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PHYSICAL AGING AND GLASS TRANSITION: EFFECTS ON THE MECHANICAL PROPERTIES OF PAPER AND BOARD

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ABSTRACT

Physical aging is a general process appearing in all amorphous or partially amorphous materials below the glass transition and is a fundamental characteristic of the glassy state. It is shown here that paper is no exception and the same behaviour is observable as in other materials. The aging process represents the slow movement of a glassy molecular network towards equilibrium and displays the 'universal' characteristics of strong age-dependence of some properties, scaling behaviour, reversibility, and relaxations which follow a stretched exponential or Kohlrausch law.

Physical aging in paper is readily reversed by moisture sorption, which lends the aging effect particular practical importance. Small-strain mechanical viscoelastic properties such as creep and stress relaxation rates are strongly affected by age; this has very significant implications for the performance of paper webs or structures subject to short or long-term endurance loading. A measurable but less important effect is also demonstrated for a very large-strain property, CD Ring Crush. The rate at which moisture is sorbed is strongly age dependent. Attempts to measure the glass-transition temperature in paper, and its dependence on moisture content, by dynamic mechanical thermal analysis are described; the results were inconclusive.

INTRODUCTION

The time-dependent properties and behaviour of amorphous and partially crystalline organic polymers and polymeric materials have been studied extensively for many years as discussed, for example, by Ferry (1). For paper, a partially crystalline cellulosic polymer structure, the characterisation of time-dependent behaviour has been more limited. The reasons for this may be the difficulties in experiment and interpretation associated with such a structurally complex and heterogeneous material which has the added complication of being softened or plasticised by water molecules, with the plasticiser concentration depending on environmental climatic conditions.

The bulk of the fruitful effort directed towards understanding the elastic mechanical behaviour of paper has been in terms of fibre network models relating bulk properties to the properties of the component fibres, the nature of inter-fibre bonding, fibre and distributional inhomogeneities, internal strains, moisture effects, and other factors. However, for insight into the time-dependence of properties, it is necessary to focus down to the molecular scale and view paper on the basis of a polymer network model. Such a model can be represented as a random network of polymer chains in which there may be small islands of local order, i.e. crystallites. The structure is far from equilibrium and is dynamically active, having a variety of modes of molecular motion and configurational relaxation which are characterised by spectra of relaxation and retardation times. It is the time, temperature and pressure dependence of the configurational relaxations which manifest as a time, temperature and pressure dependence of the bulk properties of the material, and give rise to characteristic transitions, such as the glass transition.

The aim of this paper is to demonstrate the existence and significance in paper of a generally unrecognised long-term relaxation known in a variety of other materials as physical aging. It has been discussed briefly in a previous publication (2). The motivation for the work is to understand the mechanism of rapid compression-creep failure of corrugated boxes during moisture sorption, which is an industry-wide problem. The significance of physical aging is far wider than this, however. Following a discussion of the nature and mechanism of physical aging, the glass transition, and their relationship, experimental results are presented demonstrating the effects of physical aging on tensile creep in the cross-machine direction (CD), tensile stress relaxation in the machine direction (MD), and CD Ring Crush, for a commercial linerboard. A strong effect of age on the rate of moisture sorption is also shown. Attempts to locate the glass transition by dynamic mechanical thermal analysis (DMTA) are discussed, but have proved unsuccessful so far.

GENERAL BACKGROUND

Glass Transition

Amorphous polymers undergo well-documented (1) major changes in properties and behaviour as they are cooled from the melt, through the rubbery or elastomeric state, to the 'solid' state, which is described as a glass because the structure remains disordered. The relatively slow change with temperature of various properties is interrupted at characteristic temperatures or temperature ranges by rapid property changes, identified as material transitions. The strongest of these is the α-transition or glass transition (GT), signified by large changes in viscoelastic properties, for example shear or tensile moduli, transport coefficients such as viscosity and the diffusion constant, and in dielectric and other properties. For partially crystalline materials (3) the transitions still occur, due to the contribution of the amorphous phase, but are much weaker. Time dependence of properties extends also to the location of the GT; its actual temperature, T_g, goes to lower values as the time scale for the measuring experiment is increased. The presence of softeners or low-molecular-weight plasticising molecules in the material structure also has a strong effect, moving T_g to lower values (4).

The nature of the GT has been studied and discussed for decades (5, 6), but is still not fully understood. It is not a thermodynamic phase transition and is most fruitfully considered in terms of molecular dynamics. Configurational relaxation of a polymer network requires the presence of sufficient 'holes', voids, or free volume in the structure for both local and extended or cooperative modes of molecular motion to be active. Free volume decreases as the temperature falls, increasing the molecular packing, hindering molecular mobility and limiting the dynamic response of the network to external disturbances, and manifests through an increase in relaxation times. Since the rate of free-volume decrease also depends on molecular mobility, the process is non-linear and subject to instabilities. A major instability is the α-transition or GT, where segmental motion of the polymer chains largely ceases and the structure is 'frozen' through the arrest of large-scale cooperative motion. Further, but much weaker, transitions may occur at lower temperatures through the inhibition of local modes of motion, such as side-chain librations. These are termed β, γ, δ etc. transitions. At all temperatures, the dynamics and the degrees of freedom of the system depend on the remaining free volume. The free-volume model serves as a useful conceptual framework and semi-quantitative theory for viscoelastic behaviour in polymeric materials. A fully quantitative free-volume theory has not been developed.

The understanding of the nature of the GT has advanced considerably in the last decade with the development of mode-coupling theories of liquids by Leutheusser, Bengtzelius, Götze and Sjögren (7). These theories have been applied successfully to transition and relaxation data obtained for atomic systems (8) and polymers (9) by neutron scattering and for polymers (10) and colloidal suspensions of spherical particles (11) by dynamic light scattering. This is a remarkable result, since the relaxation time scales in atomic systems on the one hand, and polymers and colloids on the other, differ by about nine orders of magnitude. Other 'universal' aspects in these systems are the existence of scaling behaviour similar to the well-known Williams-Landel-Ferry time-temperature superposition for polymers above T_g, and relaxation functions which follow a stretched exponential law first discovered by Kohlrausch last century, i.e:

$$f(t) \;\alpha\; \exp\left(-\frac{t}{\tau}\right)^{\beta} \tag{1}$$

where ß is a stretching parameter, $0<ß<1$, and τ is a characteristic relaxation time.

Physical Aging

An extensive study of physical aging in amorphous polymers is presented in a monograph by Struik (12). Physical aging occurs below T_g and exists because glassy or amorphous polymers, or the amorphous phase of partially crystalline polymers, are not in thermodynamic equilibrium and are therefore unstable. Aging represents a slow, gradual, process towards equilibrium which is usefully visualised as a continuing slow collapse or relaxation of the remaining free volume, following the rapid collapse during the approach to the GT from higher temperature. The process has numerous significant features and implications. Those considered the most important are summarised below.

1. Physical aging is a self-retarding process and therefore the aging rate becomes increasingly slow. This is so because the rate at which free volume decreases depends on the molecular mobility and the mobility in turn depends on the remaining free volume. Aging will therefore go on for a long time. However, at temperatures below the ß-transition, aging will not occur because all significant molecular motion has been frozen.

2. The properties most strongly affected by aging are those which were changed most extensively during the glass transition. For mechanical properties, aging should produce an increase in the elastic moduli and a decrease in creep and stress relaxation rates. For partially crystalline materials such as cellulose or paper fibres, the moduli changes may not be extensive.

3. Physical aging is easily reversed, i.e. materials in the aging range below the GT can be de-aged readily. One method is to take the material above the GT and quench it back down through the GT. The aging process then begins again. However, any process resulting in an increase in free volume can be assumed to cause at least partial de-aging. De-aging therefore has particular significance for paper, which is a plasticised system in which increases in free volume can be induced rather easily (2) by moisture changes. The formation and breakage of inter-chain hydrogen bonds during aging and de-aging is not actually necessary for the mechanism; of course it probably happens.

4. For partially crystalline polymer networks, aging may persist to some extent above the GT. This may be a result of broadening of the glass transition due to the presence of a partially ordered inter-phase region surrounding the crystallites.

5. The major importance of aging, particularly for small-strain mechanical properties such as creep compliance, lies in the enormous but predictable increases in the relaxation times for the very limited segmental motion of the polymer chains which is still possible below the GT. For small strains, within the linear range, all relaxation times increase by the same factor at any given age, allowing creep and stress relaxation curves at various ages to be superimposed on each other by appropriate shifts along the time axis. A 'master' creep or relaxation curve can be constructed. Using more recent terminology, below the GT the development with age of these properties is predictable through a 'scaling' law, which amounts to a rescaling of the time axis with age-dependent scale factors.

6. All glassy polymers and a range of other materials apparently age in a similar way, irrespective of the details of their composition. This 'universal' behaviour seems to be a further aspect of the universality of the dynamics of the glass transition, outlined above, and implies that aging is an inherent feature of 'glassiness' which is not influenced by structural detail.

EXPERIMENTAL ASPECTS

Material

The material tested was a 210 g/m^2 commercial linerboard, 340μm thick, composed of a mixture of long-fibre kraft and short-fibre NSSC pulps.

Creep Measurement

Tensile test geometry was used for the obvious reason that it is experimentally simple. It is also perfectly adequate for demonstrating the effects of a basic process related to the molecular dynamics of polymer networks and disordered materials. The effects of aging will also manifest in compression, shear and torsion.

Tensile creep experiments were done at 23°C and 50% RH on CD strips of 15mm width and 157mm gauge length, using dead weight loading. Strain was measured with a linear variable differential transformer with 0.1μm measuring repeatability; the strain data were logged into a computer. The constant applied load was 40% of the breaking load, at the limit of the proportional region. The initial strain under these conditions was 0.40%. The constant load was approached at a 15% per minute strain rate.

Stress Relaxation

Tensile stress relaxation was measured on MD strips of the same dimensions as in the creep measurement, using an Instron Model 4501 Testing Machine, again at 23°C and 50% RH. The constant applied strain was 0.43%, close to the proportional limit. The constant strain was approached at the rate of 3% strain per minute.

Moisture Measurement

Isothermal sorption and sorption-rate data were obtained with a Cahn 2000 Recording Electrobalance, with flow-through of air of controlled relative humidity.

Relative Humidity Control

Relative humidity in the Cahn balance and in the sample space of the DMTA was controlled with a flow-through of air of accurately known and selectable humidity. The humid air was supplied from a Tecnequip Enterprises RH generator.

The generator works on the principle of precise division of a flow of dry air into two streams, using critical flow nozzles. One stream remains dry, while the other is fully saturated with water vapour. The two streams are then rejoined; the flow ratio in the streams determines the RH of the air mixture. RH is selectable between 0 and 100% in 5% steps, or between 1 and 99% in 1% steps. Typically an air flow rate of approximately 10 litre/minute was used in our experiments. The internal volume of the sample spaces in the Cahn balance and the DMTA is approximately 0.5 litre; RH changes are therefore rapid.

Dynamic Mechanical Thermal Analysis

This technique, also known as mechanical or relaxation spectroscopy, is a powerful method for characterising the time-dependent mechanical properties of viscoelastic polymers and locating strong relaxations, such as the glass transition, in the temperature and the time/frequency domains (1). A sinusoidally varying stress is applied to the sample, in some appropriate geometry. The strain response is resolved into components in-phase and out-of-phase with the stress. The in-phase component represents the elastic response, characterised by an elastic or storage modulus, and the out-of-phase component represents the dissipative response of the material, characterised by a loss modulus. For tensile or bending geometries, these moduli are usually denoted by E' and E", respectively. The dissipative response is commonly presented as a loss factor or coefficient, $\tan\delta$, where $\tan\delta = E''/E'$ and δ ($<90°$) is the phase lag of the strain with respect to stress.

The apparatus used in the present study was a Polymer Laboratories "Dynamic Mechanical Thermal Analyser" (DMTA). The particular instrument head used applies a strain-controlled sinusoidal load in bending mode with single or double-cantilever geometry. Strain frequency is variable between 0.01 and 200 Hz in 16 steps and peak-to-peak strain amplitude can be varied between 11 and 256μm in 10 steps. Temperature is controllable between -150 and +300°C. Entrance and exit ports allow gases or humid air to be introduced into the sample environment. Instrument control and data logging and analysis are done by a computer. Data logging is done at time intervals commensurate with the frequency used and signal-to-noise limitations.

RESULTS AND DISCUSSION

De-aging Processes

The samples used in this study were stored undisturbed under standard atmospheric conditions of 23°C and 50% RH for a minimum of 6 months, except where stated otherwise. Hence the term 'old' is taken to mean an age of 6 months or longer. Two de-aging regimes were used prior to beginning any experiment in which age was a variable. One is based on the de-aging method used by Struik (12) in his studies of the aging of polymers: the sample is taken up through the GT and brought back down through the GT. For synthetic polymers this is conveniently done by heating above T_g, followed by 'quenching' to any desired temperature below T_g. The zero of age occurs as the sample temperature falls below T_g. For paper, T_g depends strongly on moisture content, i.e. plasticiser content. Borrowing from the discussion of the GT in paper given later in this work, a value $T_g \approx 23°C$ is assumed when the moisture content is in the range 11 to 13%, probably around 12%; higher moisture content lowers T_g. All that is needed, then, to take the sample above the GT is to increase its moisture content above this level. Accordingly, a regime was adopted where the sample is exposed to 100% RH for 1 hour, followed by a return to 50% RH conditions. The time of the initial re-exposure to 50% RH is conveniently taken as zero age. The error involved in this is small, since it takes only about 3 minutes for the moisture to fall below 12%. Curve 1 of Fig.1 shows the time variation of moisture content which takes place during this procedure. Note that if this de-aging regime is repeated 'soon' after requilibration at 50%, curve 2 is followed. This will be discussed further in the section, below, on the effect of aging on sorption rate.

The youngest age at which tests were performed was 0.032 days, or about 45 minutes. The sample is still about 0.3% above its equilibrium moisture at this time, so there may be a small moisture contribution to the results for this age. It should be noted, however, that the ISO specification for the control of conditioned test rooms permits a RH variation of ±2%, which corresponds to a moisture variation of ±0.3% for a typical paperboard.

FIGURE 1

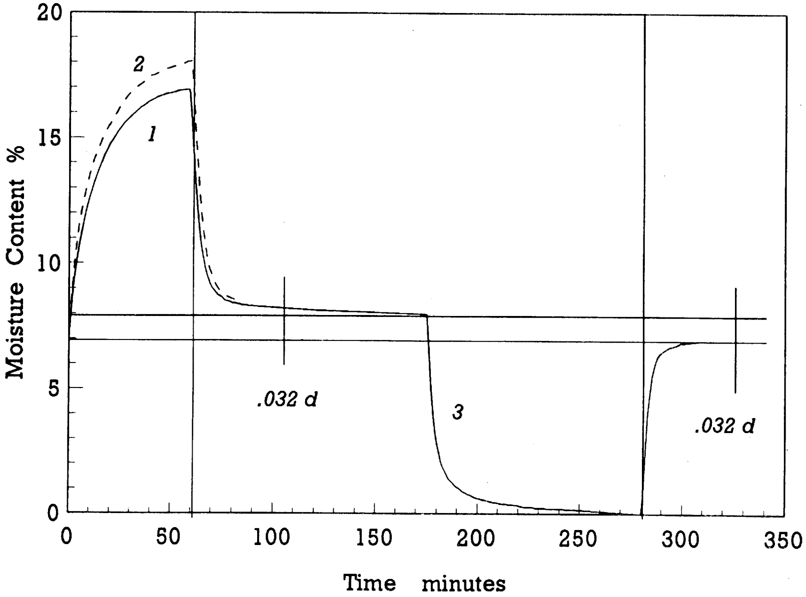

Fig. 1 Time variation of sample moisture content during two types of de-aging regime used in this study. Curve 1: moisture change during de-aging of an 'old' sample by exposure to high RH. Curve 2: effect of a second de-aging. Curve 3: moisture change during de-aging by exposure to 0% RH.

The other de-aging regime used is not at all explicable in terms of the GT, but simply relies on the assumption that any sorption, even desorption, generates some increase in free volume in the cellulosic polymer network. The assumption is based on evidence presented previously (2) that both adsorption and desorption result in mechano-sorptive transient responses in paper in dynamic mechanical measurements. It was proposed that these transient responses were in fact real-time manifestations of the de-aging/re-aging mechanism. The regime involves exposure of the sample to 0% RH for 1 hour, followed by re-equilibration to 50% RH. The time variation of moisture in this procedure is also shown in Fig.1 (curve 3). Adsorption at 50% RH is so rapid that the sample is effectively at moisture equilibrium well before age 45 minutes or 0.032 days.

Stress Relaxation and Creep

Following de-aging of a sample, it was allowed to age for a selected period before testing. The duration of all stress-relaxation and creep measurements was kept to a maximum of 20% of the previous aging time, in order to minimise the effect of aging during the actual test. For stress relaxation, the maximum testing time was limited to 10 hours by the software used. This limitation is being rectified.

MD tensile stress relaxation results are set out in Fig.2. Figure 2(a) shows the effect on relaxation at age 0.032 days of repeated high-moisture de-aging of the same specimen. The result is highly reproducible. Small variations may be contributed by the absence of extensometer control of the Instron crosshead, although crosshead positioning itself is accurate to 1 micron. The enormous increase in the relaxation rate and the large decrease in relaxation modulus compared to the 'old' sample is also apparent. Some of the change must be due to the removal of dried-in strains from the old sample and the approximately 1% higher moisture in the de-aged sample ascribable to sorption hysteresis. The reproducibilty on repeated de-aging implies that a single exposure to high RH is apparently sufficient to remove the internal strains imposed during drying on the paper machine.

FIGURE 2

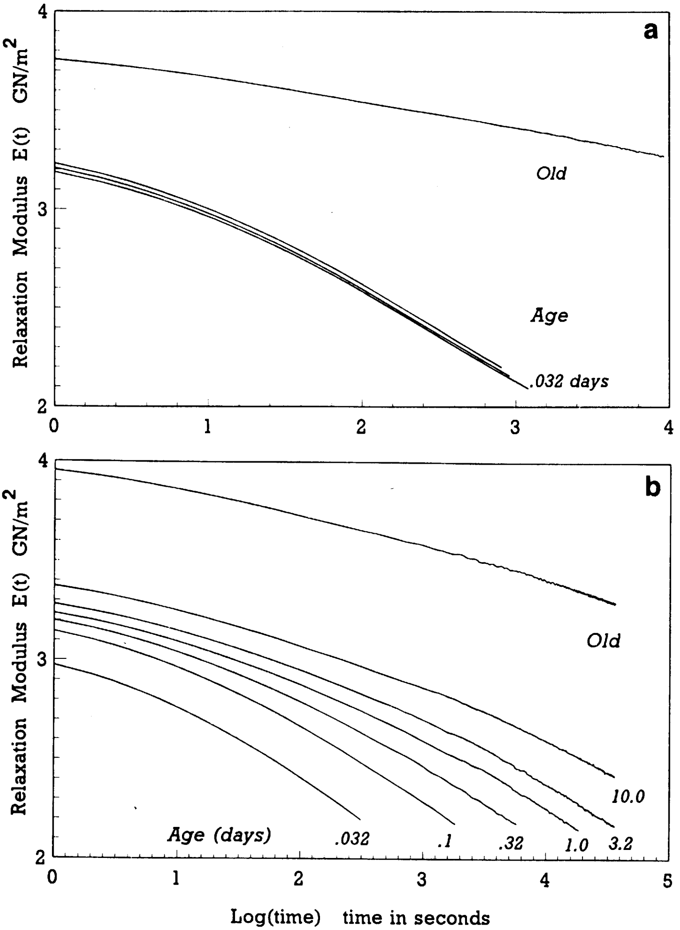

Fig. 2 Dependence of MD relaxation modulus on age, following high-moisture de-aging. (a) Effect of repeated de-aging on relaxation modulus at age 0.032 days. Sample age before de-aging was >6 months ('old'). (b) Effect of increasing age, up to 10 days. Each aging period was preceded by de-aging at high moisture. (a) and (b) refer to different specimens.

Figure 2(b) shows the effect of aging on MD stress relaxation modulus. All the results again refer to a single specimen, which was de-aged by exposure to high moisture following each relaxation test. The regularity and the enormity of the dependence on age will be discussed in more detail together with the creep results, below. However, the approximate shift down the relaxation time axis by one decade of time for each decade increase in age is apparent. On this basis the relaxation curves for ages 32 days and 100 days are quite predictable and experimental verification of this is anticipated with some confidence.

The results of CD creep tests following de-aging are shown in Fig.3. For the behaviour illustrated in Fig.3(a), the same specimen was de-aged at high moisture several times, each de-aging being followed by aging and testing. The same procedure was carried out on another specimen, with de-aging by exposure to 0% RH. The results are presented in Fig.3(b).

The effect of de-aging at 0% RH is not as strong and the aging process appears not to persist for a long time, but it is remarkable that it exists at all. However, it is consistent with the earlier finding (2) that desorption as well as adsorption results in transient property changes in dynamic mechanical measurements. In terms of the free-volume model the result implies that there is an increase in free volume on moisture desorption, whatever the mechanism may be. The evidence is mounting for the proposition that any moisture sorption causes some de-aging.

The extremely strong effect of de-aging at high moisture, i.e. by crossing the GT, and the subsequent re-aging is evident for creep compliance just as it is for relaxation modulus. This is hardly surprising since both are governed by the same molecular relaxation mechanisms. To a good approximation, for both creep and stress relaxation, the curves at different ages can be superimposed on each other by horizontal shifts along the logarithmic experimental or loading time axis and it is also possible to construct a so called 'master' curve. Small vertical shifts are also required. The necessary shift factors do not vary quite as regularly with age as in the studies by Struik (12) for other polymers, probably because of small variations in the method of initial loading of the samples. However the pattern and the magnitudes are similar.

FIGURE 3

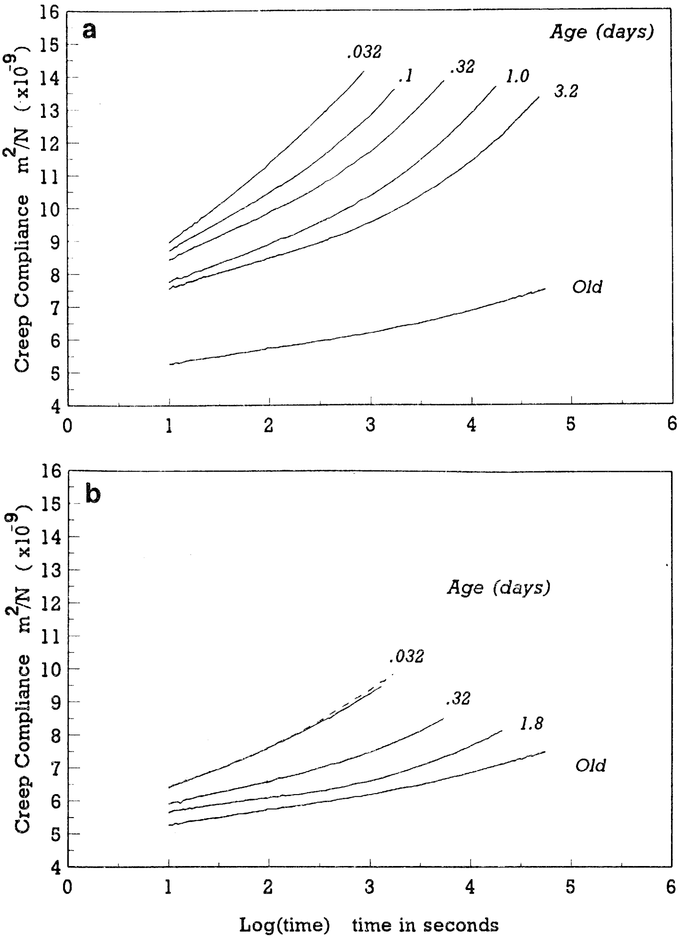

Fig. 3 Dependence of CD creep compliance on age. (a) Effect of de-aging, followed by aging, up to 3.2 days. Each aging period was preceded by de-aging at high moisture. (b) Effect of de-aging at low moisture, followed by aging, up to 1.8 days. Successive creep measurements at 0.032 days show the reproducibility of the de-aging effect.

Specifically, if t is the creep time and t_e is the time elapsed since de-aging, i.e. the aging time, then in comparing the creep compliance C(t) at two different ages t_e and t_e':

$$C_{t_e'}(t) = C_{t_e}(at) \qquad (2)$$

where a is a time-scaling factor which depends on t_e and

$$a > 1 \text{ for } t_e' < t_e$$
$$a < 1 \text{ for } t_e' > t_e.$$

Creep curves at different ages can therefore be superimposed by an appropriate rescaling of the time axis. Since the creep time is represented logarithmically, the horizontal components of the shifts are simply loga and are positive for a shift to the left and negative for a shift to the right. In other words, creep accelerates on de-aging and decelerates on aging. The same is true for stress relaxation.

Inspection of the families of curves in Figs 2(b) and 3(a) reveals that

$$\mu = -\frac{d \log a}{d \log t_e} \sim 1 \qquad (3)$$

where μ is a double-logarithmic shift rate, and this has been found to be true for all glassy polymers in the aging range below the GT, provided they are far from equilibrium (12). Struik argues persuasively that this is a result of an increase in molecular relaxation times in direct proportion to the aging time. In addition, all the relaxation times in the relaxation spectrum, or the retardation times in the retardation spectrum of the material, must change with age by the same factor, otherwise the shape of the curves would be affected by age.

The magnitude of the aging effect is best conveyed by specific examples from the results. At, say, 1000 seconds after loading, creep compliance is lower and relaxation modulus is higher by ~60% for a sample at age 3.2 days compared to one at age 0.032 days (45 minutes). On the time scale, the differences are far greater. For every increase in age by a factor 10 the molecular relaxation times increase by the same factor and the creep or stress relaxation curves move by a decade along the log(time) axis. Molecular relaxation times at age 3.2 days are 100 times slower than at age 0.032 days. It is unfortunate that these beneficial effects of aging are easily lost through a moisture sorption process.

Both creep and stress relaxation curves can be fitted by the stretched exponential or Kohlrausch law of equation (1) (for creep the exponent is positive), and particularly well for the time interval above about 100 seconds, with the stretching parameter β in the range 0.05 to 0.06. This differs markedly from $\beta \sim 0.3$ found for other materials. The difference is not understood at present, but may be related to the crystallinity and plasticisation of paper.

Ring Crush

In work done by E. Zubryn of this laboratory, the effect of aging on CD Ring Crush was observed over a 10 month period, at 23 °C and 50% RH. The results are reproduced in Figure 4, with the permission of the originator. The first measurement was made within hours of the manufacture of the linerboard. De-aging was not done in this work; it is simple to demonstrate, however, that high-moisture de-aging decreases the RC value.

The increase in RC value of about 10% over the 10 month period is not a strong effect. A similar increase in extensional stiffness was also noted (not shown). However, it is remarkable that the aging effect is detectable at all in such a test. The applied strain is very large and the result is an indication of large-scale structural failure. The strain rate is such that only local modes of molecular relaxation with short relaxation times are activated in the test, rather than the slower longer-range cooperative modes, to the extent that they still exist below the GT. The response of the sample in the early phase of the test is likely to be predominantly elastic. The elastic moduli of partially crystalline polymers do not generally undergo a strong change through the GT and therefore their further slow change below the GT will be small.

FIGURE 4

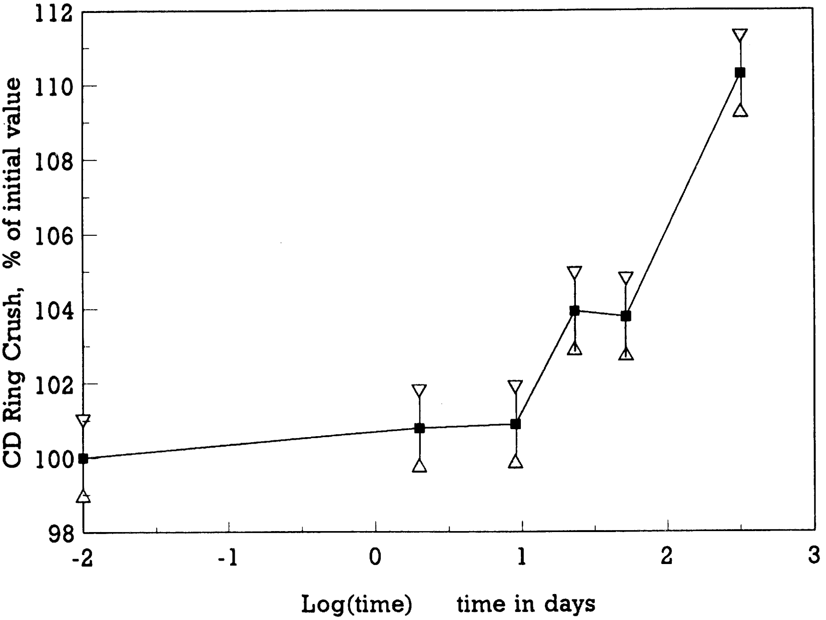

Fig. 4 Increase in CD Ring Crush with age over a 10 month period, starting on the day of manufacture of the paper on the paper machine.

Moisture Sorption Rate

An increase in free volume in the molecular network through de-aging should also affect the diffusion rate of gases and vapours through the network. In particular, changes in the diffusion coefficient of water vapour should be measurable through changes in the sorption rate. This is demonstrated in Figure 5 which shows the effect of de-aging and aging on adsorption and desorption.

FIGURE 5

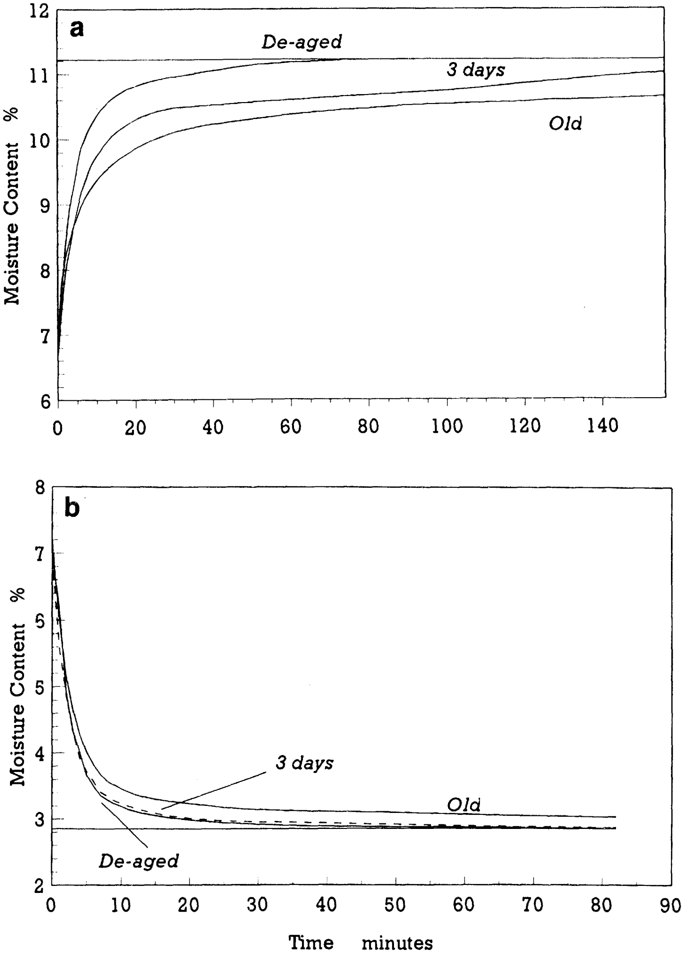

Fig. 5 Influence of age on rate of moisture sorption. (a) Moisture change on RH change from 50 to 80% for a specimen at age >6 months, after de-aging and at age 3 days. De-aging was done at 100% RH. (b) Moisture change on RH change from 50 to 10% for a specimen at the same ages as for (a), with de-aging done at 0% RH.

Figure 5(a) illustrates the strong effect of age on adsorption rate following a step change in RH from 50% to 80%. For the 'old' sample the rate is slow and the equilibrium value indicated by the asymptote was not reached in 6 hours of observation. The sample was then de-aged by increasing the RH to 100% and allowing the moisture content to rise to about 16%. Subsequent exposure to low RH prior to re-equilibration at 50% RH then ensured that the initial moisture content of the now 'young' sample was the same as in its previous 'old' state. On renewed exposure to 80% RH the sample reached equilibrium rapidly. The same procedure was then followed, but the sample was allowed to age at 50% RH for 3 days prior to testing. The approach to equilibrium was found to be slower, consistent with the older state of the sample.

Figure 5(b) shows the result of a similar series of tests, this time for desorption from 50% to 10% RH. De-aging for these tests was done by exposure to 0% RH after each test, followed by equilibration at 50% RH. The differences in desorption rate between the young, old and intermediate states is now smaller. However, the 'old' state is recovered more slowly, which is not consistent with the creep experiments with 0% RH de-aging. This difference is not understood at present.

These results lend further support to the free-volume model for aging and de-aging and to the proposition that both adsorption and desorption increase the free volume. The results may also have implications not only for moisture conditioning of paper, involving sorption rates on a relatively long time scale, but also for converting processes such as adhesive bonding, particularly those relying significantly on vapour-phase transfer of moisture, involving sorption rates on a short time scale. A detailed study of the effect of age on the initial, rapid, sorption rate has yet to be made.

Glass Transition in Paper

The central role of the GT in these discussions poses the obvious question: where is it? There is little information in the literature on the GT in paper and its dependence on moisture content. The 1980 work of Salmén and Back (13) is still the most informative, as far as we are aware. They measured the elastic modulus for a kraft paper over a range of temperatures and moisture contents, and were able to deduce the value of T_g at several moistures. The results were consistent with their theoretical calculations which were done according to a method due to Kaelble (14).

Based on the data provided by Salmén and Back, and assuming crystallinity between 50% and 60% for the linerboard used, T_g should be 23°C for moistures between 13 and 11%. For 55% crystallinity, the following values would be expected:

T_g (°C)	Moisture Content (%)
55	7
23	12
-10	16

Experimental verification by direct measurement was attempted, using dynamic mechanical thermal analysis (DMTA) or relaxation spectroscopy. This is a sensitive technique for the measurement of molecular transitions and relaxations. At T_g there is a change in the gradient dE'/dT and tan δ(T) goes through a maximum. T_g also depends on the frequency of the sample oscillation, going to lower temperatures at lower frequencies, i.e. longer experimental time scales.

Two methods of approach are possible, given satisfactory techniques for achieving them. One is a temperature ramp at constant moisture, the other a moisture ramp at constant temperature. Both methods were attempted. Keeping the sample moisture constant at varying temperature was an ambitious undertaking which did not quite succeed, but is continuing. Samples were extrusion coated on both sides with 20μm thick polyethylene, cut to specimen size, conditioned to the desired moisture by edge diffusion, then saturated with inert silicone oil, again by edge diffusion. Temperature intervals appropriate to the moisture content were scanned at 1°C/minute, spanning the range -40 to +60°C, at frequencies between 0.1 and 10 Hz. The GT for the paper could not be identified due to complicating factors related to interference from a broad but weak GT in polyethylene at -20°C, viscous effects from the silicone oil, and slow moisture losses through the sample edges.

FIGURE 6

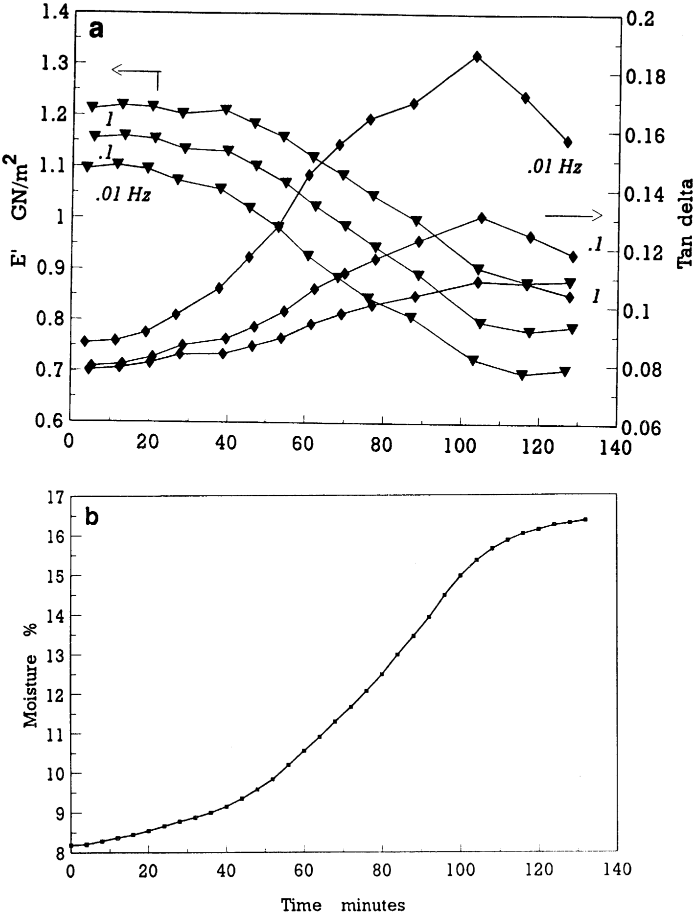

Fig. 6 (a) Storage modulus, E', and loss factor, tan δ, for a sample subjected to steadily changing moisture, as shown in (b). Frequencies: 0.01, 0.1, 1 Hz. Sample width 10mm, span 2mm, single-cantilever bending geometry, 0.36% maximum strain.

Moisture ramping at 23°C was easier to perform, by increasing the RH in the DMTA by 1% every 2 minutes, from 50 to 99% RH, using a flow-through of humid air from an RH generator. The moisture ramp was very slow in order to avoid the generation of mechano-sorptive transients in the sample response. The results are shown in Figure 6. The variation in moisture content of the sample with time in Fig.6(b) can be used to determine the moisture content of the sample in the DMTA at any desired time.

In Fig. 6(a), the onset of the rise in tanδ and fall in E' at all frequencies coincides with the onset of moisture rise. The tanδ maxima and the levelling out of E' at high moisture coincide with the decline in the moisture ramp at high moisture. Tanδ actually falls at high moisture.

These observations indicate that the observed behaviour is due to a combination of a mechano-sorptive effect, ie. free-volume generation, and both a general (plasticisation) and the sought-for moisture-content effects. The glass transition seems to be obscured in the process. The humps on the rising slopes of the tanδ curves are in the right moisture range for the GT, but they occur over the same moisture range at all three frequencies (0.01, 0.1, 1 Hz), which makes their identification as a transition doubtful.

It must be concluded that direct verification of the expected location of the GT has not been successful at present and further work is required.

CONCLUSIONS

1. Physical aging in paper is an important but unrecognised phenomenon. It is a long-term configurational relaxation of the molecular network occurring below the glass transition, and has serious short-term consequences in many situations.

2. It has been shown in this work that physical aging in paper conforms to the 'universal' pattern characteristic of the glassy state while it is far from equilibrium. These characteristics are a strong time or age dependence of some properties, particularly small-strain mechanical behaviour such as creep and stress relaxation, reversibility, scaling behaviour with a double-logarithmic shift rate of about 1, and

relaxation which follows a stretched exponential or Kohlrausch law. Paper differs from other glassy polymers in the value of the stretching parameter, and in its sensitivity to de-aging when plasticising water molecules are exchanged with the environment.

3. Physical aging and de-aging have a strong effect on the rate at which paper sorbs moisture. Sorption rate decreases with aging. This may have important consequences for conditioned testing and for converting processes which are influenced by vapour-phase exchange of moisture between paper and other materials, e.g. corrugating adhesives.

4. The drying of paper on a paper machine may be regarded as a 'quench' though the glass transition, during which imposed configurational constraints are 'frozen' in. Aging begins at this time. However, both the effects of aging and the frozen-in strains are easily reduced or removed by moisture sorption. Evidence has been presented that desorption as well as adsorption is a de-aging process. The practical consequences of highly accelerated creep and stress relaxation rates following de-aging can be profound in many situations, for example in the compression-creep failure of corrugated boxes. The 'runnability' of paper webs in converting operations may also be affected.

5. In the comparative testing of paper materials and structures, for creep, stress relaxation and properties which are known to be markedly viscoelastic or strain-rate dependent, age is a parameter as important as temperature and RH.

6. Extensive further work is required to clarify issues such as the location of the glass transition, expected to be 23°C at about 11-13% moisture for the paper used in this study, the effect of temperature, the effect of aging and de-aging under load, the limits of the aging range, and the possibility of other de-aging processes.

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Transcription of Discussion

PHYSICAL AGEING AND GLASS TRANSITION: EFFECTS ON THE MECHANICAL PROPERTIES OF PAPER AND BOARD

V Padányi

ERRATA

1. On page 525, equation (1), the negative sign should be outside the parentheses, i.e.

$$f(t) \quad \alpha \quad \exp - \left(\frac{t}{\tau} \right)^{\beta} \tag{1}$$

2. On page 536, paragragh 2, replace '100 seconds' by '10 seconds' and replace 'β in the range 0.05 to 0.06' by 'β in the range 0.14 to 0.16'.

ADDENDUM

Additional stress-relaxation data and a quantitative analysis of the relaxation data were presented at the symposium. This new material is set out below.

Figure 7 re-presents the relaxation data of Fig.2(b), together with relaxation curves for ages 31.4 and 100 days. These two curves have fallen in their predicted positions, where the prediction was based on shifting of curves measured at lower ages to the right along the time axis, using shift factors calculated from the data.

FIGURE 7

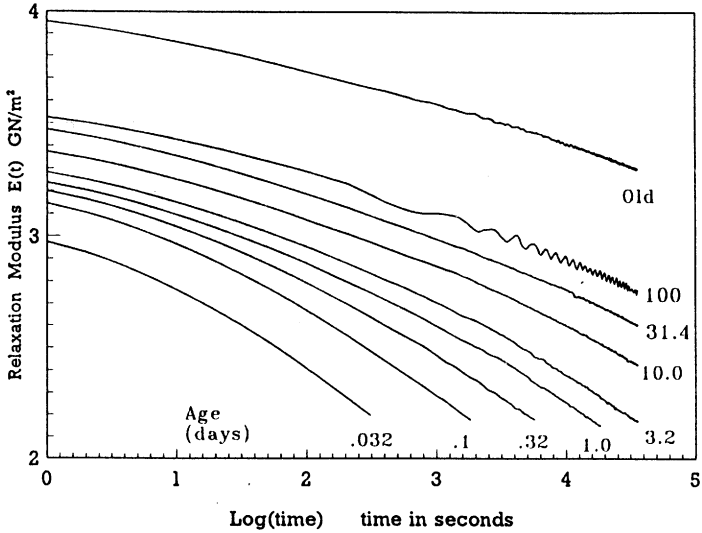

Fig.7 Data of Fig.2(b), augmented by relaxation curves for ages 31.4 and 100 days. The sinusoidal variation in the 100 day curve was caused by a sinusoidal oscillation in the test-room RH during the experiment, with period 24 minutes and peak-to-peak variation in RH of ~1.5%.

With one exception, the data on each curve can be fitted very well to the Kohlrausch 'stretched' exponential relaxation law of equation (1), where f(t) is the relaxation modulus E(t). The exception is the curve obtained for the 'old' state of the specimen, prior to the first de-aging; the presence of dried-in strains in this state may be the reason for the different behaviour. The parameters required for fitting the data are the initial relaxation modulus, E(0), which is the proportionality constant, the characteristic relaxation time, τ, and the stretching parameter, β. The fitted values of these parameters are set out in Table 1.

The data in the table reveal several interesting features. A single relaxation time is sufficient to describe the relaxation process, at least over the time interval of the experiment. An assumption of complex behaviour involving several or many molecular relaxation modes and a spectrum of relaxation times is therefore not necessary.

TABLE 1

Age days	E(0) GN/m ^{2}	τ days	β
0.032	3.38	0.16	0.153
0.10	3.34	1.25	0.153
0.32	3.39	4.0	0.153
1.0	3.37	12.5	0.153
3.2	3.36	35	0.153
10.0	3.32	140	0.153
31.4	3.40	370	0.142
100.0	3.62	1200	0.142
Old	?	?	?

Table 1 Parameter values required to achieve a very good fit of the stress relaxation data to the Kohlrausch law, equation (1).

The characteristic relaxation time is directly proportional to the specimen age, to a good approximation; the proportionality constant is about 12. This can be seen by inspection of the table and is also demonstrated in Fig.8, which plots log τ versus log(age). The plot approximates a straight line with gradient 1. The only major deviation from the straight line occurs for age 0.032 days (46 minutes). This is the experimental point most sensitive to a correct identification of the sample age, i.e. to the correct choice of zero for the aging 'clock'. For convenience this was chosen arbitrarily to coincide with the removal of the specimen from the 100% RH atmosphere in the de-aging process. Since rapid desorption is taking place for several minutes after this event, and desorption is also a de-aging process, this choice for zero age is clearly incorrect. The deviation from linearity is corrected if the specimen age for this point is assumed to be 20 minutes. This puts the onset of the aging process at 26 minutes after removal from 100% RH. Curve 1 of Fig.1 shows that this time agrees well with the end of the rapid part of moisture desorption, not far from moisture equilibrium, with further desorption towards equilibrium occurring much more slowly. It is reasonable to expect aging to begin at about this time. What, if anything, happens to the aging process while the relaxation (or creep) experiment is proceeding will need to be considered in further work.

FIGURE 8

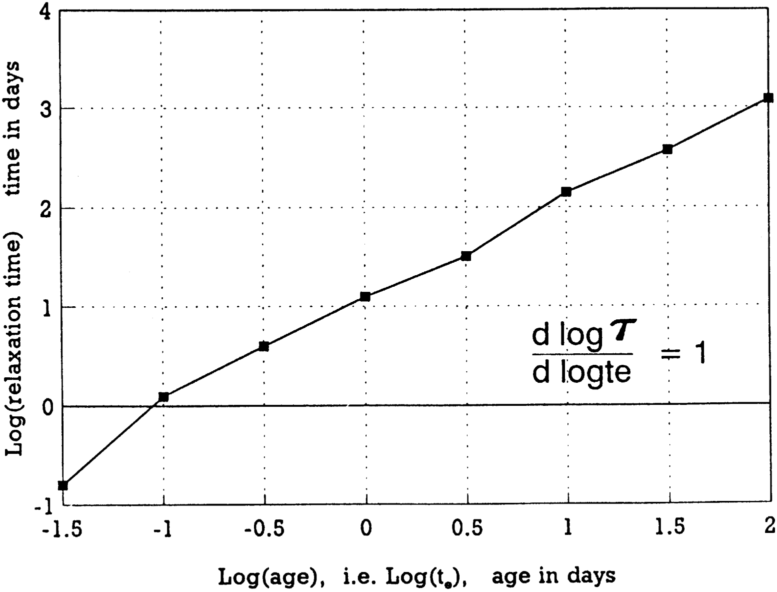

Fig.8 Dependence of relaxation time, τ, on age, t_e, for the relaxation curves of Fig.7.

Comparing the gradient, $d \log \tau / d \log t_e = 1$, with the relation of equation (3), it is clear that the shift factor or time-scaling factor, a, is inversely related to the relaxation time, τ. This is a perfectly sensible result and it is actually the reason why time-age superposition works, and it is also the reason why time-temperature superposition works for amorphous polymers above the glass transition.

The stretching parameter, β, has the value 0.153 for relaxation data up to and somewhat beyond age 10 days and changes to 0.142 by age

31.4 days. The sensitivity of the fit does require 3 decimal places. The change in β is puzzling and may be related to the choice of the zero of time in the relaxation experiment, i.e. should t=0 be at the beginning or at the end of the loading phase? This question is expected to be resolved by current work, together with more general questions such as: Does β have a 'universal' value, or a narrow range of values, for paper? How is it affected by stress and environmental conditions?

The success in describing the stress-relaxation process with the Kohlrausch law permits a very convenient, if unusual, way of plotting the data on a 'master' curve. If ln(-ln(E(t)/E(0))) is plotted against ln(t/ τ), then all curves with the same value of β should lie on a straight line of gradient β. This is shown in Fig.9.

FIGURE 9

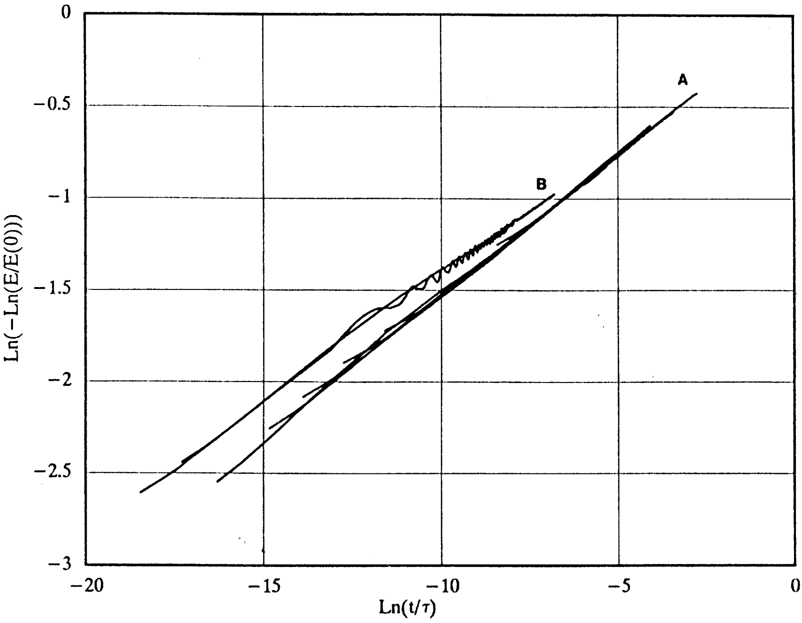

Fig.9 Master curves for the MD stress-relaxation data. Line A, of gradient 0.153, is the master curve for ages from 0.032 to 10 days. Line B, of gradient 0.142, is the master curve for ages 31.4 and 100 days.

A similar analysis can be done successfully for the family of creep curves shown in Fig.3(a), which has since been extended to age 32 days.

In view of the expected generality of the behaviour described above, future work will need to investigate a connection with another general result for stress relaxation, in a range of materials including cellulose, paper and wood, found by J.Kubát and co-workers (15,16,17,18). In the absence of internal stresses, the maximum or inflexion slope of the stress-log(time) curves is equal to one tenth of the total decrease in stress. In terms of relaxation modulus:

$$\left[\frac{dE(t)}{d(\ln t)}\right]_{\mathrm{max}} = (0.1 \pm 0.01)\Delta E, \qquad \Delta E = E(\infty) - E(0). \tag{4}$$

The beginnings of a connection can be made by noting that for the Kohlrausch law:

$$\left[\frac{dE(t)}{d(lnt)}\right]_{\mathrm{max}} = -\frac{\beta E(0)}{e}\ . \tag{5}$$

If it is assumed that E(∞) = ½E(0), which needs to be investigated experimentally, then:

$$\left[\frac{dE(t)}{d(lnt)}\right]_{\mathrm{max}} = 0.104\ \Delta E, \qquad \textit{for}\ \beta = 0.142$$

and

$$\left[\frac{dE(t)}{d(lnt)}\right]_{\mathrm{max}} = 0.110\ \Delta E, \qquad \textit{for}\ \beta = 0.153.$$

The molecular mechanism behind the phenomenon of physical aging and the analysis provided above, continues to be visualised usefully in terms of the qualitative free-volume model outlined in the body of this paper. However, alternative models may make useful contributions; for example, the role of crystallite formation and melting, and the part played by the movement of water molecules in this, needs to be considered. Ultimately, the most general and valid approach may be from the consideration of paper as a non-equilibrium dissipative structure (19).

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Dr R Popil, MacMillan Bloedel Research, Canada

I was wondering how were you able to deduce that the glass transition temperatures were so low, for instance, on page 540 of the text at a moisture content of 12%, the glass transition temperature is 23°C., and you are quoting the work of Salmen and Back. As recently as this morning we have had Fig. 24 (Page 406) presented for example by Lennart Salmen, where the glass transition temperature at 10% moisture is of the order of about 90°C or so. How do you account for your discrepancy in terms of high glass transition temperatures of about 100°C or so for a moisture content of 10%?

V Padányi

Well, the glass transition temperature I assumed, 23°C at 12% moisture, is based totally on that work by Salmen and Back. I have no other source of information. The results presented this morning are entirely new to me. If the glass transition temperature is not around the 12% mark at room temperature, then that explains why I can't find it.

Dr L Salmén, STFI, Sweden

Just a point of clarification. The figures that you have given for the glass transition are comparable to the ones in my presentation (see figure 8, p383) because yours refer to the conditions in the paper and the ones I have given are for the pure materials. However, one must recognise when measuring in this complicated paper system that the glass transitions for carbohydrates are very broad and may be difficult to detect.

As I have the opportunity I may now ask you. In your diagram where you have plotted 'Tan delta' as a fraction of time under moisture uptake (Figure 6(a), p 541) you have a very peculiar change in the strength of the 'Tan delta' with frequency; could you explain why this is happening - why is 'Tan delta' increasing with decreasing frequency?

V Padányi
Well this is one of the reasons that I am assuming that this is not a glass transition. In a glass transition you do expect the amplitude of the "Tan delta" peak to be frequency independent. These "Tan delta" curves are more reminiscent of what you get in a melting process rather than in the glass transition process. This is one of the problems I have, just like you. I don't really know why I am getting this unexpected frequency dependence unless we are really looking at some sort of melting of the crystallites in this process, which then reform during the ageing process. That is a very complex subject, that is, the role of water molecules in crystallite formation. All the information I have on that, and there is not much of it, is about the ageing and staling of bread - it is the same sort of process.

J F Waterhouse, Institute of Paper Science & Technology, USA

I have trouble with the term "ageing", in fact after your last presentation in Hawaii I looked at a number of standard text books on polymer science and did not see this. I wonder if "annealing"/toughening may be more suitable terms. How did you come up with the term ageing? The other point I would like to raise, you mention J. Kubat's work and I remember the constant of 0.1 (and I can't remember the other two sides of that relationship), but it would be interesting to hear your connection between Kubat's work, which obviously deals with stress relaxation.

V Padányi

The term physical ageing is very commonly used in the polymer literature for this process, for this change in the viscoelastic properties of plastics and other synthetic polymers and is a standard term, so that is obviously where I got it from. It is in the literature, but if it is confusing I apologise. I borrowed the term from elsewhere. There is also a text book on the subject entitled "Physical Ageing in Amorphous Polymers and Other Materials" by Struik (Ref. 12).

(The Chairman took the next question at this stage, and there was no opportunity to discuss the relationship to Kubat's work. This is addressed in the addendum to Dr Padányi's paper)

Prof E Back, Feedback Consulting E&E Back KB, Sweden

I enjoyed your experimental data. Let me comment on your last question "alternatives to physical ageing". Chemical ageing as I understand it, is auto crosslinking of cellulose and hemicelluloses and linear lignin in the cellulosic material. With time it will have just the same effects as you have shown here today. It will reduce the moisture absorption rate, and will affect creep and stress relaxation in the way you have shown here. Due to swelling forces, most of these bonds can be broken on humidification. We can promote or reduce the rate of chemical ageing by chemical means* so I would like to encourage you to do a few experiments to differentiate between chemical ageing and physical ageing by promoting the chemical ageing and reducing it. That is one way to differentiate between these two ageing methods.

* Back, E; Pulp and Paper Mag Can 68 (1967) p165

V Padányi
That is where the commercial significance lies, of course, ie what to do about all this, and I am certainly interested in your suggestion - thank you.

Dr D Page, Pulp & Paper Research Institute Canada
If you make a handsheet under normal conditions, you normally leave it to dry at room temperature and it dries rather slowly so maybe it takes 24 hours to dry - is that then an aged sample or an un-aged sample?

V Padányi
This is a question of definition - I suppose.

D Page
No, I don't mean definition, does it follow the curve of an aged sample or the curve of an un-aged sample?

V Padányi

That is a young sample. If you do the tests after specific time delays, a year even, the results will change continuously.

D Page

What effect does this have in practice on other properties such as tensile strength, tear or any other property that we tend to measure?

V Padányi

Inasmuch as many of the properties that we measure are measured at a high strain rate, then these effects are not as noticeable because the viscoelastic nature does not manifest as strongly when you are doing tests at high strain rates. In the Proceedings (Fig. 4) there is a result showing what happens to Ring Crush over a long period of about 6 months. The effect is not very strong but it is there. In fact, I was very surprised that it was there because it is not a small strain test, it is a test to destruction and it is at a high strain rate, so viscoelastic behaviour does not manifest very strongly in the Ring Crush test, as it also does not in the many other tests that we do. But, in the end use out there in the field I am sure the low strain rate performance is important. We are not measuring it routinely, unfortunately.

C Soremark, Assi Kraftliner, Sweden

These results are most interesting. I have a question of a more philosophic character because, you say there is a de-ageing occurring when you adsorb and desorb water into the paper is that correct?

V Padányi

Yes, I am trapped by my own terminology.

C Soremark

When does the ageing take place - because most of the papers are always subjected to changes in relative humidity during their lives?

V Padányi

I am saying any change in relative humidity causes a de-ageing and a consequent effect on the viscoelastic properties of the material. The ageing takes place whenever the sample or the material is left undisturbed, for example in the reel. The changes are when it comes out of the reel and if it is subjected to a moisture change as a result of environmental humidity, then it is immediately de-aged. It may not be completely de-aged but, on the free volume model, there will be an increase in the free volume and an acceleration in the creep rate and the stress relaxation rate, which can make the reel very difficult to control when you are trying to control the tension in a converting process.