its temperature dependence are very similar in all pure polysaccharides.

4.4. Chain dynamics in acetyl-starches

It can be expected that a derivatization will modify the local dynamics of the helical chain of the starch. In Ref. [7] we published results for amylo-maize-starches, which are substituted in a regioselective or statistical like way at the AGU. In this paper we have presented dielectric spectra for tri-acetates of AMS and WMS and 2-*O*-acetyl-AMS with a degree of substitution DS = 0.6 (see Figs. 11 and 12). In all these systems investigated the β-process is detected (in the first paper [7] still interpreted as OH(6)– relaxation). For our discussion in this article it is interesting that this local

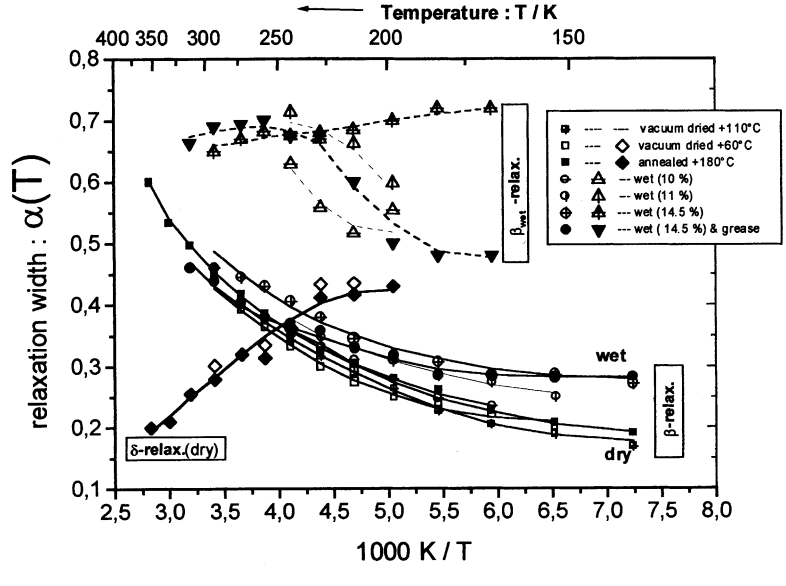

Fig. 17. Activation plot of the relaxation times for the β-relaxation detected in pure starches and acetyl- starches. In addition, the γ-relaxations for the acetyl-side group in position C2 (and C3) at the AGU and in position C6 of the derivatives are sketched β-relaxation: circles and full lines; γ(2,3-*O*-Ac) relaxation up-triangles and dotted lines, and γ(6-*O*-Ac) relaxation down-triangles and broken lines.

Table 3
Dynamic parameters for the different relaxation processes detected in acetyl-starches

Degree of substitution $\mathrm{DS}_{\mathrm{Ac}}$	β-relaxation		γ(2,3-*O*-Ac)-relaxation		γ(2,3-*O*-Ac)-relaxation	
	E_a (kJ/mol)	τ_0 (10^{-17} s)	E_a (kJ/mol)	τ_0 (10^{-17} s)	E_a (kJ/mol)	τ_0 (10^{-17} s)
Regioselective 2-O-acetyl amylo-maize starches						
0.00	55.2 ± 0.5	7.8 ± 0.5	–	–	–	–
0.34	52.4 ± 1.5	2.7 ± 2.0	61.8 ± 2.5	2.7 ± 2.0	–	–
0.60	51.0 ± 1.5	6.6 ± 1.5	72.3 ± 2.5	6.6 ± 1.5	–	–
0.79	43.6 ± 2.0	106 ± 12	64.0 ± 2.0	106 ± 12	–	–
1.00	45.0 ± 1.0	27.3 ± 3.0	60.0 ± 2.0	27.3 ± 3.0	–	–
tri-acetyl-amylo-maize starch						
3.0	48.0 ± 1.0	34 ± 5	57.8 ± 3.0	18 ± 3	33.7 ± 3.0	$(1.6 \pm 1.5)10^5$
Tri-acetyl-waxy-maize starch						
3.0	51.2 ± 1.5	26 ± 5	54.0 ± 3.0	1100 ± 300	36.4 ± 3.0	$(1.1 \pm 1.5)10^5$

chain dynamics is modified especially in its frequency width (see Figs. 11 and 12) but not much in its frequency position as shown in Fig. 17.

The side group motion in position C2 or C3 at the AGU (γ(2-*O*-Ac)– or γ(3-*O*-Ac)-relaxation) depends on the $\mathrm{DS}_{\mathrm{Ac}}$– value and shifts to lower frequencies, whereas the motion of the side group in position C6 has a frequency position similar to the main chain motion but with a lower activation energy (see Table 3).

This fact should be explained by the realistic assumption that all polymer motions are determined by cross-correlations between different motion modes. By sterical hindrance the side group orientational motion is coupled with the chain motion and the slowest motion determines the position of the relaxation peak in the frequency scale. The C2-side group connected by a simple O-bridge with the AGU is more sterically hindered in its orientation that slows down the total dynamics. The C6-side group is coupled by a $-\mathrm{CH_2}-\mathrm{O}-$ bridge and has a higher mobility relative to the polymer chain and the time-determining process is also the segmental motion. In pure polysaccharide the C6- side group is the methylol-group showing a dynamic, which is much faster than our experimental time resolution and thus not detectable for pure polysaccharides in the dielectric spectroscopy up to a maximum frequency of 5 MHz. This statement was also experimentally confirmed in other papers [4,24].

5. Conclusions

In the range of the water content lower than 15% w/w three relaxations connected with the polymer dynamics: the β-relaxation, the δ-relaxation and the β_{wet}-relaxation are only found. An α-type relaxation connected with the glass transition and characterized by a non-Arrhenius activation plot was not found in starches or other polysaccharide samples investigated. The β-relaxation in the starches is associated with the segmental motion of the polymer chain and it is also detectable in all starch derivatives in a little modified form. This process is Arrhenius-like in all cases investigated. A low water content of the starch increases the activation energy of this dynamics and decreases the pre-exponential factor of the relaxation times; the last fact must be interpreted as an increase of the entropic character of this motion mode by water bridges along a polymer chain and between different chains. The biological origin, the type of the starch or its physical preparation has no influence on the local chain dynamics or these effects are very small for well-dried samples.

It means that the investigation of the β-relaxation for well dried starches is no good analytic tool for the starch diagnostic. This situation is different for wet starches, because the water influence on starches — and other polysaccharides — is different for different types of starch and this effect can be detected with the help of the dielectric spectroscopy. In general, this dynamic method is limited to low water contents of the substances investigated. In the range of gelantinization it is impossible to compare dielectric measurements with and without mixing with grease or to select individual orientational processes. The conductivity effect covers up all dielectrical processes.

The experimental method of mixing wet starches with a suitable vacuum grease has a few advantages for the depressing of conductivity effects and the MWS-relaxation. The β-relaxation is hardly effected by the grease content. The β_{wet}-relaxation presenting a collective motion of a water–polymer-mixing phase is little affected in a direction that the water content in the starch granules increases by the water-repelling properties of the grease in the hole and capillary system of the starch. The findings for starches and starch derivatives are very similar to the experimental results for cellulosic materials and other polysaccharides. The local chain motion is more influenced by the type of glucosidic bridge between the repeating units than by the orientation or the position of the C-atoms in the AGU between which the linkage is formed.

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