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# **DEGRADATION OF THE POLYMER STRUCTURE OF WOOD BY WETTING AND DRYING. VISCOELASTICITY AND MORPHOLOGY OF THE COMPOSITE CELL STRUCTURE**

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## **ABSTRACT**

The cracking and destruction of wood by inner and outer stresses is discussed in the light of previous works and the spectral (NMR and FTIR), microscopic (SEM), and mechanical stress experiments of the authors. The physical properties of wood are compared with those of synthetic high polymers. Wood components swelling in water, such as extractives and hemicellulose and lignin and their hydrogen-bond-forming power, are important chemical factors determining the mechanical stability of wood. Anisotropic shrinking of wood cells, resulting in cracking on drying, is a time-dependent process which has few analogues in synthetic polymers and their composites. This behavior lessens considerably the areas of technical use of wood.

## **INTRODUCTION**

Wood is a high polymer composite and a versatile construction material which competes favorably with synthetic polymers and their composites. However, in many outdoor applications the use of wood is hampered by its cracking and defor-

mation on repeated drying and wetting which promote the access of microorganisms to the interior of the material. Technically, the difficulties may partly be avoided by forming wood-plastic composites (WPC) using chemical or radiation curing of polymer-impregnated wood [1].

Although the mechanism of cracking is of central importance for the practical use of wood, its origin and mechanism is still only partly resolved. In the following pages some aspects of the problem are discussed in the light of earlier theoretical and experimental findings.

### WATER IN A LIVING TREE

Water is a natural constituent of all parts of a living tree. In the xylem part forming the woody tissue, water in the form of moisture commonly makes up over half of the total weight. Thus, the weight of water in green wood is normally equal to or greater than the weight of the dry wood substance [2]. The water is partly present as free water, but also to a marked degree dissolved and associated with the other wood components [3]. Therefore it influences the physical properties of living wood. In addition to its nutrient and growth factor transport function, it also forms a lubricant for the reinforcing and supporting viscoelastic structural network.

For the stability and viscoelasticity of the living tree, certain simple regularities have been observed. For example, McMahon and coworkers found that under ideal conditions the base diameter of the trunk of a living soft wood tree is proportional to the  $3/2$  power of its height. The variation in the data was about 25% owing to growth place and other conditions. This state of neutral engineering stability of the tree at equilibrium moisture has a technical safety factor of about 4, which is surprisingly high. Wood cracks or breaks only at extreme conditions of low temperature or in strong storms and hurricanes. Technically, the wood trunk may be compared to a conically shaped longitudinally reinforced plastic and elastic composite structure lubricated with water and extractives.

### THE NONLIVING TREE

When a tree dies and a log is processed into lumber, veneer, or other technical products, the wood immediately begins to lose some of its moisture to the surrounding atmosphere. If the drying continues long enough, the dimensions and the physical properties of the wood begin to undergo changes. The physical and mechanical properties, resistance to biological deterioration, and dimension stability are affected by the residual amount of water which may fluctuate with time, temperature, and atmospheric conditions. The favorable elastic properties of living wood are also partly lost.

It is evident that the drying or wetting processes make the theoretical problem of wood viscoelasticity still more complicated. However, certain regularities have also been noted here. Thus, Ashby and coworkers [4, 5] calculated for dried cork, balsa, and other woods the moduli and other mechanical characteristics of the materials. They concluded that these can be broadly explained in terms of the deformation of the honey-comblike cell-wall structure.

When cork deforms, the cell walls bend and buckle. Tensile deformation along the cell prism axis unfolds the corrugation and straightens the prism walls. At an extension greater than 5%, the cell walls become straight, and further tension at first stretches and then breaks them. Deformation by compression, on the other hand, folds the corrugations. The folding is unstable, and at about 10% compression a layer of cells collapses completely, suffering a large compressive strain. Further compression makes the boundary of the layers propagate and the cells to collapse. According to the mentioned authors, the collapse moves through the cork structure like a Luders band through steel or a drawing band through polyethylene.

Ashby et al. calculated theoretically the moduli and collapse stresses for cork. The results compared well with experiments. In particular, they were able to explain the isotropy in the plane normal to the radial direction, the factor of two difference between the radial direction and the other two directions, the striking difference in the values of Poisson's ratio, and the elastic collapse load. Interestingly, variations in cell shape and orientation seemed to cause a discrepancy between theory and experiments in Poisson's ratios  $\nu(23)$  and  $\nu(32)$ . Interestingly, their theory is also consistent with the observation by Kelvin (1890) that a cork cube immersed in water sinks when a pressure of about 2 MPa is applied to the water.

Models similar to those described above but connected with thermal parameters have been presented among others by Salmen [6] in his thesis on the temperature and water-induced behavior of wood-fiber-based materials. Björkman [7] compared tensile strength, creep, and stiffness of wood samples from which hemicellulose or lignin were chemically extracted with the original samples. He concluded that especially hemicellulose strongly influences the mechanical properties of wood. This view, and especially the role of lignin, was newly supported by the calorimetric measurements on resin-free wood of Olsson and Salmen [8]. Basing his proposals largely on experimental material, Schulgasser [9] recently proposed that upon moistening, the expansion of wood, particle board, and paper in a certain direction is essentially proportional to the inverse of the modulus of elasticity in that direction. From the data of Gardner et al. [10] on swelling effects of solvents and the infrared spectroscopic measurements by Lindberg et al. [11], it is evident that the above phenomenon is closely related to the number of hydrogen bonds working in the structure in the direction under test.

A more detailed physicochemical study of the problem encounters some mathematical difficulties. The penetration of water and/or chemicals in the cell structure is a temperature-dependent, diffusion controlled, partly nonlinear process which strongly influences the mechanical and viscoelastic properties of wood [12, 13]. The accumulated stress relaxes upon rapid drying through extensive radial and longitudinal cracking. Similar phenomena are found in strongly crosslinked reinforced synthetic composites on swelling with solvents when the elastic strength is exceeded.

### GENERAL THERMODYNAMIC PROBLEM OF CRACKING OF MATERIALS

A discussion of the above phenomena may be based upon various theories. The most general treatment uses the first law of thermodynamics of energy conservation and the well-known Griffith fracture theory for solids [14], which seems to

be valid both for wood and synthetic polymers. The combined processes of humidity diffusion, drying, and fracture are then expressed in terms of the rates of the work input to the system being equal to the work absorbed by the system [15].

In accordance with the law of the conservation of energy, the thermodynamic requirement in a deformable solid demands that the rate of inputting work,  $dI/dt$ , plus the rate of adding heat,  $dQ/dt$ , must equal the rate of increase of kinetic energy,  $dK/dt$ , plus internal energy,  $dU/dt$ , plus the rate of work absorbed in generating a new fracture surface,  $d\Gamma/dt$ . For isothermal systems, the internal energy is composed of two parts, the intrinsic internal strain energy of deformation and the internal temperature change.

$$\frac{dI}{dt} + \frac{dQ}{dt} = \frac{dK}{dt} + \frac{dU}{dt} + \frac{d\Gamma}{dt} \quad (1)$$

From the general definition of the integrals of the above terms, it is possible to deduce the internal strain-energy rate,  $dW/dt$ , in terms of the heat flux vectors and the stress and strain tensors.

With known diffusion rate, specific fracture energy, body forces, and heat fluxes, one may solve the equilibrium and compatibility equations with boundary conditions appropriate for the given physical problem. Here it is represented by the swollen or deswollen cell wall network. The solution of the equations leads to the desired fracture criteria.

A general and working model is obtained by solving the integro-differential equations for the crack history in terms of the constitution law, the specific fracture energy, and the loading history.

It is evident that the total problem is very complicated, and many attempts have been made during the last decades to resolve the inherent mathematical difficulties in the general problem. A nice review on recent results in using thermodynamics and deformation kinetics to solve the fracture mechanics of wood has been given by van der Put [16] who analyzed the limitations of present theories and developed a general rheological model for wood. It is evident that the thermodynamic and mechanic views of wood strength are strongly interrelated, and that the semiempirical WLF equation for polymers may be partially applied, as also anticipated by Salmen. The technical problem of the structural anisotropy of wood and the uniqueness of every specimen are evidently too complex questions to be totally solved analytically. The final numerical evaluation must therefore be made by using the finite element method (FEM) or similar empirical methods of structural analysis [17].

## SIMPLIFIED TREATMENT OF TANGENTIAL DEFORMATION

In the case of the trunk of a tree with cylindrical symmetry and hexagonal cell cross sections, the mathematical treatment of the viscoelastic strength by van der Put may, for our purposes, be considerably simplified. The conditions of cracking on drying in the radial direction of a branch-free stem of wood may be roughly estimated from the following deductions made by one of us (M.L.). The following discussion will be principally limited to softwoods and especially those with heart- and sapwood.

The fiber saturation point (FSP) is defined as a state of wood where the cell wall is saturated with water (at room temperature, about 30%) but the cavities are empty. In wood with a higher moisture content ( $u$ ) than FSP at room temperature, the wood trunk is in a nondeformed state. Below this point, shrinking begins, which varies with the symmetry directions. Its magnitude, when going from 30 to 0% moisture for a softwood in Nordic conditions is 10% in a tangential direction, 5% in a radial direction, and 0.1–0.3% in a longitudinal direction.

The dimensions of a piece of wood also vary with time of growth of the section studied. Thus, the density of summer wood  $\rho/(su)$  is proportional to  $2.5 \times$  density of springwood  $\rho/(sp)$ . The shrinkage may be estimated from the approximate formula

$$AL/L = Au\rho \tag{2}$$

where  $A$  is the area of the piece of wood and  $L$  is its length.

Shrinkage is greatest in the tangential direction for the following reasons. The strongly shrinking summer wood forces the more weakly shrinking spring wood to deform in a similar manner. The shrinkage of summer and spring woods are nearly equal in the radial direction. Therefore, the cracking of the wood structure is caused by the difference in shrinkage between the tangential and radial directions.

$$dL = \frac{2\pi R[a(t) - a(r)]}{100} \tag{3}$$

where  $a(t)$  is the percent shrinkage in the tangential direction,  $a(r)$  is the percent shrinkage in the radial direction, and  $R$  is the radius.

Using a piece of maximum dimensions,  $AL = (0.3R)(0.15d)$ , where  $d$  is the thickness of the sample. The shrinkage  $AL/L$  is about 0.05.

On rapid drying (time scale: up to a few hours), the forces and moduli involved may be calculated from the usual Hooke's law,

$$\sigma = E\epsilon \tag{4}$$

where  $\epsilon = AL/L$  and  $\sigma$  is the applied force per area.

Experimentally, we know that the tangential modulus of tension is about  $E(\text{tan}) = 400$  MPa and the breaking force is  $\sigma(\text{break}) = 4$  MPa. Therefore, the maximum change in dimensions may be about  $\epsilon = 0.01$  before inner cracking of the wood structure occurs.

In a slow drying process (time scale: weeks and months), the conditions are quite different and the conditions may be roughly calculated from the viscoelastic Maxwell equation,

$$\frac{d\epsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (\text{Maxwell}) \tag{5}$$

where  $t$  is the time and  $\eta$  is the viscosity of the material.

The influence of solvent diffusion on the radial stress profile of the wood may be incorporated in the deduction using Fick's first law and, for simplicity, a parabolic radial humidity distribution in the wood trunk,

$$\frac{dm}{dt} = -D \frac{du}{dx} \quad (\text{Fick's first law}) \tag{6}$$

where  $m$  is the mass diffusing,  $D$  is the diffusion coefficient, and  $du/dx$  is the moisture diffusion gradient. Attempts to solve the entire very difficult problem have been made by several authors (cf., e.g., Ref. 23 and 24).

### MICROSCOPIC ASPECTS

The anisotropic swelling on humidification and shrinking on drying is related to mechanical, structural, and chemical factors. As mentioned above, an especially important point seems to be the FSP. To mimic the situation in a wood trunk where the dimensionally very stable softwood (pine) heartwood cylinder is surrounded by a more easily deformable sapwood core, the following experiment was performed.

We measured the tangential stress on ring-formed softwood samples prepared by a method devised by Ranta-Maunus [18] and spanned on a metal bar in a humidity chamber. We found that the cracking of the sample occurs on drying, often before the FSP. The deformation of the cell dimensions were nearly unchanged before rupture as inspected on the macro level.

Electron scanning micrographs combined with computer-aided image analysis showed, however, that the rupture nearly invariably proceeds along the middle lamella (Fig. 1) which is poor in cellulose fibers but rich in lignin and other amorphous substances. The process is very rapid and chaotically unforeseeable.

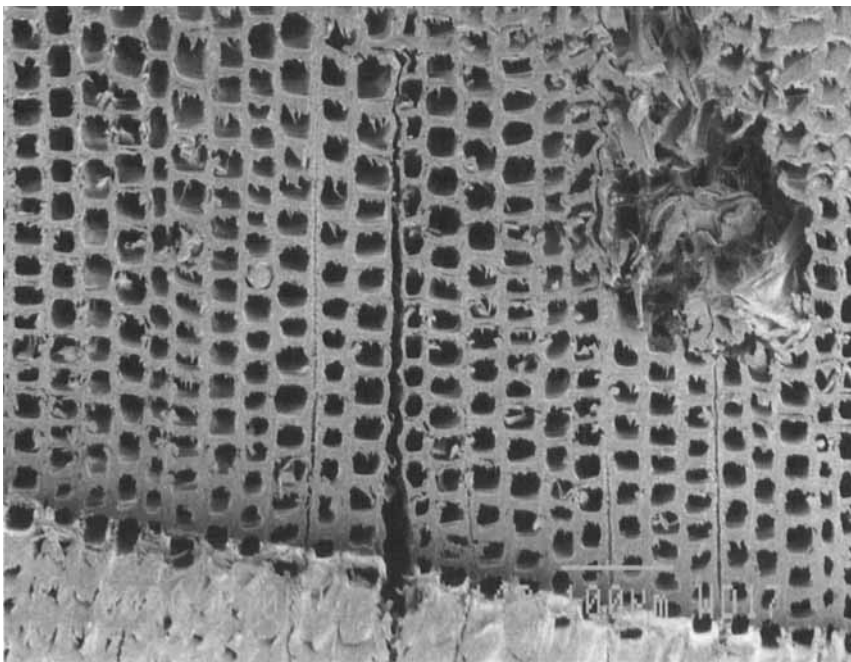


FIG. 1. SEM photograph of cracking in the middle lamella in the radial direction of a circular spanned section of drying pine wood (see text). Magnification:  $500\times$ .

For spanned samples, a statistical treatment with computer-aided picture image analysis showed that marked changes in cell dimension anisotropy was observed on the microscopic level around and before the FSP.

The dimensions of the lumen of the cells change on drying from a value of 1 for the radial to tangential diameter ratio to about 0.9.

The cell wall thicknesses in the radial direction diminished between 10 and 30%.

In the beginning the thicknesses of the radial direction middle lamellas shrunk about 30% but increased later to their original dimensions.

The cell thickness in the tangential direction decreased about 30%.

The dimensions of the resin ducts remained unchanged.

For unspanned samples a similar analysis of the general cell organization and neighbor relations of the cells by fractal number analysis also indicated marked shifts around the FSP (Fig. 2). On drying, the anisotropy of the cell diameter increased rapidly from about 40% humidity. On the other hand, the fractal number showed a minimum at about 30% humidity.

It is evident that comparatively rapid drying and deswelling (a time scale of some few hours in comparison to the technical and/or outdoor process of weeks or months) accumulates large tangential stress forces in the cell network, and these cause deformation and cracking.

### CHEMICAL AND SPECTROSCOPIC ASPECTS

The above discussions regarding the relationship between mechanical properties and the physical and chemical structure of wood have been confirmed by spectroscopic and chemical experiments on wood samples.

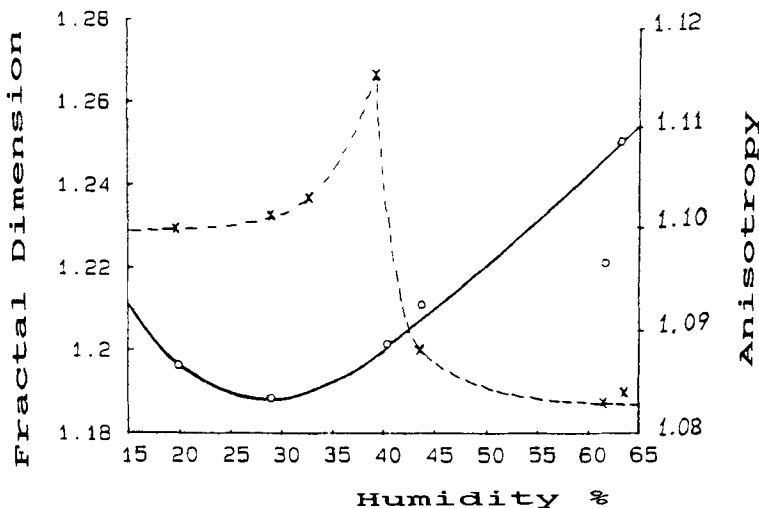


FIG. 2. Fractal number (○) and mean anisotropy (×) (ratio of diameter in direction 135° to 45°) of pine wood around the fiber saturation point, FSP, about 30% relative humidity. Statistics of 200 cells.



Solid-state CP/MAS  $^{13}\text{C}$ -NMR measurements on the amount and state of cellulose in dried and moistened wood (spruce, humidity about 10% by weight, resinous and resin-free samples) indicated that up to this level of humidity no substantial changes were observed in the position and intensities of the cellulose peaks.

We earlier [19] reported a similar behavior for chemical treatment of resin-free wood. Chemical treatment seems not to influence the general cellulose structure. On the other hand, the peaks referring to hemicellulose and lignin seem to change on various chemical treatments. On the contrary, treatment with ammonia gave marked changes in the bands belonging to cellulose and were caused by transitions from the crystalline I state to the III state.

The relaxation times of the NMR bands seem to be more sensitive to environmental changes of secondary valence forces connected with the glucose unit of the cellulose chain. In the present case (Table 1), we found a definite increase in the relaxation times of all carbon atoms for spruce wood samples after deresinification. In resinous specimens, the relaxation time was highest at 10.5% humidity for all the carbon atoms, C1–C6. For a sample with higher humidity (22.5%), the relaxation time decreased again except for the side-chain C6 atom. The effects may be explained as a change in the hydrogen bond network around the cellulose chain caused by the penetration of water. At high water content, and equilibrium force state nearly similar to that of dry resinous or resin-free wood seems to have been reached again. The experiments regarding this question will be continued.

### TECHNICAL ASPECTS OF SWELLING OF WOOD BY SOLVENTS

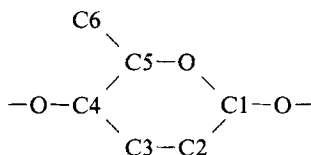
With regard to the diffusion of various solvents and water vapor, we substantiated the findings of earlier investigators [3, 10, 22]. The diffusion rate and swelling

TABLE 1.  $^{13}\text{C}$ -CP/MAS NMR Relaxation Times for Glucose Ring Carbon Atoms of Moistened Acetone Extracted or Nonextracted Spruce Wood at Room Temperature

Sample <sup>a</sup>	Relaxation times (ms); accuracy, 0.1 ms				
	C1	C2, C3	C4	C5	C6
Spruce, carbon atoms <sup>b</sup>					
Dry, extracted with acetone	3.83	4.65	3.93	4.02	7.52
Dry, nonextracted	3.48	4.47	2.95	3.69	4.52
10% humidity, nonextracted	5.41	6.58	3.99	5.81	9.74
22.5% humidity, nonextracted	3.53	4.35	3.02	3.31	8.39

<sup>a</sup>No change in type of crystallinity of the cellulose chain was detected by CP/MAS  $^{13}\text{C}$ -NMR spectroscopy.

<sup>b</sup>Numbering of carbon atoms in the glucose monomer:



power of the solvents are proportional to the solubility parameter of Hildebrand and the hydrogen bond capacity parameter of Gordy of solvents and solvent mixtures. The markedly high solubility parameter of water, 23.4, and its high Gordy parameter indicate the unique properties of water against wood.

The presence of hydrophilic low-molecular extractives (resins) and amorphous polymers (lignin and hemicelluloses) in the cell wall are of central importance for understanding the instability of the wood structure under drying and wetting. These views have been stressed by several of the authors named in the present discussion. However, the lenticular trellis theory of Boyd [13] on the important influence of resins on the structural stability of wood under swelling is especially worthwhile mentioning as an explanation of the phenomena studied.

From a technical point of view, it is well known that logs can be stored for a long time in water before being processed in saw mills, but other methods of dimensional preservation have also been tried. In the spirit of Boyd's idea, it has been proposed that the stability of wood logs and lumber should be preserved by treatment with hot acetone to remove, at least partly, the extractives [20]. This method is not economically profitable despite its marked energy-saving properties [21].

To obtain a simple measure of the mechanical changes on deresinification, we compared the tensile strength of resinous spruce dry wood with that of acetone-extracted samples and found the following relations,

$$E(t,r) = 1.5E(t,rf) \quad (7)$$

$$\eta(t,r) = 0.5\eta(t,rf) \quad (8)$$

where  $E(t,r)$ ,  $E(t,rf)$ ,  $\eta(t,r)$  and  $\eta(t,rf)$  refer the tangential tensile strength and viscosity for resinous and resin-free spruce wood samples, respectively.

The above equations indicate quantitatively the great decrease in Young's modulus and increase in viscosity on deresinification of wood, which explains the importance of the resins.

## DISCUSSION

The above discussion indicates that the problem of wood instability and cracking on drying is a serious but resolvable one. At present the increase of wood quality for constructional purposes involves economic loads which partly diminish its ability to compete with synthetic high polymers and their composites for cheap construction. Wood's other excellent properties and friendliness to environments in comparison to many presently used materials and composites will, however, increase its future constructional uses.

## EXPERIMENTAL

The wood samples from South Finnish spruce and pine were prepared by the group of Ranta-Maunus [18] by cutting radially ring-shaped samples with a cross section of 10 mm width and 4 mm thickness and an outer radius of 50 or 70

mm. For the spectroscopic measurements of these samples, specimens were cut tangentially and ground in a mill.

The electron micrographs were measured with a JEOL JSEM-820 scanning electron microscope (SEM) from gold ion sputtered samples. The micrographs were analyzed with a Robotron K 7067.15 graphic unit equipped with a video camera. The data were processed with the picture analysis program Image C version 3.0 working with PC XT/AT computers in MSDOS version 4.01. The following parameters were calculated: total area of windows, particle area, length of limiting border, projections in eight directions (0–180°), and Euler's number. As secondary cell parameters, the following were calculated: area, perimeter, maximum/minimum diameter, convexity, form factor, and fractal number. All data were taken as a mean of 100–200 cells. Before the SEM measurements, the samples were examined with an optical microscope to obtain representative areas.

The FTIR spectra were recorded in the 400–4000  $\text{cm}^{-1}$  region from KBr pellets (3 mg/400 mg) using a Nicolet 205 Fourier transform spectrometer. The spectral resolution was 2  $\text{cm}^{-1}$  in the entire range.

The solid-state carbon-13 spectra were recorded on a JEOL FX 200 FT NMR spectrometer at 50.1 MHz with the CP-MAS technique. The contact time was 1 millisecond, and the delay time between the pulse sequence repetitions was 1 second. In the experiments, 500 scans were collected. The chips were packed in Macor-rotor cells and spun at speeds of 3 kHz. Chemical shifts of the spectra were calibrated with hexamethylbenzene. The relaxation times were carried out by means of a modified inversion-recovery-T1 experiment. The relaxation curves were numerically resolved into their components. Curve fitting was done by using a least-squares technique. At most, two components could be obtained. In the present case the slower component was used for the evaluation of the influence of humidity.

The change in water content was followed by using a humidity chamber installed in a microbalance. This was equipped with a fan circulating the humidified air with a velocity of 0.5 m/s. A similar system was also used to follow the cracking behavior of the circular ring specimens. The tensile strength of the wood specimens were measured at room temperature by using a tensile tester, model Instron TM-SM model 1026.

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