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Cellulose/Poly(vinyl alcohol) Blends. 1. Influence of Miscibility and Water Content on Relaxations

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ABSTRACT: This contribution is concerned with cellulose/poly(vinyl alcohol) blends, and it concentrates on the influence of miscibility and the presence of water on relaxations. The blends were characterized by small and wide angle X-ray scattering as well as by dielectric and dynamic mechanical spectroscopy. They display no residual crystallinity and are characterized by a molecular mixing of the components with microheterogeneities on a nanometer scale. The water is bonded yet mobile. A temperature increase leads to an enhanced mobility of the water as well as to the onset of main-chain rearrangements and of decomposition. A secondary relaxation occurs in all blends: the relaxation behavior is similar for the blends and the pure cellulose. A major result is that the presence of water influences the relaxation in the blends more strongly than the presence of the blend component poly(vinyl alcohol).

I. Introduction

Cellulose is a polymer provided by nature which is suited in principle for technical applications. The concept is to exploit the optimization performed by nature. Yet an industrial use of cellulose with the aim to replace synthetic organic polymers meets with several difficulties. A major problem is processing in the molten state. One way to overcome this problem consists of blending cellulose with synthetic polymers of appropriate chemical structures. Blends of cellulose and synthetic polymers meet with interest also for other reasons: recycling problems of synthetic polymers may be reduced to a certain extent.

The requirement for two polymer species to become miscible is frequently that favorable intermolecular interactions exist. Cellulose containing hydroxy groups has therefore the potential to be miscible with synthetic polymers due to the ability to form hydrogen bonds. Homogeneous blends are thus expected for polyamides, polyesters, and vinylic polymers.[1−5] This contribution is concerned with cellulose/poly(vinyl alcohol) blends.

Major problems to be considered for such blends are miscibility and the role of water which is, in general, present in natural polymers. The morphology of polymer blends is often significantly influenced by the interaction between the components of the blends which in turn affects also the properties of the blends. Previous investigations on biopolymer materials and their blends have revealed, in addition, a strong influence of the absorbed water on the structure and molecular mobility.[6] The water content has been reported to affect macroscopic properties strongly. The microscopic origin is often not well understood. This particular contribution is concerned in this context with an analysis of the effect of miscibility and of water on relaxations in the blends. The reason is that relaxations play a considerable role in controlling macroscopic properties such as mechanical or diffusion properties. The methods employed were small and wide angle X-ray scattering and dielectric and dynamic mechanical spectroscopy.

II. Experimental Section

Preparation of the Films. Blends were prepared from cellulose (Danufil-Zellstoff) and poly(vinyl alcohol) (Mowiol 8−88). Different amounts of the blend components (cellulose/poly(vinyl alcohol) 100/0, 90/10, 80/20, ..., 0/100) were mixed in *N*-methyl-2-pyrrolidinone (NMP)/3 wt % LiCl solutions. The polymer solutions (about 6 wt %) were dried for 2 days on a glass plate and coagulated in ethanol. The self-supporting films were subsequently dried in vacuum. Blends containing more than 70 wt % cellulose are optically clear; blends with more than 40 wt % poly(vinyl alcohol) were inhomogeneous. Only the homogeneous blends containing more than 60 wt % cellulose were used for the investigations to be described in the following.

X-ray Investigations. Wide angle X-ray scattering (WAXS) curves were obtained using a Siemens D-5000 diffractometer, the data were taken in the scattering range from $2\theta = 1$ to 60°. A linear background was subtracted prior to performing Lorentz and polarization corrections. The small angle X-ray scattering (SAXS) was investigated with a Kratky camera equipped with a one-dimensional position sensitive detector (OED; Braun). Ni-filtered Cu Kα radiation was used in all cases. The samples were exposed to room atmosphere for several weeks to ensure identical moisture for all films.

Dielectric Investigations. The dielectric analysis covered a frequency range from 20 Hz to 1 MHz (Hewlett-Packard impedance analyzer HP 4284 A). A nitrogen gas heating system and the fully computer controlled measurement ensured a precision of 0.2 K within a temperature range of 100−470 K. The samples were kept between two electrodes (diameter 20 mm), and they were sputtered at both sides with a gold layer to obtain a perfect electric contact with the electrodes of the condensator. The films were exposed to the atmosphere for about 1−2 days, 1 week, and 3 weeks. We also investigated samples dried at temperatures of about 460 K.

DMTA Investigations. The dynamic mechanical measurements were performed using the DMTA (dynamic mechanical thermal analyzer) equipment manufactured by Polymer Laboratories. The temperature was varied in the tensile mode from 120 to 570 K and the frequency from 0.1 to 30 Hz.

III. Results and Discussion

III.1. Crystallinity and State of Mixing. Blends of cellulose and poly(vinyl alcohol) have been analyzed previously with respect to the structure and crystallinity.[1−5] It was found that both properties depend on

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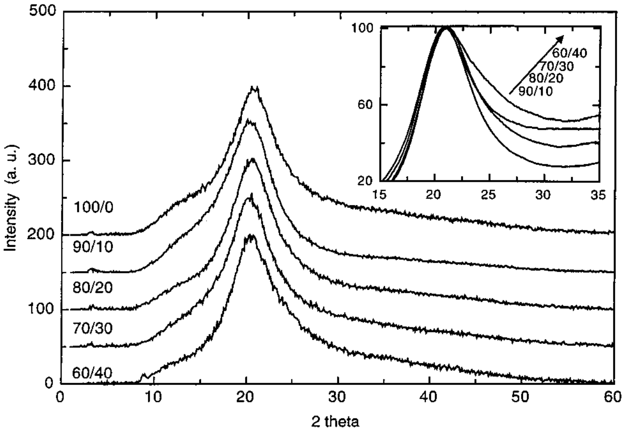

Figure 1. WAXS curves for cellulose and cellulose/poly(vinyl alcohol) blends, taken at room temperature. The concentrations are given in wt % cellulose/poly(vinyl alcohol). The insert displays an enlarged and smoothed portion of the large angle tail of the halo.

the concentration range considered and the solvent used. The nature of the cellulose and the molecular weights of the compounds used also play a major role. It is for this reason that we have to consider the structure and state of mixing for our systems in some detail in order to be able to address the relaxation behavior. In any case we were interested only in homogeneous and amorphous materials because crystallization tends to suppress molecular motions and to cause phase separation.

The DSC investigations gave no indications for the occurrence of melting or crystallization processes either for the pure samples or for any blend. These results are in agreement with those obtained by X-ray investigations. The wide angle X-ray scattering (WAXS) curves of cellulose films and blends containing poly(vinyl alcohol) in a range from 10 to 40 wt % are shown in Figure 1. The scattering curve of pure cellulose displays a broad halo centered at a scattering angle of 20.6°. This location is slightly different from the one of the (101) and (002) reflections of crystalline cellulose (at 20.0°) reported in the literature.[1] Additional diffraction features indicative of a crystalline structure, such as the (040) reflection at 34.7°,[1] were not detected. A further halo occurs in the scattering range from 12 to 14°. This halo has been attributed to the presence of guest molecules[7] in our case possibly water. This detail will be discussed later.

The cellulose films prepared as described above evidently are amorphous. Indeed, the diffraction pattern shown in Figure 1 are similar to those obtained by Gert et al. for amorphous cellulose produced from solutions involving ethyl acetate$-$$N_2O_4$ mixtures.[7] Blends containing up to 40 wt % poly(vinyl alcohol) exhibit no evidence for the presence of crystals.

Blending gives rise to a broadening of the halo at a scattering angle of 20.6°, as shown in the insert of Figure 1, the amount of broadening depending on the concentration of poly(vinyl alcohol). The shape of the halo can be analyzed with respect to the state of mixing of the two components, as shown in the following.

In a first approach we assumed that the broadening originates from a superposition of the scattering curves of the pure components, indicating immiscibility. We tested this assumption by fitting the scattering curves to a superposition of the two halos characteristic of the scattering of the pure components using appropriate weights. The fit fails. These results indicate that the system is not totally phase separated. A second approach involved the consideration of an additional halo originating from the local packing of unlike polymer chains (partial miscibility). This fit also failed. This can be taken as an indication for mixing on a molecular scale although a quantitative analysis is unfortunately not possible in this case.

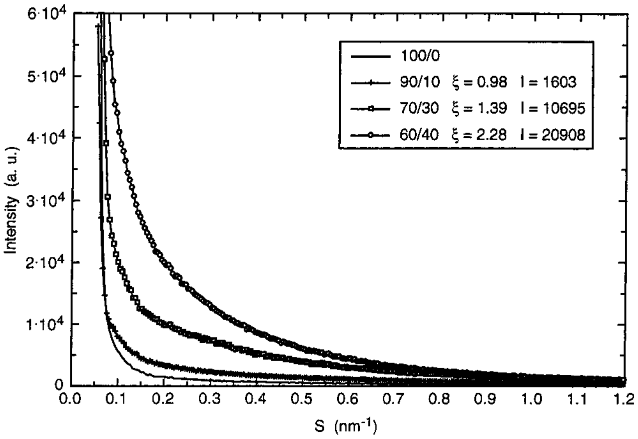

Figure 2. SAXs curves for cellulose/poly(vinyl alcohol) blends taken at room temperature. The insert displays the corresponding correlation lengths and scattering intensities (in arbitrary units) at $s = 0$ nm^{-1}.

To obtain additional information on the state of mixing, we performed small angle X-ray scattering investigations (SAXS). The SAXS curves are shown in Figure 2. Pure cellulose films exhibit no s-dependent small angle scattering in an s range down to $s = 0.2$ nm^{-1} ($s = 4\pi/\lambda \sin\theta$), yet the blends containing poly(vinyl alcohol) display a scattering intensity which increases with decreasing s, starting at about $s \approx 1$ nm^{-1}. The small angle scattering of blends is known to be controlled by electron density fluctuations, which depend both on variations of the particle density and on the concentration. Density fluctuations lead predominantly to a constant SAXS curve, whereas the scattering caused by statistical concentration fluctuations or the presence of phase-separated regions tends to increase at small scattering angles.[8]

The intensity $I(s)$ of the blends considered here can be decomposed into a constant component which will not be discussed further and an additional component which depends strongly on s. We found that the latter can be represented by an exponential electron density correlation function

$$C(r) = e^{-r/\xi} \tag{1}$$

where ξ is the correlation length and r the distance between the sample volumes considered. This leads to an s dependence of $I(s)$, as described by Debye and Bueche.[9,10] For the case of a slit-smeared scattering intensity one obtains

$$I(s) = \frac{I(s{=}0)}{(1 + \xi^2 s^2)^{3/2}} \tag{2}$$

It turned out that the small angle scattering is controlled by a dominant correlation length; the values are shown for various blends in Figure 2. They are in the range between 1 and 2.3 nm. Microheterogeneities of the same scale were also estimated on the basis of 2D-WISE experiments[11] for our systems. Microheterogeneities with similar and larger dimensions have previ-

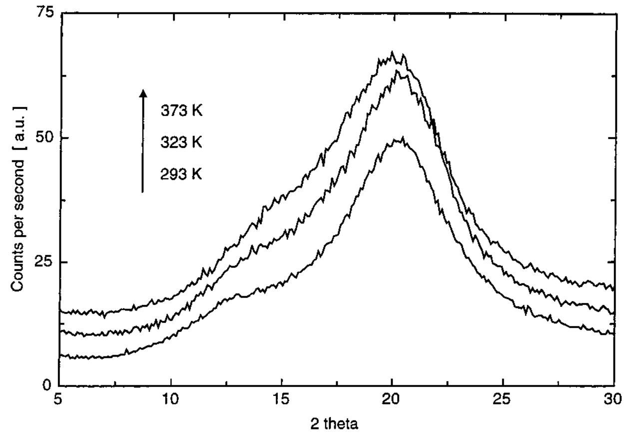

Figure 3. Temperature dependence of WAXS curves for pure cellulose.

ously been reported for various blends of cellulose with synthetic polymers.[21] Our result shows that the microheterogeneities have to be considered in terms of a kind of local phase aggregation with phase boundaries rather than in terms of statistical concentration fluctuations since the latter would give rise to a different kind of correlation function[12] to which the data could not be fitted.

The integrated scattering intensity is certainly related to the concentration of such aggregates. The observation is that this value increases with increasing concentration of the poly(vinyl alcohol) (see insert of Figure 2), as expected. A further finding is that the removal of water does not change the aggregate structure. A quantitative analysis requires, however, knowledge of the electron density contrast between the aggregates and the nonaggregated regions which we do not know.

III.2. Water Content of the Blends. ^{1}H-NMR, ^{2}H-NMR, and 2D-WISE investigations have shown[11] that two distinct components of water molecules, weakly and strongly bonded, occur in the materials. The weakly bonded water is desorbed on heating whereas this does not hold for the strongly bonded one. Heating leads to a loss of water in a temperature range above about 330 K although only slowly. The amount of water which is weakly bonded was found to be 6% for pure cellulose and to decrease significantly with the increasing concentration of poly(vinyl alcohol). The expectation is that the desorption as well as the different states of water present in the samples affect both the structure and the relaxation behavior.

It was already mentioned above that the halo in the range from 12 to 14° has been attributed to a local swelling by inclusion compounds, i.e. by water in the case considered here.[7] Systematic changes should occur in this scattering range when the films are dried, for instance by heating them. This expectation actually holds. Heating gives rise to a loss of water amounting to about 6 wt % (see above) and simultaneously to strong changes of the shape of the wide angle X-ray diffraction curve. It seems that one of the features characteristic for the changes in the peak shape is a shift of the small halo localized at $2\theta = 12.5°$ for room temperature to higher scattering angles. This is apparent from Figure 3 for pure cellulose films. A similar result was obtained for the blends. This result indicates a reduction of the local swelling with increasing temperature. Such structural changes are, of course, expected to influence the properties of the films.

III.3. Dynamics of Dried Samples. Influence of Miscibility on the Secondary Relaxations. The results obtained from the dielectric relaxation analysis are displayed in Figure 4 for dried samples. We have chosen to represent the results in terms of tan δ to make the comparison with the dynamical mechanical data easier. The dimensionless value tan δ is given by the ratio ϵ''/ϵ'; it corresponds to the mechanical quantity tan $\delta = E''/E'$ usually considered in the analysis of mechanical properties.

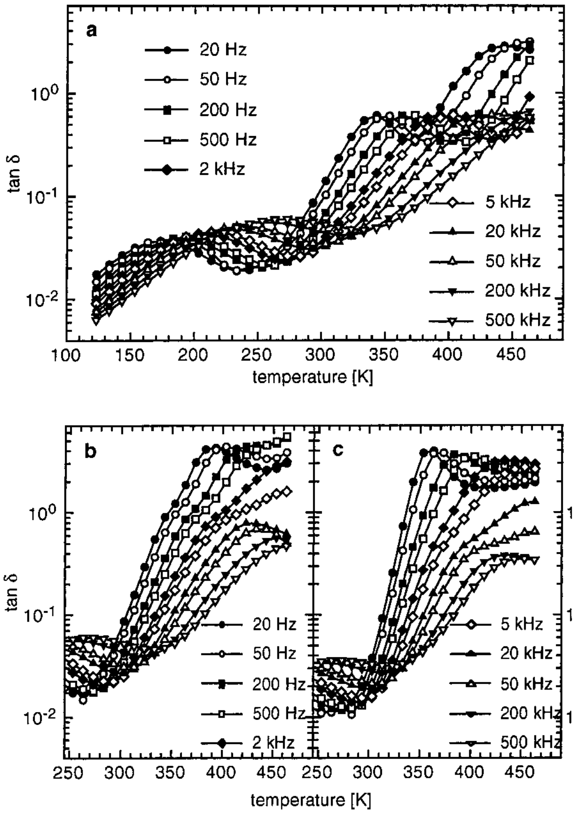

Figure 4. Dielectric results on dried blends of cellulose/poly(vinyl alcohol): (a) 100/0; (b) 90/10; (c) 60/40 tan δ (log scale) versus temperature.

Cellulose displays a secondary relaxation process at lower temperatures in the range between $T = 140$ and 290 K in the frequency range considered here (Figure 4a). The process is thermally activated; i.e. the frequency $\nu_{\max}$ at which the maximum of the ϵ'' peak occurs is shifted with temperature according to the Arrhenius equation.

$$\ln(\nu_{\max}) = \ln(\nu_0) - E_a/RT \tag{3}$$

with an activation energy E_a amounting to 40.8 ± 2 kJ/mol. The activation energy and the constant ν_0 determine the temperature/frequency range.

The relaxation can be described by the empirical Havriliak–Negami equation.[13–15] The complex dielectric function ϵ^* is given by

$$\epsilon^* - \epsilon_\infty = \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (i\omega\tau_{\mathrm{HN}})^{1-\alpha}]^\beta} \tag{4}$$

where ϵ_∞ describes the real part of the dielectric function for $\omega \gg 1/\tau_{\mathrm{HN}}$ with τ_{HN} being the mean Havriliak–Negami relaxation time. $\epsilon_0 - \epsilon_\infty$ is the dielectric relaxation strength. The parameters α and β, respectively, describe the symmetric and asymmetric broadening of the relaxation time distribution.

Figure 5 shows as an example the experimental data and the fitted functions for ϵ' and ϵ'' versus log frequency

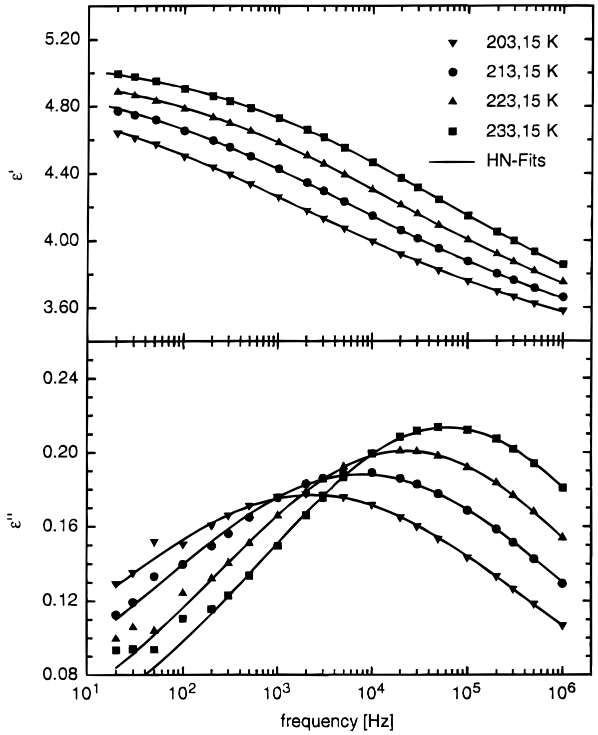

Figure 5. Secondary relaxation and HN fits (Havriliak–Negami) for cellulose, ϵ' and ϵ'' versus frequency (log scale).

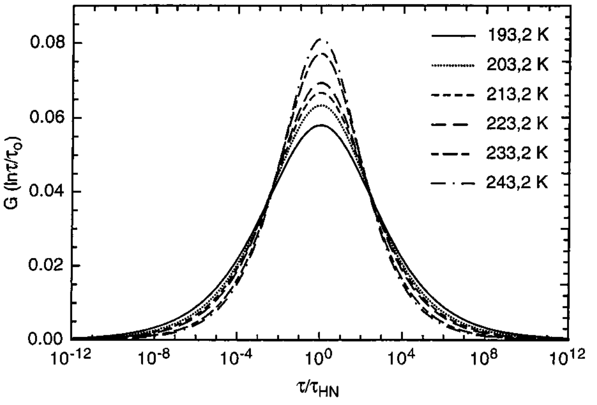

Figure 6. Relaxation time distribution of cellulose as a function of the temperature ($\tau_{\rm HN}$: τ (Havriliak–Negami)).

for the cellulose film at different temperatures. It is obvious that the empirical Havriliak–Negami equation is able to represent in a quantitative manner.

The relaxation time distribution $G(\ln \tau)$ is given by

$$G(\ln \tau) = \frac{1}{\pi}\,\frac{(\tau/\tau_{\rm HN})^{\beta(1-\alpha)}\sin\beta\theta}{\{(\tau/\tau_{\rm HN})^{2(1-\alpha)} + 2(\tau/\tau_{\rm HN})^{(1-\alpha)}\cos\pi(1-\alpha) + 1\}^{\beta/2}} \qquad (5)$$

where θ denotes

$$\mathrm{arctg}\left[\frac{\sin\pi(1-\alpha)}{\{(\tau/\tau_{\rm HN})^{(1-\alpha)} + \cos\pi(1-\alpha)\}}\right] + \begin{array}{ll} 0 & \text{for } [...] > 0 \\ \pi & \text{for } [...] < 0 \end{array} \qquad (6)$$

Figure 6 shows the corresponding distributions. The distribution is extremely broad and becomes narrower with increasing temperature. The relaxation strength is surprisingly large for a secondary relaxation which is typically of the order 0.1–0.5;[16,17] it amounts in our case to 1.87. This large relaxation strength indicates reorientational motions of strong dipoles taking part in the relaxation.[16,18] Such strong dipoles are not present in the cellulose but rather in the absorbed water. We therefore attribute the relaxation to the strongly bonded water fraction, in agreement with the discussion in the literature.[16,19]

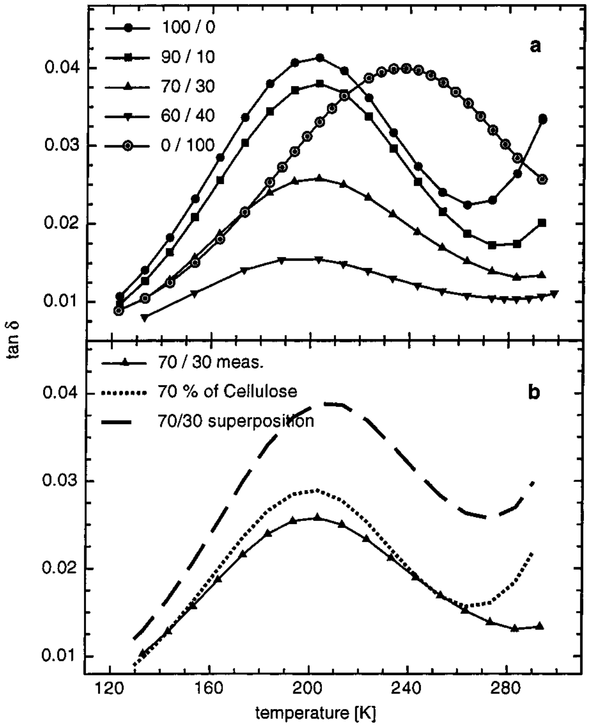

Figure 7. Dielectric relaxation results on blends, tan δ versus temperature: (a) secondary relaxation dependent on poly(vinyl alcohol) content; (b) simulation of the loss spectrum.

Poly(vinyl alcohol) also displays a secondary relaxation in the temperature and frequency range considered here. The surprising result is that all dried blends show clearly only one secondary relaxation (Figure 7a) and that this secondary relaxation occurs in all blends in exactly the same temperature/frequency range as the relaxation of the pure cellulose: it is characterized by an activation energy of $E_{\rm a} = 40.8 \pm 2$ kJ/mol and by $\ln(\nu_0) = 31.6 \pm 1$ (Figure 8a and Table 1). It thus seems that the low-temperature relaxation characteristic of poly(vinyl alcohol) is not present in the mixtures. To show that the relaxation behavior of the blends does not correspond to a superposition of those of the pure materials, we simulated the dielectric loss spectrum of a 70/30 blend (a) by a superposition of the relaxation of the two components and (b) by considering just the relaxation characteristic of pure cellulose.

The result is shown in Figure 7b; only approach b works. It seems as if the molecular interactions totally suppress the secondary relaxation of the poly(vinyl alcohol) but not the one characteristic of cellulose. Both the dielectric secondary relaxations of cellulose and poly(vinyl alcohol) are caused by the motion of water.[16,19] We thus propose a strong absorption of water just by the cellulose backbone in agreement with the results of NMR studies. These revealed a direct dependence of the water content on the composition of the blend: the water molecules are located within the cellulose rather than within the poly(vinyl alcohol) segments.

The relaxation strength decreases with the decreasing ratio of cellulose (Table 1 and Figure 7a): the relaxation

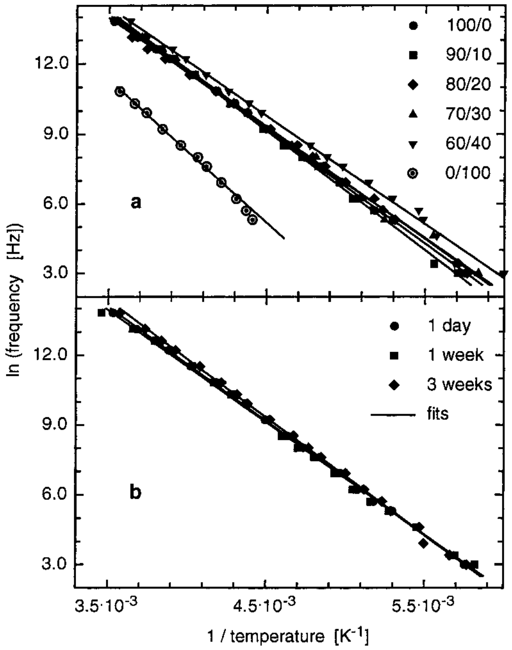

Figure 8. Relaxation results for blends (Arrhenius plots), frequency (log scale) versus 1/temperature: temperature/frequency behavior dependent on (a) poly(vinyl alcohol) content and (b) water content (time of exposure to ambient conditions).

Table 1: Relaxation Results for Blends (T = 203.15 K)[a]

	100/0	100/0*	100/0**	90/10	80/20	70/30	60/40
E_a (kJ/mol)	40.8	40.05	41.88	42.74	39.3	40.26	38.71
$\ln(\nu_0)$	31.26	30.79	31.99	32.25	30.5	31.1	30.71
α	0.759	0.772	0.747	0.716	0.778	0.763	0.769
β	1.0	1.0	1.0	0.643	0.772	0.798	0.65
$\epsilon_\infty - \epsilon_0$	1.846	3.068	3.366	2.282	1.469	1.186	0.702

[a] Activation energy, ln (ν_0), HN parameters α and β, and relaxation strength dependent on the water and poly(vinyl alcohol) content.

strength is proportional to the amount of cellulose present. This fact confirms the conclusion that the blends show a similar relaxation behavior as the pure cellulose. The α and β parameters are given in Table 1 for a temperature of 203.15 K for the different blends. The variation of these parameters with changing composition shows that the relaxation time distribution becomes broadener and more asymmetric with increasing concentration of poly(vinyl alcohol). The interpretation is as follows. The secondary relaxation taking place in the blends is predominantly controlled by the relaxation of cellulose rich regions as far as the relaxation strength, the activation energy, and the characteristic relaxation time are concerned. This would be consistent with a phase-separated state. Yet the broadening of the relaxation time distribution has been traced back to the presence of poly(vinyl alcohol) on a molecular scale since the secondary relaxation happens on a local scale. The systematic change of the relaxation time distribution thus indicates mixing on a molecular scale.

Influence of Miscibility on the Primary Relaxations. The dielectric measurements performed on dried samples reveal, in addition to the secondary relaxation process discussed above, two distinct processes (Figure 4a). The process occurring at intermediate temperatures in cellulose can be attributed to a glass relaxation process. This is obvious from the observation (Figure 9) that the temperature–frequency dependencies correspond to a WLF behavior.[20] With the frequency positions we found:

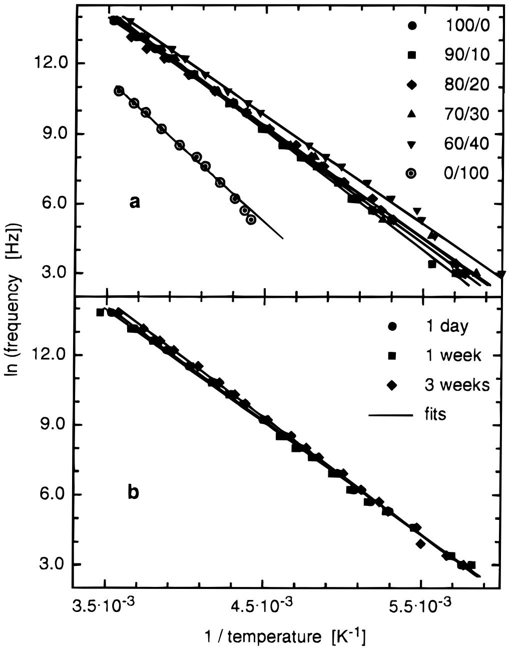

Figure 9. WLF plot of the dielectric results for cellulose and poly(vinyl alcohol).

$$\log\left(\frac{\nu_T}{\nu_{T_g}}\right) = \frac{c_1(T - T_g)}{c_2 + (T - T_g)} \tag{7}$$

(ν_T is the maxima of ϵ'' and ν_{T_g} = 0.01 Hz for the calorimetrically measured T_g; c_1 and c_2 are WLF parameters.

The WLF fit yielded the following parameters: c_1 = 14.1 and c_2 = 163.7 K for the cellulose. The quasi-static glass transition derived from this plot is located at about 292 K. The poly(vinyl alcohol) displays a glass relaxation which is very similar to that of cellulose. This is apparent from the corresponding activation curve also shown in Figure 9. The WLF parameters turned out to be c_1 = 10.3 and c_2 = 85.0 K, respectively, and the quasi-static glass transition temperature to be 307.8 K. It is not surprising in view of the close resemblance of the glass relaxations of the pure components that the blends display a glass relaxation behavior which is independent of composition.

Parts a–c of Figure 4 reveal the presence of a further high-temperature process which depends on the composition of the blends. We are not able to assign a special molecular motion to this process at higher temperatures since the observed features do not agree with those expected for dipolar reorientations: the magnitude of ϵ'' is too large, the quantity $\tan\delta = \epsilon''/\epsilon'$ shows values greater than 1. The observed spectrum is evidently controlled by the onset of decomposition of the cellulose which gives rise to a polarization of the electrodes and to changes of the dipolar structure of the molecules. It is not possible to interpret the values quantitatively because of the experimentally limited temperature and frequency range and the decomposition. The variation of the relaxation behavior with composition nevertheless points to an influence based on miscibility, the reasoning being that the dielectric relaxations tend to be rather localized.

III.4. Effect of Water on the Dynamics. Influence of Water Content on the Secondary Relaxations. A comparison of the dielectric results obtained for dried samples after different times of exposure to the atmosphere shows the dependence for the secondary

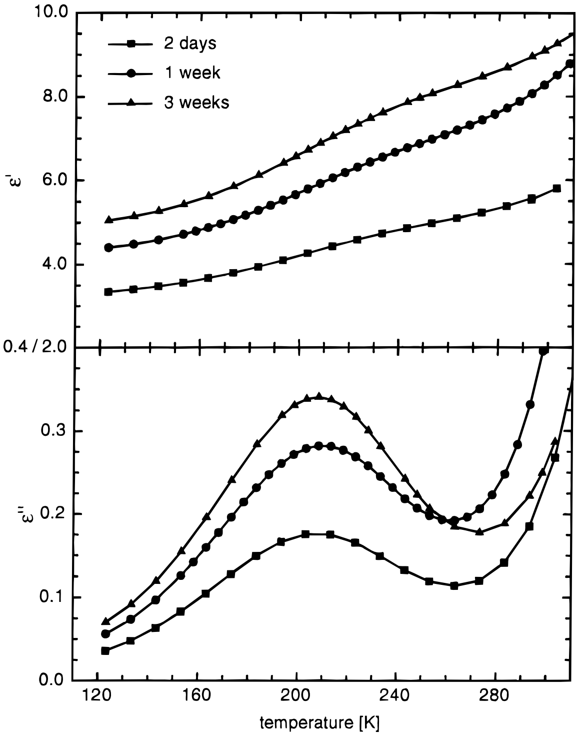

Figure 10. Relaxation results for blends, ε′ and ε″ versus temperature: secondary relaxation dependent on the water content (time of exposure to ambient conditions).

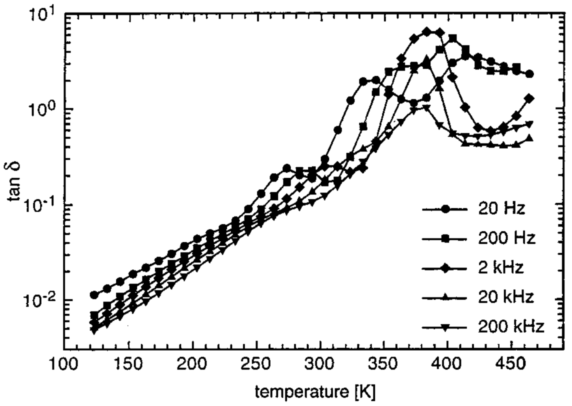

Figure 11. Dielectric results on water-containing cellulose. (Note that no change of the water content is expected during the experiments for temperatures below 330 K.)

relaxation on the water content at low temperatures. The relaxation strength increases clearly from 1.85 to about 3.4 (Figure 10, Table 1), whereas the activation energy and the temperature range of the relaxation stay the same (Table 1 and Figure 8b).

We conclude that the low-temperature relaxation is strongly influenced by motions of absorbed water molecules located in the cellulose rich regions (see discussion above). The molecular origin of this secondary relaxation has to be bonded water: it can only partially be removed by drying. The relaxation strength is decreased by drying yet it remains unusually large (see above).

Influence of Water Content on the High-Temperature Relaxations. The dominant influence of the water content on the microscopic mobility and thus on the macroscopic properties is manifested by comparing the dielectric results for dried (Figure 4a) and undried samples shown in Figure 11. We detect first of all a relaxation in a temperature range from 250 to 340 K for lower frequencies. This relaxation completely masks the low-temperature ranges: the low-temperature relaxation can only be detected as a shoulder. The relaxation strength depends clearly on the water column; it increases with increasing content by more than 1 order of magnitude.

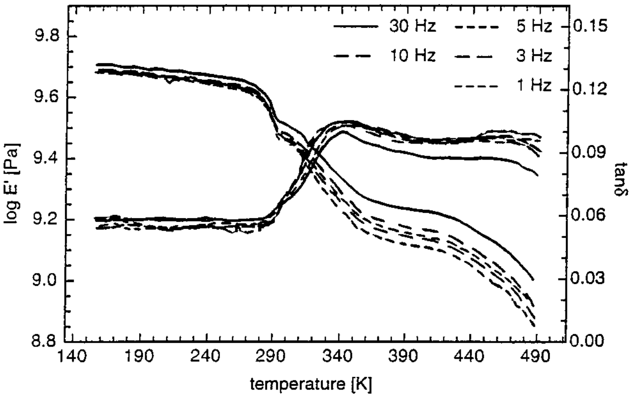

Figure 12. Results of dynamical mechanical studies on cellulose, *E*′ and tan δ versus temperature.

Water-containing samples furthermore display a strong tan δ peak in a temperature range between about 330 and 400 K. The experimentally observed variation of tan δ with frequency and temperature indicates, however, that reorientational relaxations of dipoles are probably not the origin of the relaxation peak. This conclusion is in agreement with statements in the literature. The dielectric spectra are probably controlled by the mobility of the weakly bonded water molecules: a desorption of the water molecules takes place above 330 K causing changes on the molecular level and an inhomogeneous distribution of dipoles in the samples. Furthermore the free water molecules probably cause polarization effects at the interface of electrodes and film.

The water content and its variation with temperature also affect the dynamical mechanical relaxation. Typical results for such investigations are shown in Figure 12. The temperature range in which the *E* modulus falls off corresponds clearly to the temperature ranges where an increase of the mobility and the onset of desorption of the water molecules is detected by the NMR and dielectric investigations. No low-temperature relaxation is detected mechanically. We have to conclude that the molecular motion causing a secondary dielectric relaxation is not able to cause a similar mechanical effect.

IV. Conclusion

The presence of water is found to strongly influence both the secondary relaxation within the glassy state and the lower frequency relaxation related to the glass transition in cellulose and its blends with poly(vinyl alcohol). The effect of the presence of poly(vinyl alcohol) on the relaxation behavior is marginal or even absent. Properties related to the relaxation properties such as transport properties are therefore expected to be approximately unaffected by blending. One is thus able to blend cellulose with poly(vinyl alcohol) in order to improve the processing without loosing the favorable properties of cellulose required for many of its applications.

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