

A model of the dynamic mechanical responses of wood, paper and some polymers to moisture changes

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The dynamic mechanical responses of Scots pine, paper, PA6, cellophane, PVAc and PUR samples subjected to changes in the relative humidity of the surrounding air from 5 to 85% and vice versa have been analysed semiquantitatively on the basis of coupled non-linear rate equations for the moisture concentration in the sample as a function of the time. Important characteristics of the diffusion of moisture into and out of the samples have been studied by measuring the sample weight as a function of time. Moisture sorption results in sample swelling in Scots pine, paper, PA6, cellophane and PUR, for all of which mechanical loss peaks were detected. For PVAc, which does not bind moisture at load-bearing hydrogen bonding sites, no mechanical loss peak could be found. Characteristic of the mechanical loss at low vibration frequencies (0.01 to 1 Hz) is a peak immediately following a change in relative humidity for all studied sample materials except PVAc. This peak is almost certainly due to modulation of the number of load-bearing hydrogen bonds in the material. The relation between the width of the mechanical loss peak and the duration of the moisture sorption and desorption processes is interpreted according to an accepted model of two water molecule binding modes, one in which load-bearing hydrogen bonds are broken unimolecularly by water molecules and one in which further water molecules form clusters on the already unimolecularly bound water. © 1998 Chapman & Hall

1. Introduction

In previous work [1, 2] it was proposed that moisture transport through samples of wood, paper, cellophane, polyamide 6 and some other polymers studied by dynamic mechanical analysis was diffusion limited. Assuming “Fickian” diffusion (often only a fair first approximation) a characteristic diffusion time t^* (approximately the time at which the sample is filled with moisture) can be defined according to $D = (\pi/16)h^2/t^*$ where h is the sample thickness (moisture allowed to diffuse into the sample from both sides). This diffusion time was then compared to the frequency f of the dynamic mechanical measurements, $\omega = 2\pi f$, using the product $\omega\tau_D$ (where ω is angular frequency and τ is relaxation time) with τ_D estimated by t^* . When the frequency is decreased from high frequencies ($\omega\tau_D \gg 1$) toward intermediate frequencies ($\omega\tau_D \approx 1$) the amplitude of the out of phase component of the oscillation and thus $\tan \delta$ is expected to increase. This was used to draw conclusions about

the order of magnitude of the (diffusion controlled) relaxation time in the dynamic mechanical experiments. In general, the estimated relaxation times were of the order of minutes.

As the sorption and desorption kinetics of moisture transport in polymer films is of central importance in the present work, we have studied the time dependence of the weight change of our samples subjected to changing humidity in the surrounding atmosphere, from which typical response times and estimates of diffusion coefficients can be extracted. In general, the diffusion coefficients estimated on the basis of our data are of the same order of magnitude as published values [3], differences being caused by the large variations in relative humidity (from 5 to 85%) used and non-“Fickian” diffusion. Typical sorption and desorption response times as measured in this way are around 40 min varying from about 10 min to about 2 h.

Since changes in the moisture content of the samples studied here lead to changes in their dimensions

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and elastic moduli, changes in the in-phase and out-of-phase parts of the mechanical response are expected. These changes take place on the same time scale as the weight changes. In a first approximation any frequency dependence of the mechanical response is caused by a frequency dependence of the material's equilibrium properties.

Another response time is that determined by the rate of the hydration reaction between water molecules and the material. The response time for the hydration/dehydration reaction is expected to be of the order of 10 s. An "extra" interaction between moisture sorption/desorption and the mechanical vibration is expected only in the neighbourhood of $\omega\tau_R = 1$.

The transport of moisture both to and from the sample and hydration/dehydration reaction taking place inside the sample are thermodynamically spontaneous relaxations towards new equilibria. Thus, when they are probed using dynamic mechanical vibrations the measured mechanical losses must be larger than the corresponding values for the sample in thermodynamic equilibrium, both for sorption and for desorption. In the present case, this means that measured $\tan\delta$ (loss tangent) transients must be positive for these spontaneous relaxations.

The $\tan\delta$ peaks observed previously are interpreted in terms of a theory due to Fukuda [4] of moisture sorption/desorption including both diffusion and a hydration/dehydration reaction. However, some of the non-"Fickian" characteristics of our results are better modelled by a theory due to Wu and Peppas [5] which is focused on the effects of plasticizing and swelling of glassy polymeric material from moisture uptake. It appears that a more complete theory of the effects studied here must include important components from both these theories.

2. Theory

2.1. Diffusion with hydration/dehydration reaction

Recently Fukuda [4] has analysed diffusion processes in polymers in a manner that is relevant to present purposes. One reason for developing the model was the observation that dehydration often takes place at a slower rate than hydration and that the time development of the dehydration, for instance the shape of the weight change versus square root of the time curve, is different to that for hydration. These differences cannot be explained solely on the basis of a concentration dependent diffusion coefficient. On the other hand, they can be explained rather well when the diffusion equation is coupled to an equation describing the chemical reaction between the diffusing species and the medium.

Fukuda's starting point is to take into account the fact that the moisture (C , g cm^{-3}) diffuses in the sample in a mobile form but when it is adsorbed it changes form (S , g cm^{-3}) and becomes essentially stationary. This is expressed in the following two equations coupled by the terms $(1/\beta)(\partial S/\partial t)$ and $k_1 C(S_0 - S)$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] - \frac{1}{\beta} \frac{\partial S}{\partial t} \quad (1)$$

$$\frac{\partial S}{\partial t} = k_1 C[S_0 - S] - k_2 S \quad (2)$$

Here $S(\text{g cm}^{-3})$ is the amount of adsorbed moisture attached to polar groups in the solid material and S_0 is its saturation value. The rate constants for the adsorption reaction are $k_1(\text{cm}^3 \text{g}^{-1} \text{s}^{-1})$ and $k_2(1/\text{s})$. The diffusion coefficient D is assumed to be independent of the total concentration C (equilibrium concentration C_0) of the moisture including the adsorbed moisture. The porosity of the sample, β , is assumed to be unity.

At equilibrium, as the relative humidity is increased the proportion of adsorbed (attached) moisture decreases from about 2/3 of total moisture for low relative humidity to about 1/3 for high relative humidity for the poly(*p*-phenylene terephthalamide (PPTA) films studied by Fukuda. The saturation value of the adsorbed moisture is reached at around 25% relative humidity while the total moisture content continues to increase as the relative humidity is increased.

Fukuda's pair of coupled rate equations is not susceptible to analytic solution. Therefore, Fukuda solved them numerically after expressing them in dimensionless form using

$$\begin{aligned} \frac{C}{C_0} &= \varphi & \frac{S}{S_0} &= \Psi & \frac{x}{L} &= X & \frac{Dt}{L^2} &= \tau_D \\ \frac{k_1 C_0 L^2}{D} &= \lambda_1 & \frac{k_2 L^2}{D} &= \lambda_2 & \frac{S_0}{C_0} &= \sigma \end{aligned} \quad (3)$$

where L is the thickness of a film exposed to moisture changes on one side only. With these new variables the rate equations become

$$\frac{\partial \varphi}{\partial \tau_D} = \frac{\partial^2 \varphi}{\partial X^2} - \sigma \frac{\partial \Psi}{\partial \tau_D} \quad (4)$$

$$\frac{\partial \Psi}{\partial \tau_D} = \lambda_1 \varphi (1 - \Psi) - \lambda_2 \Psi \quad (5)$$

For sorption, at the boundaries of the sample ($X = 0$ and $X = 1$) the solution of the equation for $\partial \Psi / \partial \tau_D$ is

$$\Psi = \frac{\lambda_1}{\lambda_1 + \lambda_2} \{1 - \exp[-(\lambda_1 + \lambda_2)\tau_D]\} \quad (6)$$

and the corresponding equation for desorption is

$$\Psi = \frac{\lambda_1}{\lambda_1 + \lambda_2} \exp[-\lambda_2 \tau_D] \quad (7)$$

When λ_1 and λ_2 are large compared to unity these processes take place correspondingly more quickly than ordinary "Fickian" diffusion-controlled moisture uptake in the material.

For the PPTA films of thicknesses 16 and 50 μm studied by Fukuda typical diffusion-controlled sorption times were 100 to 400 min and desorption times were several times longer. Diffusion coefficients were between $2 \times 10^{-11} \text{cm}^2 \text{s}^{-1}$ and $20 \times 10^{-11} \text{cm}^2 \text{s}^{-1}$, increasing with moisture content. The reaction rates

for the formation of hydrogen bonds with amide groups were orders of magnitude faster: $k_1 \approx 20 \text{ cm}^3 \text{ g}^{-1} \text{ s}^{-1}$ for typical moisture concentrations C around 0.03 g cm^{-3} and $k_2 \approx 5 \times 10^{-2} \text{ s}^{-1}$. With $\tau_1 \approx 1/(k_1 C + k_2) \approx 1.5 \text{ s}$ and $\tau_2 \approx 1/k_2 \approx 20 \text{ s}$ this means that there are two quite different characteristic times in the process, one characteristic of moisture diffusion and one (or a pair) characteristic of chemical bonding of moisture to the polymer.

2.2. Diffusion with sample swelling

Only three years before Fukuda's work was published, Wu and Peppas [5] attacked the problem of analysing non-"Fickian" (case II) transport since deviations from "Fickian" behaviour (case I transport) are commonly observed in, for instance, glassy polymers. Instead of considering chemical bonding to the polymer explicitly, they studied the swelling and plasticizing of the glassy polymer that must be the result of moisture uptake. This involves internal stresses and strains in the polymer which are related to moisture content and material constants through constitutive relations. Obviously these stresses and strains relax to equilibrium values under suitable conditions. Their characteristic relaxation time τ_s in a Maxwell model is given by a (moisture content dependent) viscosity η divided by an elastic modulus E . Thus, there are two time scales also in this case, one defined by the (moisture content dependent) diffusion coefficient $D(c)$ divided by L^2 where L is half the sample thickness (exposed to moisture changes on both sides) and the other by the ratio of a viscosity to an elastic modulus, η/E .

Again, two non-linear differential equations are obtained, this time expressed in terms of the penetrant volume fraction y_1 (more or less corresponding to C , the total moisture concentration, in Fukuda's work) and of the stress σ_{xx} for a one-dimensional analysis (more or less corresponding to the bound moisture S in Fukuda's work). Because of the swelling the spatial co-ordinates of the equations are not at rest, which must be taken into account. Again, the equations are put into dimensionless form and solved numerically.

The result of the numerical solution depend strongly of the Deborah number, defined as the ratio of the stress relaxation time η_0/E where η_0 is the viscosity in the glassy polymer with zero penetrant (moisture) concentration divided by the diffusion characteristic time D/L^2 evaluated when the polymer is swollen and at equilibrium. When the Deborah number is very small, less than 0.01, the absorption process is almost completely diffusion controlled and "Fickian" (case I) transport is observed. On the other hand, when the Deborah number is of the order of unity or more there is a relatively sharp transition between the swollen and unswollen polymer, characteristic of case II absorption. This transition moves into the sample at an almost constant linear rate, making the mass uptake linear in time. Also noteworthy is that an induction time, that is, a delay between the change in humidity and the beginning of the mass increase in the sample, is observed in this case. In the intermediate case a plot of the mass uptake against the square root of the time

typically leads to an S-shaped curve instead of a linear one characteristic of "Fickian" transport. The initial part of the S-shaped curve is the remains of the induction time observed in the high Deborah number case.

The numerical results reported by Wu and Peppas do not include desorption of a penetrant in a polymer, only absorption. In contrast, the numerical results given by Fukuda show differences between absorption and desorption curves but no tendency toward S-shaped curves or induction times. As will be seen below, our experimental results include both S-shaped curves and differences in curve shapes for absorption and desorption.

2.3. Loss tangent under varying external conditions

The loss tangent $\tan\delta$ of a vibrating system is relatively easy to define and understand when analysed on the basis of a linear differential equation with constant coefficients for a harmonic oscillator. The situation is far less clear when the constant coefficients in the harmonic oscillator equation are replaced with variable coefficients in order to model what happens when external conditions are changed during the oscillations.

To show more clearly what we mean, let us consider the differential equation for a harmonic oscillator with variable $x(t)$ and driving force $F(t)$,

$$a_2 \frac{d^2x(t)}{dt^2} + a_1 \frac{dx(t)}{dt} + a_0 x(t) = F(t) \quad (8)$$

where the a 's are constant coefficients, a_2 relating to mass or density, a_1 to damping (for instance, viscous) and a_0 to elasticity or stiffness. By multiplying each term of the equation by $(2\pi)^{-1/2} \exp(-i\omega t)$ and integrating term by term from minus infinity to plus infinity an expression for the Fourier transformed variables (denoted by $\hat{x}(\omega)$ and $\hat{F}(\omega)$) is obtained after partial integration of the terms containing derivatives

$$-a_2 \omega^2 \hat{x}(\omega) + a_1 (i\omega) \hat{x}(\omega) + a_0 \hat{x}(\omega) = \hat{F}(\omega) \quad (9)$$

The Fourier transformed amplitude $\hat{x}(\omega)$ is easily expressed in terms of the Fourier transformed driving force $\hat{F}(\omega)$ and the frequency ω . The loss tangent is then obtained as $\tan\delta = -\omega a_1/a_0 - \omega^2 a_2$ while the resonance frequency is given by $\omega_0^2 = a_0/a_2$. The loss tangent is an intrinsic variable describing the properties of the material. Such variables are obtained by measurements when the material is at (or very near) equilibrium (chemical, thermal, etc.).

When the driving force $F(t)$ is plotted against the response $x(t)$ a closed loop is obtained. The area within the loop is a measure of the amount of energy required per cycle to maintain the motion. It is clearly directly related to the loss tangent.

When a (hygroscopic) material is allowed to absorb or desorb moisture during measurement of the loss tangent the requirement above on equilibrium is explicitly violated.

The constants a_2 , a_1 and a_0 in the above equations are no longer independent of the time. In general,

the differential equation cannot be solved when the coefficients are variable in this way. It is reasonable to assume that approximate solutions might be obtained using a kind of perturbation theory such that the changes in the coefficients are assumed to happen relatively slowly (compared to say the inverse of the resonance frequency) and to be small relative to the sizes of the coefficients themselves. Then one can hope for solutions only slightly different to those for the constant coefficient case. In the present case the most important difference is in the size of the loss tangent.

The exact solution to the above differential equation with varying coefficients corresponds to a complicated spiral in the $F(t) - x(t)$ plane. The approximate solution proposed here means that the closed loops are replaced by distorted open loops, the amount of the distortion and the amount of "openness" depending on how fast the coefficients a_2 , a_1 and a_0 change compared to the frequency ω .

To go further, suppose that a_0 can be replaced by $a_0(1 + b_0h(t))$ where b_0 is zero when the perturbation is turned off and unity when it is turned on. The function $b_0h(t)$ is always much less than unity and assumed to be slow compared to the inverse resonance frequency. Carrying out the steps of multiplying the individual terms of the differential equation by $(2\pi)^{-1/2} \exp(-i\omega t)$ and integrating as above results in an "extra" term

$$\begin{aligned} a_0b_0(2\pi)^{-1/2} \int_{-\infty}^{+\infty} h(t)x(t)e^{-i\omega t} dt \\ = a_0b_0(2\pi)^{-1/2} \int_{-\infty}^{+\infty} \hat{h}(\omega - \acute{\omega})\hat{x}(\acute{\omega})d\acute{\omega} \quad (10) \end{aligned}$$

where the second expression is the *Faltung* of the two functions $h(t)$ and $x(t)$. In general we do not know the exact form of $\hat{x}(\omega)$ since it is the solution of the differential equation with variable coefficients. However, suppose that the *Faltung* can be well approximated by a function of the form

$$a_0b_0(2\pi)^{-1/2} [Re\hat{h}(\omega) + iIm\hat{h}(\omega)]\hat{x}(\omega) \quad (11)$$

where $\hat{h}(\omega)$ is not too much different to $\hat{h}(\omega)$. *Re* and *Im* denote taking the real and imaginary parts of the arguments. These are reasonable approximations at least from the point of view of physics if the perturbation is both weak and slow. The resulting Fourier transformed equation has two more terms than before, one including $Re\hat{h}(\omega)$ modifying the resonance frequency of the system and one including $Im\hat{h}(\omega)$ modifying the damping, that is, the loss tangent. With this approximation the value of $\hat{x}(\omega)$ is easily determined by the same method as before. From this a new resonance frequency and a new "loss tangent" can be calculated. At best this is still only an approximation, but it can give some insight to the nature of the exact solution when the coefficients a_2 , a_1 and a_0 do not change too much or too fast. The new "loss tangent" is no longer a measure of an intrinsic property of the material but a hybrid which includes information about how the perturbation $h(t)$ developed in time as well as information about the material.

Obviously, the same procedure can be carried out on the derivative terms in the differential equation as

well. As long as the perturbation is not too strong and not too abrupt the solutions to the resultant equations should be sinusoidal with damping. An important question is how the damping is influenced by these weak slow changes in the coefficients a_2 , a_1 and a_0 . Here some results from thermodynamics are useful.

The Q value of a system at or near resonance is the ratio of the energy stored in the vibration to the work done per cycle by the external force. In terms of the above differential equation (Equation 8) the Q value can be expressed as

$$Q = \frac{\omega^2 + a_0/a_2}{2\omega a_1/a_2} \quad (12)$$

This number is obviously related to $\tan\delta$ since the coefficient a_1 is directly involved. Clearly, the larger the value of a_1 , the smaller the Q value, that is, the greater the amount of work by the external force needed to maintain a given vibration amplitude and the larger the value of $\tan\delta$. Conversely, the larger the value of $\tan\delta$, the more work must be done by the external force to maintain a given vibration, or, the faster the decay of the vibration amplitude.

According to thermodynamics a process such as absorption or desorption of moisture in a material can only happen spontaneously and irreversibly if it leads to an increase in the entropy of the system. When it comes to equilibrium at constant volume and temperature the Helmholtz free energy $F = U - TS$ of the system is a minimum. Thus thermodynamics indicates that for absorption and desorption of moisture the contribution of the irreversible approach to equilibrium must be to decrease the Helmholtz free energy as quickly as possible. This is achieved by increasing the loss tangent and dissipating energy as quickly as possible. Thus the change in the loss should be "positive", that is, the loss tangent should be increased by this irreversible process, thus hastening the approach to equilibrium. Note that this assertion is valid irrespective of the "direction" of the change in the external conditions as long as the response of the system is spontaneous and irreversible in the thermodynamic sense. In particular, the loss tangent is increased both during absorption and desorption of moisture by the material under study.

This loss tangent is essentially different to the loss tangent measured at equilibrium in that it includes an intrinsic part, $\tan\delta_i$ and an "external" part $\tan\delta_e$ dependent on the manner in which the experiment is carried out (the form of the function $h(t)$ and related functions for the other coefficients). It is not necessarily true that the "total" $\tan\delta$ is the sum of the two parts, the intrinsic and the "external" $\tan\delta$, as in principle they can be mixed in some complicated way. On the other hand, it is not fair to say that $\tan\delta$ measured during transients is an "artefact". Especially if the transients are slow and weak the difference between the loss tangent measured under varying external conditions and the loss tangent measured at equilibrium should be small.

3. Experimental estimation of diffusion times

It is relatively straightforward to measure diffusion times in thin polymer samples by measuring the weight of the sample as a function of time when subjected to a change in the surrounding humidity. A common and useful way of analysing this data is to plot the weight change against the square root of the time. An example of such a plot is shown in Fig. 1 for 52 μm thick PA6. For “Fickian” absorption and desorption the initial weight increase should be proportional to the square root of the time, but finally it should level off to be independent of the time. The characteristic time t^* is given by the intersection of the tangent to the initial part of the curve and the tangent to its final (level) section. In Fig. 1 there is only a hint of possible non-“Fickian” behaviour in the beginning of the curves and the characteristic times for sorption and desorption are similar. The determination of t^* is then fairly easy and accurate.

In several of our experiments the initial part of the weight increase curve was not linear but rather somewhat S-shaped, making determination of t^* difficult and uncertain. An example is shown in Fig. 2. This deviation from “Fickian” behaviour can be caused by difficulties in determining the zero of time (the weight being determined at certain finite intervals of time) or by the large differences in humidity used in our experiments as well as to possible non-“Fickian” behaviour of the samples as discussed in the theory section above. If the latter is the correct explanation, it could be interpreted as meaning that sample swelling has a limiting effect on the diffusion of moisture into and out of the sample. Finally we note that diffusion constants determined on the basis of the first absorption and desorption of moisture can differ significantly from corresponding diffusion constants determined on the basis of subsequent absorptions and desorptions.

Table I is a summary of our experimental results for sorption (increase of the relative humidity of the surrounding atmosphere at room temperature from 5 to 85%) and desorption (reduction of the relative humidity from 85 to 5%) for six different materials. The amount of water involved varied from only about 3% of the sample weight for Scots pine and PUR to 8 to

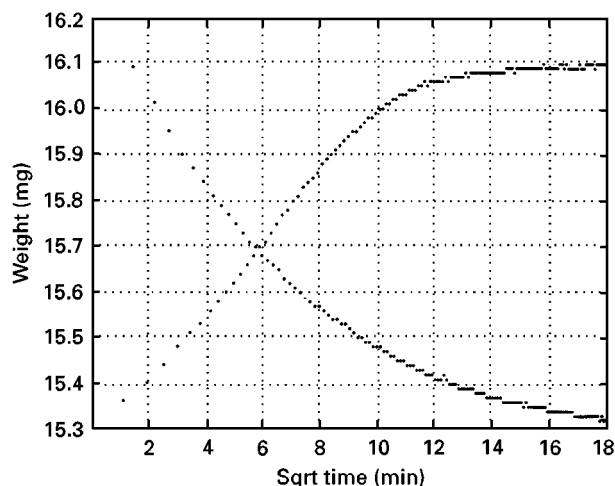


Figure 1 Weight of a PA6 sample (thickness 52 μm) versus the square root of the time in minutes in absorption followed by desorption.

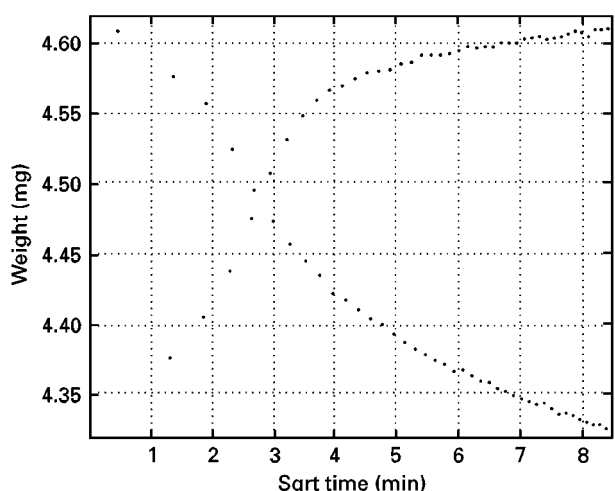


Figure 2 Weight of a cellophane sample (thickness 20 μm) versus the square root of the time in minutes in absorption followed by desorption.

10% for PVAc and paper and up to 22 to 45% for PA6 and cellophane. Included in the table are literature values of the diffusion coefficient taken from an article by Barrie [3]. In general the agreement between our values of the average diffusion coefficients

TABLE I Results of measurements of sorption and desorption times based on weight change measurements for six samples

Material	Thickness (μm)	t^* sorption (min)	t^* desorption (min)	D absorp experiment $10^{-8} \text{ cm}^2 \text{ s}^{-1}$	D desorp experiment $10^{-8} \text{ cm}^2 \text{ s}^{-1}$	D average experiment $10^{-8} \text{ cm}^2 \text{ s}^{-1}$	D literature $10^{-8} \text{ cm}^2 \text{ s}^{-1}$
Paper	110	11	28	2.5	2.1	2.3	–
Scots pine	800	40	36	53	58	55	–
PA6	20	25	30	0.043	0.053		
	30	56	30	0.052	0.097	0.071	≈ 0.1
	52	121	81	0.073	0.11		
Cellophane	20	18	42	0.071	0.031	0.15	< 0.1
	40	34	16	0.16	0.33		
PVAc	150	121	56	0.61	1.3	0.96	4.3
PUR		28	10	0.012	0.033	0.022	–

Diffusion coefficients evaluated according to the formula $D = (\pi/16)h^2/t^*$. Literature values from Barrie [3].

and the literature values is fair, but the scatter in our experimental results, due to the difficulties mentioned above, is great.

As expected, our “diffusion coefficients” for wood and paper are much greater than those for the other materials because of the macroscopic porosity of wood and paper (much larger for wood than for paper). For PA6 agreement between the literature value and the average of our experimental values is good. As noted above in connection with Fig. 1 the sorption and desorption curves indicate that the diffusion is “Fickian” to a good approximation. For cellophane our average value is larger than the literature value and the variation in the calculated diffusion coefficients is large. Our cellophane sample contained plasticizing additives including a mixture of glycerol and a poly(ethylene oxide) adduct which could not be identified. Several other substances appearing in mass spectrometric analyses also remain unidentified [2]. This could be an explanation for the difference between our value of the diffusion coefficient and the literature value. Also, for cellophane our sorption and desorption curves are indicative of non-“Fickian” behaviour, as illustrated in Fig. 2. Our average diffusion coefficient for PVAc (nearly “Fickian” behaviour) is only a fourth of the literature value, for reasons unknown. Finally, the diffusion coefficients calculated for PUR foam (nearly “Fickian” behaviour) make use of our estimated average foam wall thickness of 10 μm . The most important conclusion to be drawn from the values in this table is that the characteristic response times for diffusion in these experiments vary between 8 min and 120 min. This should be compared with the lowest frequency used in our dynamic mechanical measurements, 0.01 Hz. Thus, the minimum product of the angular frequency and the characteristic response time, $\omega\tau$, is 30.

4. Results of dynamic mechanical measurements

In previous work [1,2,6] the in-phase and out-of-phase parts of the applied oscillatory force on a sample in three-point bending, uniaxial tension or compression have been measured, normally at 1 Hz but sometimes at 0.1 Hz or 0.01 Hz. The ratio of the out-of-phase part of the force to the in-phase part thereof, designated $\tan \delta$, was displayed and discussed in detail. Fig. 3 shows results for a sample in uniaxial tension at 1 Hz. The measured force changes are caused by changes in the dimensions of the sample due to swelling and to changes in the elastic modulus, the latter changes being far more important than the former ones. The figure illustrates several typical characteristics of the results of our dynamic mechanical measurements:

- the in-phase part of the force changes significantly according to whether the sample is moist or dry, with relatively smooth transitions between the two levels;
- with the exception of PVAc, the force transitions from dry to moist samples are quicker than the

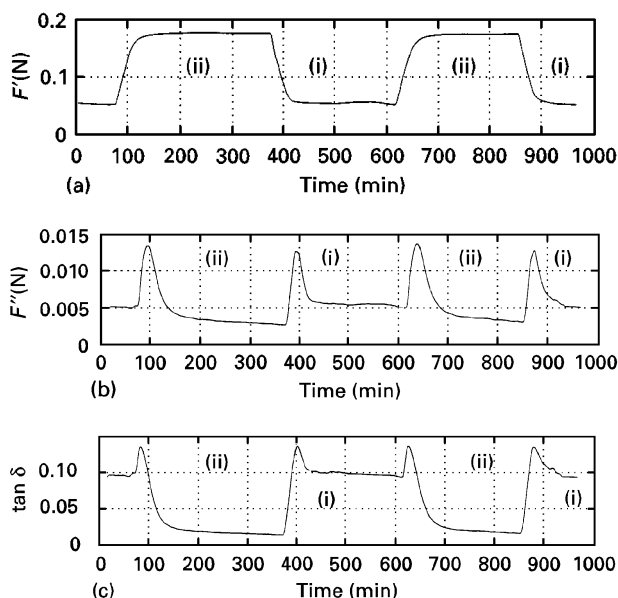


Figure 3 Dynamic mechanical measurement results for a PA6 sample (dimensions 22 mm \times 2.5 mm \times 30 μm) in uniaxial tension at 0.1 Hz subject to moisture changes from 85% relative humidity to 5% relative humidity and vice versa at room temperature. (a) The measured (in-phase) force F' as a function of time, where F' is higher for the dry sample than for the moist sample. (b) The measured (out-of-phase) damping F'' measured at the same time as the (in phase) force F' . (c) The ratio of the (out-of-phase) damping to the (in-phase) force, designated $\tan \delta$.

force transitions from moist to dry samples, and for paper and Scots pine much quicker;

- with the exception of PVAc, the durations of the force transitions from dry to moist samples are shorter than the measured diffusion times as determined in the weight change experiments;
- the durations of the force transitions from moist to dry samples are more often longer than the measured diffusion times as determined in the weight change experiments;
- the out-of-phase part of the force varies similarly to the in-phase part thereof, although in this and most other cases less strongly, except that there is a pronounced peak in the out-of-phase part of the force at the beginning of each transition,
- the width of each peak in the out-of-phase part of the force is quite comparable to the duration of the corresponding transition in the in-phase part of the force.

In most cases the strength of the peak in the out-of-phase part of the force versus time plot increases when the measurement frequency is lowered to 0.1 or 0.01 Hz. The only exception to this is the case of PVAc in which no peak could be found at any measurement frequency. This we link to the fact that water does not form load-bearing hydrogen bonds in PVAc, as it does in the other five sample substances studied here. This supports the proposition that the peak in the out-of-phase part of the force versus time plot is due to the interaction of water molecules with the polymer through the formation and breaking of load bearing hydrogen bonds (to be discussed below) rather than for instance to mechanical loading effects.

5. Analysis

We base our semiquantitative analysis of our measurement results on the assumption that the mechanical moduli (Young's modulus, loss modulus, etc.) of the samples are affected by moisture uptake only through the water molecules' making and breaking load-bearing hydrogen bonds in the polymer. This primary effect is of main interest here. Secondary effects of moisture uptake are dimensional changes in the samples, affecting their stiffness, and increased losses due to changes in the sample properties happening at rates comparable to the measurement frequency.

We have noted previously [2] that the dimensional changes due to moisture uptake are small. Their effect on the measured stiffnesses of the samples is small, usually less than 10% of the observed change in the stress necessary to achieve a given strain. Thus this effect will not be discussed further here.

As we noted above in Section 2.3 a change in the mechanical properties of a sample can lead to an increased loss tangent if the change in the mechanical properties takes place on a time scale similar to that of the measurement. In our experiments the weight changes of the samples take place on a time scale of the order of 40 min. On the other hand, the lowest measurement frequency used in our experiments is 0.01 Hz, making the weight change rate (and corresponding change rates of mechanical properties) much slower than the inverse of the measurement frequency. Thus this effect should not contribute significantly to the value of $\tan \delta$ in our experiments. Support for this conclusion is provided by the experiments on PVAc in which no transient in $\tan \delta$ was observed, even at the lowest measurement frequencies, this being connected with the fact that moisture does not form load-bearing hydrogen bonds in PVAc. Thus, we can disregard this secondary effect in the following analysis.

Instead we note that the reaction times for moisture sorption and desorption in PPTA film observed by Fukuda were of the order of 10 s. Reaction times of the same order of magnitude as in PPTA films can be expected in our samples since in both cases the basic phenomenon involved is the formation and disruption of hydrogen bonds. This makes the product $\omega\tau$ near unity when τ is the reaction time and ω corresponds to 0.1 or 0.01 Hz. Thus, as long as the hydrogen bonding reaction is underway and the concentrations of both the unbound water and the water binding sites on the polymer are significant an increase in the mechanical loss and thus in the loss tangent is expected. Obviously, when the reaction has hardly begun or when it is near completion little energy is developed by modulating it and its contribution to the mechanical loss is insignificant.

During the initial phases of moisture uptake the water molecules are adsorbed in the sample and most if not all are bound to the material at hydrogen bonding sites on cellulose molecules or amide or urethane groups. The mechanical properties of the sample are changed due to the disruption of the hydrogen bonds, of which a few per cent are responsible for the ability of the material to bear loads. In fact, the elastic

modulus of paper can be understood in terms of this small fraction of hydrogen bonds [7–10]. The first water adsorption "layer" has somewhat different properties to the following perhaps six to eight "layers". In particular, in the first or low moisture content range (in cellulose for water contents up to around 5% by weight [8, 9]) one water molecule breaks one hydrogen bond and if that hydrogen bond is a load-bearing one a corresponding decrease in the elastic modulus results. In the second or high moisture content range more water molecules attach themselves to the first one, thus forming a cluster; further hydrogen bonds between polymer molecules are broken co-operatively and a relatively large change in the elastic modulus results. Because, at room temperature and 50% relative humidity, the equilibrium weight fraction of moisture in cellulose is about 0.08, the experiments carried out here mainly concern the second or high moisture content range where water molecules typically form clusters which break hydrogen bonds co-operatively. In this range ($w > 0.045$) the relation between the elastic modulus E and the moisture content w (weight fraction) is approximately $\ln(E/E_0) = -6.41w + 0.24$ [7, 8]. In the first or low moisture content range ($w < 0.045$) the appropriate relation is approximately $\ln(E/E_0) = -w$.

In the case of paper, when the relative humidity of the surrounding air is changed quickly from 5 to 85% the elastic modulus is expected to decrease, quickly at first because moisture transport to the cellulose is relatively fast, and then more slowly when the rate of change of the elastic modulus with moisture content decreases with the logarithmic dependence shown above. This means that the apparent duration of the reduction of elastic modulus should be a little shorter than the duration of the transport of moisture into the sample. On the other hand, when the relative humidity of the surrounding air is changed quickly from 85 to 5% the elastic modulus is expected to increase, again quickly at first since moisture transport from the sample is relatively fast and then somewhat less quickly because the rate of moisture transport decreases and the (absolute) rate of change of the elastic modulus with moisture content decreases as the moisture content decreases toward 0.045. Thus, the apparent duration of the increase in the elastic modulus is expected to be a little longer than the duration of the diffusion controlled moisture transport process. This scenario is in good agreement with the first four typical results of our dynamic mechanical measurements, as summarized above.

A second consequence of the above model is that moisture diffusion in the sample is not a simple monomolecular process but, rather, dependent on a number of steps and the formation of clusters of molecules leading to sample swelling. This is taken into account in the model developed by Wu and Peppas [5].

The details of the above description of hydrogen bond breakup and formation are thought to be more correct for paper than for instance for polyamides [4, 11, 12] or polyurethanes [13]. The latter materials have not been studied with respect to their interaction with moisture to the same extent that paper has been.

Further, wood is morphologically and structurally much more complicated than paper and some aspects of the above description may have to be adjusted somewhat to achieve an exact description corresponding to that appropriate for paper.

Also the mechanical damping is affected by sorption of moisture. At vibration frequencies such that the product $\omega\tau$ is within an order of magnitude of unity there is a contribution to the mechanical damping due to the breaking and re-establishment of load bearing hydrogen bonds. We have no independent estimate of τ , either for the initial adsorption or for cluster formation. The rate constants for the biomolecular reaction between a water molecule and an amide group given by Fukuda [4] can be correct to within an order of magnitude or so also for the other materials studied here. On the other hand, the process of cluster formation is most likely not characterized by the same reaction rate constants. Because it is more complicated and involves more molecules than the initial biomolecular reaction it can be expected to be slower, that is, characterized by a longer τ than the bimolecular reaction. Some evidence presented by Nissan [7] in connection with a discussion of the mechanical properties of hydrogen-bonded solids indicates that for paper the reaction rate constant for the initial biomolecular adsorption reaction may be around 10^{-2} s^{-1} and for the co-operative cluster forming reaction it may be only half of that value or less. In this case, as the vibration frequency is lowered the product $\omega\tau$ decreases toward unity for sufficiently low frequencies, with the faster bimolecular adsorption reaction being more important in the relaxation process than the cluster forming reaction for all frequencies used here.

When the relative humidity of the air surrounding a sample increased from 5 to 85% moisture is first adsorbed according to the bimolecular reaction and then according to the cluster forming reaction. At the relatively high vibration frequencies used here ($\omega\tau > 1$ for all investigated frequencies) the increase in the mechanical damping caused by the adsorption is expected to be strongest when the bimolecular reaction involving load-bearing hydrogen bonds is under way. After it has been essentially completed, further moisture adsorption takes place via cluster formation, but this process does not contribute as strongly to the mechanical damping because of the longer reaction time associated with it. The result is a peak in the mechanical loss versus time curve or in the $\tan\delta$ versus time curve. The time required to reach the new mechanical quasi-equilibrium must be shorter than or at most equal to the time taken to complete the weight changes in the weight change experiments. As noted above, this is true of all our experimental results for moisture uptake, with the exception of PVAc where no peak in the mechanical loss versus time curve could be found.

During sample drying the situation is a little different since the moisture associated with water molecule clusters can be expected to leave the sample either before or at the latest concurrently with the initially bound moisture. The contribution to the mechanical

losses due to modulation of the amount of hydrogen bonds being formed or destroyed by the vibrations (again assuming sufficiently low frequencies) is therefore delayed compared to the case of moisture uptake. The time required to reach this new mechanical quasi-equilibrium is therefore similar to or longer than the time required to complete the weight changes in the weight change experiments. This is true of all our experimental results for sample drying.

6. Conclusions

We believe that the above semiquantitative analysis based on the theoretical models of Fukuda and of Wu and Peppas and our observations concerning the durations of the weight change transitions and of the changes in mechanical characteristics of the samples is a fair summary of the physical phenomena that we have observed and presented in previous articles and in the present one. In particular, we associate the peak observed in the out-of-phase part of the force with mechanical losses caused by modulation of the number of load-bearing hydrogen bonds in the sample. The phenomena involved are complex and difficult to sort out, as the extensive literature of mechanosorptive effects suggests. We have not been able to present an independent measure of the reaction rates for formation and disruption of hydrogen bonds in our sample materials, which would have been useful in testing the validity of our model. On the other hand, we wish to point out the significant fact that for PVAc no peak in the mechanical loss versus time or the $\tan\delta$ versus time curve could be found for mechanical frequencies of 0.01, 0.1 or 1 Hz. PVAc does not bind water molecules at load-bearing hydrogen bonding sites although it does absorb water. Thus, according to our model, there should be no $\tan\delta$ peak to observe in PVAc.

Another important conclusion of this work is that there are two different time scales to be taken into account in these experiments. One is the time it takes for moisture to diffuse into the heart of the sample, obviously increasing with sample dimensions. The other is the chemical reaction time, in the present case the time for formation and disruption of hydrogen bonds, which is a property of the sample material and its interaction with water molecules and independent of the sample dimensions. It is important to differentiate between these two time scales when considering what might happen when the sample size is scaled up or down, for instance.

The present model depends on the absorbed water interacting with the material in such a way that the mechanical strength of the sample is changed. Without this coupling no peak in the mechanical loss on sorption or desorption would be observed. Further, our interpretation of the relation between the width of the mechanical loss peak to the duration of the moisture sorption process makes use of the fact that there are two types of water binding in wood and paper (and perhaps also in PA6, cellophane and polyurethane). In these respects, even our semiquantitative analysis lends support to a presently accepted model of the

interaction between water and cellulosic and other material in which hydrogen bonds contribute significantly to the mechanical strength.

We note that it has not been possible to use published diffusion coefficients to accurately predict characteristic times for moistening or drying the samples as there are significant differences between the measured sorption and desorption times not usually taken into account with regard to the diffusion constants, and because the process is decidedly non-“Fickian” in many cases where sample swelling probably slows the diffusion process. Especially in the case of mechanosorptive effects a combination of the chemical reaction theory of Fukuda and the mechanical swelling theory of Wu and Peppas seems a likely candidate for a better description of the phenomena taking place. Such a theory, while conceptually not too difficult, might be rather complicated in its details and obviously not amenable to analytical solution. More recently a somewhat different approach has been taken by Hedenqvist *et al.* [14] in their study of propane in medium density polyethylene pipes. They let the diffusion coefficient be concentration dependent, allowed the stress developed due to solute absorption to relax slowly in time and made use of free volume models in order to analyse their experimental data. However, as the concentration of the solute propane was always relatively small, changes in the specimen geometry, that is deformation of the spatial co-ordinates, was not included in the analysis. Analytical solutions to the diffusion equation were shown not to be as accurate as numerical solutions including more details of the interaction between the solute and the solvent. Thus it appears that the detailed interpretation of diffusion measurements in polymeric materials has not yet been fully elucidated.

In the above treatment, the diffusion of water molecules into the hygroscopic material was analysed mainly with reference to the “chemist’s” view as presented by Fukuda [4] with less attention to the effects of swelling as treated by Wu and Peppas [5]. This should not be taken to mean that we are unaware that sudden volume changes caused by a stepwise change in temperature do not correspond to an equilibrium arrangement of the molecules. Instead, a relatively slow, thermally activated equilibration process sets in until the molecules have resumed their minimum-energy positions. For thermally induced volume changes this process is known as physical ageing. Recently Hunt and Gril [15] pointed out that processes similar to physical ageing are likely to take place also when the volume variation is caused by sorption/desorption, especially since the volume changes occurring in the latter case are significantly larger than those normally caused by thermal expansion.

Physical ageing is normally considered as a rearrangement process with a maximum intensity immediately following the temperature step. Unfortunately the very beginning of the process is not amenable to measurement with the techniques normally used in the field because of the finite period of time needed for the temperature gradients in the sample to fade away. In our case, the $\tan\delta$ value is determined throughout the humidity steps. The additional mobility of the structure because of its consolidation is likely to result in a higher mechanical loss level, at least during the initial stage of the sorption/desorption process. The $\tan\delta$ transients observed in our work [1,2,6] thus appear to be related to such a consolidation process. The term “chemical reaction” is used in the present paper to denote in a neutral sense a second stage of the sorption/desorption process can thus be related to the physical ageing phenomenon.

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