

RHEOLOGICAL PROPERTIES OF CHEMICALLY MODIFIED WOOD: RELATIONSHIP BETWEEN DIMENSIONAL AND CREEP STABILITY

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ABSTRACT

A typology of chemical modifications of wood based on the interaction of water with the molecular constituents of the lignocellulosic material is proposed. The model accounts for both the moisture expansion and the so-called mechanosorptive creep induced by moisture changes under load. Anti-creep efficiency (ACE) values were obtained for wood specimens modified with fourteen different types of chemical treatments and subjected to a 4-day creep-recovery test under cyclic humidity conditions. The relationship between dimensional stability, as measured by anti-swelling efficiency (ASE), and ACE was determined for the different treatments. Treatments such as polyethylene glycol impregnation or etherification with epoxides, in which the hydrophilic nature of the bulking agent is not counter-balanced by crosslinking, yielded high ASE values but increased mechanosorptive creep instead of reducing it.

Keywords: Rheology, creep, dimensional stability, chemical modification.

INTRODUCTION

One main reason to modify wood chemically is to improve its dimensional stability;

that is, to reduce the free swelling or shrinking of a modified unloaded specimen submitted to humidity change as compared to the swelling of untreated wood under like conditions. The anti-swelling or shrinkage efficiency (ASE) factor is commonly used to quantify this effect (Rowell and Banks 1985). However, in many situations where wood-based materials are used as structural members, the materials undergo

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other types of dimensional changes such as creep deformations resulting from the application of static loads. In the field of wood rheology, the occurrence of abnormal creep in wood under load and subjected to humidity variations has been the object of many studies since creep was first observed 30 years ago (Armstrong and Kingston 1960; Grossman 1976). This so-called mechanosorptive effect may result in high levels of strain or early failure of wood members. On the other hand, it can have positive consequences in operations used to form composites (Norimoto and Gril 1989).

It may seem quite natural to assume that dimensional stability as quantified by ASE implies dimensional stability in a broad sense, including such phenomena as creep stabilization and acoustical stabilization (Norimoto et al. 1988). In other words, a treatment that prevents shrinkage and swelling should also reduce mechanosorptive creep (Norimoto et al. 1987). As will be shown in this report, this would be an erroneous assumption, although in many cases it may be true. Some treatments, well known for producing a high degree of dimensional stability, actually increase mechanosorptive creep instead of reducing it. The explanation for this must be sought at the molecular level by considering the interactions of moisture with the components of the cell wall.

Perhaps the term *mechanosorptive creep* is not totally accurate for the phenomenon we are studying. Creep implies a time dependency; Grossman (1976) indicates that mechanosorptive effects are not directly dependent on time. Perhaps the term *mechanosorptive deflection, strain, or distortion* would be more appropriate, but since the term *creep* has been used in past references in this subject area, we will continue to use it.

The purpose of this research was to characterize the ability of a chemical treatment to stabilize mechanosorptive creep. To do this, an anti-creep efficiency (ACE) factor was obtained through a 4-day creep-recovery bending test. Spruce wood was subjected to fourteen chemical treatments, and ASE, ACE, and other

conventional strength properties were measured and compared. Based on the data obtained, we propose a simple molecular model to account for both moisture expansion and mechanosorptive creep of wood. We suggest a typology of chemical treatments based on this model.

EXPERIMENTAL

Chemical modification treatments

Spruce specimens 100 by 12 by 2 mm (longitudinal by radial by tangential) were used for mechanical tests; 20- by 12- by 2-mm (longitudinal by radial by tangential) specimens were used for dimensional stability tests.

Fourteen chemical modification treatments were used: formalization (F1, F2, F3), impregnation with maleic acid (M) or maleic acid glycerol (MG), heat (H1, H2), acetylation (A), etherification with the epoxides propylene oxide (PO) or butylene oxide (BO), impregnation with polyethylene glycol (PEG), formation of a wood/inorganic material composite (WIC), impregnation with phenol-formaldehyde resin (P), and formation of a wood-plastic composite (WPC).

For the formalization treatments, F1 was done in liquid phase by immersing the wood in a water solution containing 3.6% formaldehyde, 3.7% HCl, and 75% acetic acid for 6 days at 25 C, followed by water washing. The F2 and F3 treatments were done in vapor phase: F2 with hydrogen chloride as catalyst, with 0.027 M formaldehyde and 0.0005 M HCl, at 150 C for 4 h; F3 with sulphur dioxide as catalyst, with 0.0215 M formaldehyde and 0.004 M SO₂, at 120 C for 24 h.

For the maleic acid treatment (M), the wood was impregnated with an aqueous solution containing 20% maleic anhydride and 1% lithium chloride as catalyst, reacted at 180 C for 3 h, then leached 10 h in boiling water. For the MG treatment, the wood was impregnated with an aqueous solution of 20% maleic anhydride and glycerol in a 2/1 ratio (v/v), reacted at 180 C for 3 h, then leached 10 h in boiling water.

The heat treatments were done at 180 C to

separate the effects of heat and chemical action in M and MG treatments. The H1-treated wood was heated for 3 h and the H2-treated wood for 10 h.

For treatment A, wood was acetylated by reaction with acetic anhydride at 120 C for 10 h (no catalyst), followed by leaching 10 h in boiling water.

Wood was etherified in treatments PO and BO by reaction in the presence of propylene or butylene oxide mixed with 5% triethylamine at 120 C for 30 min in an autoclave at 1,030 kPa. The wood was not leached to avoid losing the reactant during the process.

For the PEG treatment, the wood was immersed in an aqueous solution containing 25% PEG 1000 and boiled at 110 C for 3 h.

The WIC was formed by immersing the wood in an aqueous solution containing 32.0% BaCl_2 and 7.2% boric acid at 60 C for 1 day, followed by a second immersion in an aqueous solution of 37.4% $(\text{NH}_4)_2\text{HPO}_4$ and 16.6% boric acid for 1 day at 60 C, and, finally, 10 h of leaching in boiling water.

For treatment P, the wood was impregnated with an aqueous solution of 10% low molecular weight phenol-formaldehyde resin. The resin-impregnated wood was cured for 30 min at 130 C.

The WPC was obtained by impregnating the wood with methyl methacrylate (MMA) containing 1% α, α' -azobis-iso-butyronitrile as catalyst, wrapping the specimens in aluminum foil, and curing them for 3 h at 80 C.

Weight percent gain (WPG) resulting from each treatment was determined based on the oven-dry weight of the specimens before and after treatment (Table 1).

Static bending tests

For each treatment, static three-point bending tests (span 8 cm) were performed on three specimens at 20 C and 65% relative humidity (RH) until failure. Longitudinal Young's modulus (E), stress at proportional limit (δ_p), strength (δ_m) and maximum strain (ϵ_m) were calculated from the load-deflection curves.

Adsorption isotherms

Adsorption isotherms were obtained for three specimens for each treatment at 29, 56, and 86% RH (30 C) by measuring the weight of the specimens after 1 week in a humidity chamber. The oven-dried state (0% RH) was obtained at 103 C.

Mechanosorption tests

Mechanosorptive creep was measured in three-point bending tests at 30 C using humidity cycles between 29 and 86% RH. The initial load was adjusted to specimen dimensions after treatment to obtain a stress level of 10 MPa in the dry state. The following procedure was imposed on all specimens: loaded at 29% RH, kept 10 min, moved to 86% RH for 24 h, returned to 29% RH for 24 h, unloaded at 29% RH, kept 10 min, moved to 89% RH for 24 h, and, finally, returned to 29% RH for 24 h. A small fraction of the initial load (5 to 9%) remained on the specimen after unloading. At the end of each humidity step, the dimensions of a control specimen were measured to estimate the current maximum strain and stress of the loaded specimen and to plot stress-strain diagrams.

To characterize the ability of the treatment to reduce mechanosorptive creep, an ACE factor was defined in the following way:

$$\text{ACE} = \frac{dJ_u - dJ}{dJ_u} \times 100$$

$$dJ = \frac{4wt^3}{Fl^3}(f_3 - f_1)$$

where

dJ = creep compliance,

dJ_u = creep compliance of untreated wood,

F = applied load,

f_3 = deflection before unloading (dry state),

f_1 = deflection after loading (dry state),

l = span, and

$wt^3/12$ = inertia of cross section.

TABLE 1. *Classification of chemical treatments.*

Treatment	Type
None (untreated wood)	I-O
Heat	I-1
Formalization, liquid phase	I-2
Maleic acid impregnation	I-3, 6
Maleic acid + glycerol impregnation	II-4, 6
Acetylation	I-5
Esterification with epoxides	I-6
Polyethylene glycol (PEG) impregnation	II-7
Formation of wood/inorganic material composite (WIC)	II-7
Phenolic resin impregnation	II-8, II-5
Formation of wood-polymer composite (WPC)	III-8
WPC for industrial use	III-0

Alternative definitions of ACE are possible, such as a definition based on relative deflection instead of compliance, depending on the aim of the research.

Dimensional stabilization tests

The ASE was calculated from five specimens for each treatment from oven-dried volume to the swollen state reached after 1 week at 20 C and 98% RH, by using the formula

$$ASE = \frac{S_u - S}{S_u} \times 100$$

$$S = \frac{w_{98} - w_0}{w_0} + \frac{t_{98} - t_0}{t_0}$$

where

- S = swelling ratio,
- S_u = swelling ratio of untreated wood,
- w = width, and
- t = thickness.

DISCUSSION

Mechanosorptive creep of wood

Figure 1A is the usual representation of a creep test in which the relative deflection is plotted against time. The initial 10-min period of creep at 29% RH is hardly visible on the graph. Previous work had shown that the change in deflection would be minimal even after a long time if the specimen were kept at

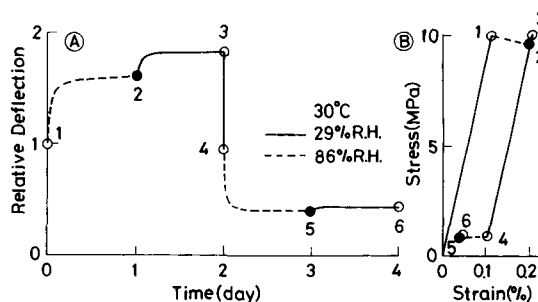


Fig. 1. Typical mechanosorptive creep-recovery test of untreated wood (fiber direction). A, relative deflection as a function of time. B, stress-strain diagram.

29% RH. Increasing the humidity induces a marked increase in deflection, and the following reduction in humidity induces another increase in deflection. After the specimen is unloaded at 29% RH, only a slight recovery will occur over a long period as long as the specimen remains at this RH level. On the other hand, high RH level induces a marked recovery, even though the recovery is slightly masked by the final equilibrium at 29% RH.

The increase in creep deflection during drying is often seen as a typical feature of the mechanosorptive effect. However, it may be explained here, at least partially, by a pure geometrical and elastic effect. At the high RH, the transverse dimensions of the specimen are bigger and the stress level is lower than at the low RH; conversely, redrying induces an increase of the stress level. The stress-strain diagram in Fig. 1 (Fig. 1B) shows the values of maximum stress and strain (estimated by assuming linearity in the cross section of the specimen) at the end of each humidity step and before and after loading or unloading. Such diagrams are commonly used by engineers but are rarely used to describe creep tests. In the present case, the time factor is of minor interest because the amount of mechanosorptive strain is largely time-independent (it depends on the applied stress, amount of moisture change, and parameters of previous hygromechanical loading history), and quasiequilibrium values are considered here.

Figure 1B is a compact representation that

contains the essential data (Gril 1988). Furthermore, the fact that little real mechanosorption occurred at the low RH is made evident by the position of point 2 (end of high RH) in the neighborhood of point 3 and line 3–4 (instantaneous response at unloading). The classical mechanosorptive creep effect is apparent with the net increase (line 1–2) during a complete low RH-high RH cycle under loading or with the residual strain after complete unloading, estimated by extending line 2–3 to the strain axis. Another typical feature is the high recovery rate after cycling in the unloaded state. The final residual strain that would have been reached if the unloading had been complete is estimated by extending line 1–3 to the strain axis.

Model of wood-water interaction

The molecular model shown in Fig. 2B accounts for both mechanosorptive and moisture expansion effects. The “chain” indicated by (a) refers to the crystalline core of a cellulosic microfibril, but it must be understood in a wider definition. The chain may be any part of the lignocellulosic material of the cell wall that is not affected by water movement during the course of the experiment. It has a water-reactive zone at its boundary, illustrated by the “hydroxyl group” (b). Neighboring chains are linked to each other by a water-reactive zone, shown here by the “hydrogen bond” (c). Water sorption on (c) has a double effect. First, it fills the space between the chains and forces them to expand laterally in the directions indicated by (d). Second, it weakens the connection between the chains and facilitates slippage in the direction indicated by (e) resulting from local shear stresses. At the macroscopic level, the first effect results in moisture expansion (swelling or shrinking) and the second in mechanosorptive creep.

In Fig. 2, the two chains are represented as two independent members for the sake of clarity, but in reality they belong to a fully interconnected framework. This fact accounts for the mechanosorptive recovery—whatever molecular movements occur in the water-reactive

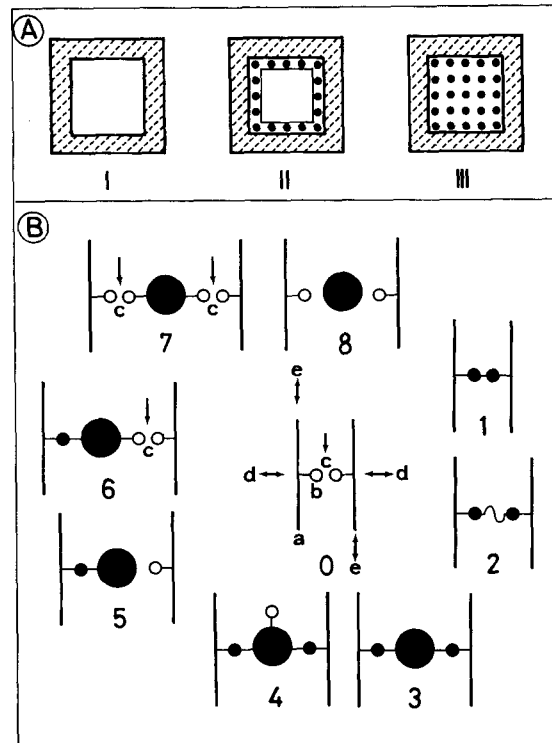


FIG. 2. Model of chemical modification of wood. A, cellular level: (I) modification of cell wall only, (II) deposition on cell-wall surface, (III) filling of lumen. B, modification of ligno-cellulosic material at molecular level. Empty circles, hydroxyl group available for hydrogen bonding; small filled circles, substitution of hydroxyl group; large filled circles, bulking agent.

parts, the surrounding framework tends to recover its original shape in a stress-free state. Moreover, the simplistic image used here suggests that the basic phenomena associated with expansion (d) and creep (e) are not connected to each other because they occur in different “directions” at the local level. Although the real wood-water interaction is more complex, the simplified model shown in Fig. 2B has some basis in regard to the anisotropic nature of the microfibrillar framework. At the macroscopic level, wood anisotropy (reduced by the inclination of the microfibrils but amplified by the cellular structure) yields a partial disconnection of two types of problems: moisture expansion occurs predominately in a transverse direction relative to the fiber, and it is domi-

nated by mechanosorptive creep in the direction of the fiber.

Classification of chemical treatments

We classify chemical treatments with respect to their actions at both the cellular and molecular levels. Figure 2A shows a model of the cross section of a single wood cell and represents three types of chemical treatments: 1) no deposit of chemical in the lumen of the wood cell, 2) deposit or coating of chemical on the internal faces of the lumen, and 3) lumen partially or totally filled with chemical. In each of these cases, the wood cell wall itself may or may not be modified.

Figure 2B makes use of the basic model (0) to analyze the possible modifications of the cell-wall material at the molecular level. The hydroxyl group represented by the empty circles is available for hydrogen bonding with water; the small filled circles indicate that the hydroxyl group has been substituted with chemical bonding and is not available. The large filled circles indicate the bulking effect caused by the introduction of large molecules between the constituents, which replace water molecules. Weak connections, such as hydrogen bonding, are represented by two hydroxyl groups (empty circles) facing each other; strong molecular bonding is shown by a line. The crosslinking effect is thus pictured by an unbroken sequence of lines and filled circles (either small or large) linking the two chains.

The initial model (0) can be modified according to the eight patterns shown in Fig. 2B. In patterns 1 and 2, crosslinking occurs without the bulking effect by using molecules of low molecular weight that link on two sides with hydroxyl groups. In pattern 1, the reaction is made in a dry state with a short linkage, preventing lateral expansion or molecular movement. In pattern 2, the reaction is made in a swollen state, so that after drying the structure develops considerable potential looseness. Both crosslinking and the bulking effect occur in patterns 3 and 4. In pattern 3, the reactant is hydrophobic, and in pattern 4, it is hydrophilic. The remaining four cases show the

bulking effect without crosslinking. In patterns 5 and 6, the reactant establishes a stable bond on one side. The reactant is hydrophobic in pattern 5 but hydrophilic in pattern 6. Thus, the reactant simultaneously suppresses a hydrogen bonding on one side and creates the possibility for a new bonding site on the other side. In patterns 7 and 8, the bulking agent does not establish any stable linkage with the constituents. The bulking agent is highly hydrophilic in pattern 7, and it establishes many hydrogen bondings with the constituents. The bulking agent is hydrophobic in pattern 8 and does not interact with water at all.

Theoretical assignment of chemical treatments

Any type of chemical treatment of wood can be described by a combination of the criteria shown in Fig. 2. Several combinations of these criteria may occur at the same time. In some cases, we are not able to determine which combinations are involved in the treatment because we do not know the mechanisms of action that underly the treatment. Other treatments can be typified as shown in Table 1.

RESULTS

The results of the static bending tests are listed in Table 2, together with ASE and ACE values. For each treatment, Figs. 3 and 4 show 1) relative deflection as a function of time, 2) a stress-strain diagram, and 3) an adsorption isotherm. For each chemical treatment shown with a solid line, control data (untreated wood) are plotted on a dotted line for comparison.

Vapor-phase formalization (F2 and F3) yielded a high ASE for a low WPG (Fig. 3). It was also the most efficient treatment regarding ACE. Its main drawbacks are a loss in strength properties and a greater degree of brittleness, caused by the acid catalysts. The use of sulphur dioxide (F3), which is milder and also cheaper, is preferable to the use of hydrochloric acid (F2) because it involves less degradation and less corresponding loss in properties. Water-phase formalization (F1) is usually performed on paper so that cohesion is retained even in

TABLE 2. Properties of chemically modified woods.^a

Treatment	WPG (%)	E (GPa)	δ_p (MPa)	δ_m (MPa)	ϵ_m (%)	ASE (%)	ACE (%)
None	0	8.02	60.3	90.4	1.40	0	0
Formalization							
F1	0.5	7.88	63.2	78.8	1.01	3	12
F2	0.7	8.10	62.4	62.4	0.61	57	87
F3	2.1	9.07	78.6	78.6	0.67	63	94
Heat							
H1	-2.4	7.81	64.2	90.3	1.23	11	16
H2	-3.5	7.86	68.5	89.4	1.02	17	22
Maleic acid	15.8	7.46	61.8	61.8	0.66	38	48
Maleic acid + glycerol	20.5	8.15	78.9	84.3	0.84	44	43
Acetylation	22.8	7.26	68.3	100.3	1.48	66	48
Etherification							
Propylene oxide	25.7	7.65	51.9	78.8	1.28	45	-186
Butylene oxide	25.5	7.07	49.4	75.0	1.23	51	-81
PEG ^b	110	6.27	24.9	46.5	1.53	81	-208
WIC ^c	42.5	7.82	56.8	87.3	1.45	0	-70
Phenolic resin	12.9	8.78	78.9	101.4	1.03	28	47
WPC ^d	105	12.07	72.9	145.5	2.07	0	6

^a Abbreviations for properties: WPG, weight percent gain; E, longitudinal Young's modulus; δ_p , stress at proportional limit; δ_m , modulus of rupture; ϵ_m , maximum strain; ASE, anti-swelling efficiency; and ACE, anti-creep efficiency.

^b Polyethylene glycol impregnation.

^c Wood/inorganic material composite.

^d Wood-polymer composite.

water. Such a treatment is of no practical interest in the case of wood, which has a natural cohesion in the green state. As a matter of fact, the treatment leads to only small improvement in ASE and ACE according to all criteria.

Heat treatment for 3 h at 180 °C (H1) was compared to treatment with maleic acid (M) and maleic acid plus glycerol (MG), which involves similar conditions (Fig. 3). The 3-h H1 treatment was also compared to a 10-h heat treatment (H2). Heat treatment alone yielded only small ASE or ACE values. Consequently, the improvements observed with maleic acid with or without glycerol must be attributed mostly to the effects of crosslinking and bulking. The same can be said of the loss of mechanical properties, especially in the case of the maleic acid treatment.

Of special interest is the comparison between acetylation (A, type I-5) (Fig. 3) and etherification with epoxides (PO, BO, type I-6) (Fig. 4); these treatments have a reputation as dimensional stabilizers (high ASE). Strength

properties were improved by acetylation and reduced by epoxides. However, the most striking difference between these treatments is the opposite effect they exerted on mechanosorptive creep: acetylation yielded positive ACE values, but both PO and BO yielded extremely negative values. This means that epoxide treatments "stabilize" stress-free wood but "destabilize" loaded wood. Interpretation of mechanosorptive creep according to the model shown in Fig. 2B (0-6) may explain this quite unexpected result. Although the reactant saturates hydroxyl groups, it produces new ones during the reaction. Furthermore, as a bulking agent, the reactant increases the accessibility of water molecules to the water-reactive regions. This results in more water sorption (when calculated on a prior-to-treatment oven-dried weight basis) and more mechanosorptive creep (negative ACE).

The PEG treatment yielded results similar to those resulting from epoxide treatments, though the PEG results are amplified (Fig. 4).

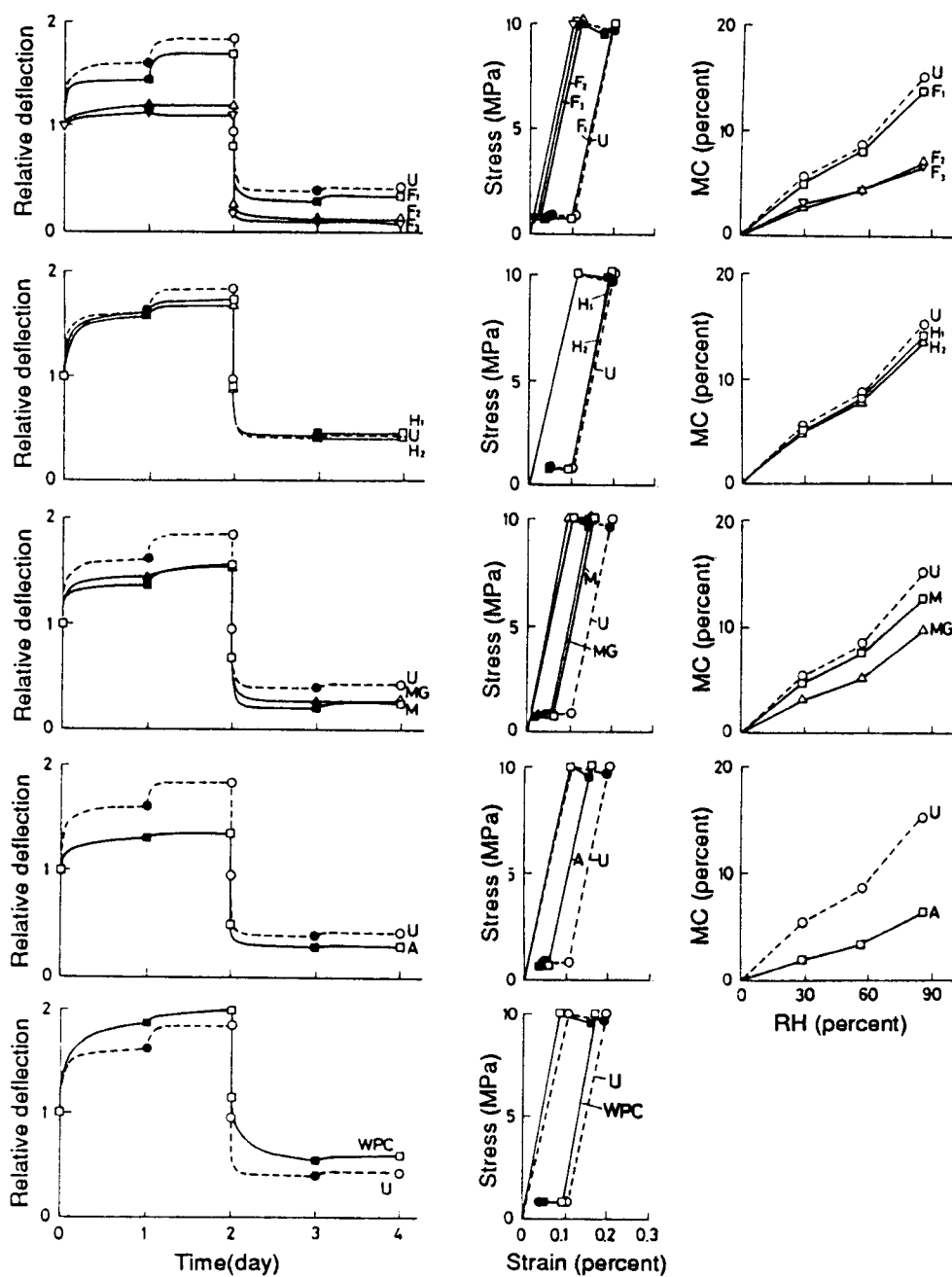


FIG. 3. Mechanosorptive creep-recovery tests and isotherms of wood chemically modified by formalization (F1, liquid phase; F2, vapor phase, catalyst HCl; F3, vapor phase, catalyst SO₂), heat treatment at 180 C (H1, 3 h; H2, 10 h), treatment with maleic acid alone (M) or with glycerol (MG), acetylation (A), or formation of a wood-polymer composite (WPC). U is untreated wood.

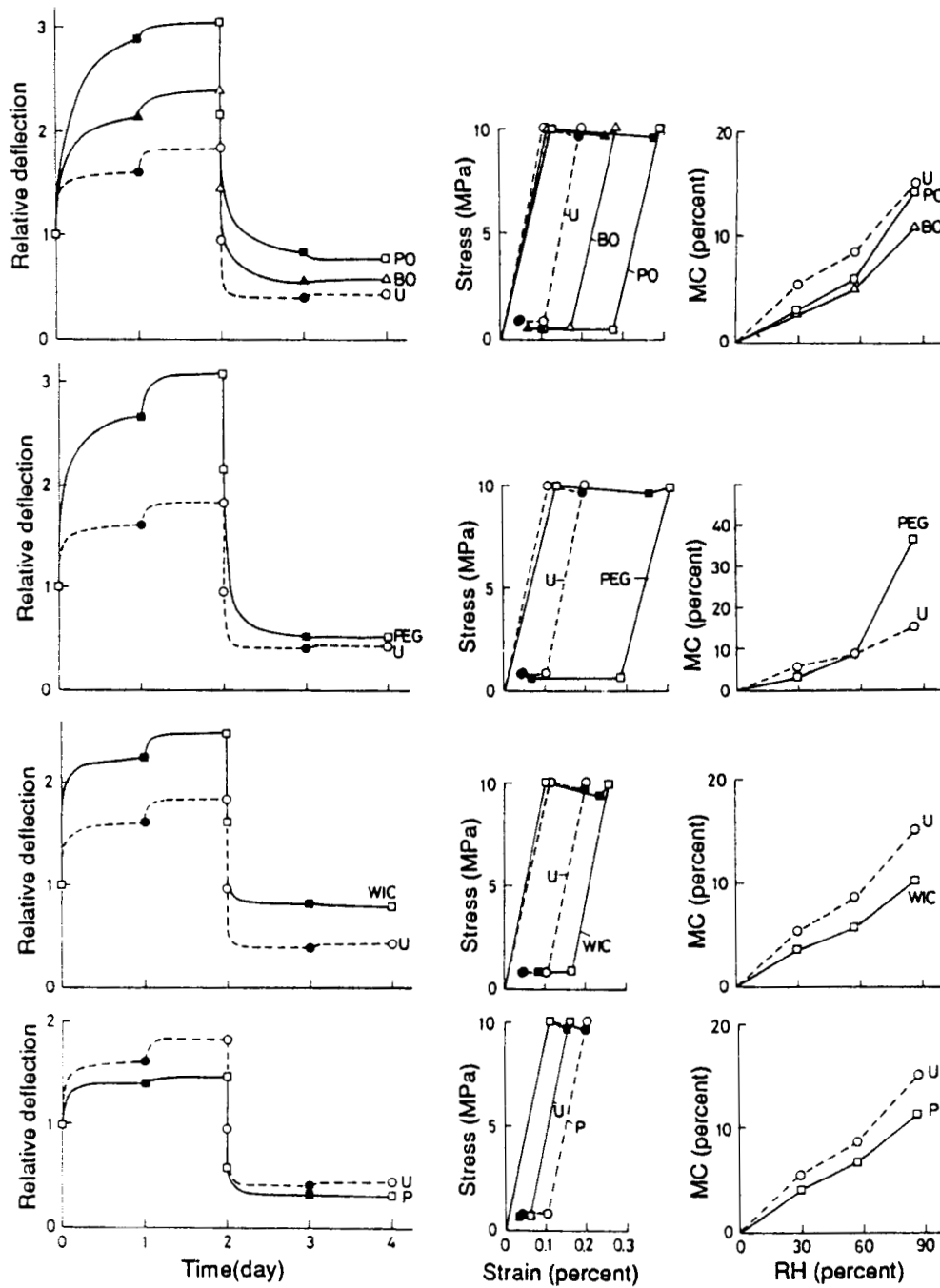


FIG. 4. Mechanosorptive creep-recovery tests and isotherms of wood chemically modified by etherification with propylene oxide (PO) or butylene oxide (BO), impregnation with polyethylene glycol (PEG), formation of a wood/inorganic material composite (WIC), or impregnation with phenol-formaldehyde resin (P). U is untreated wood.

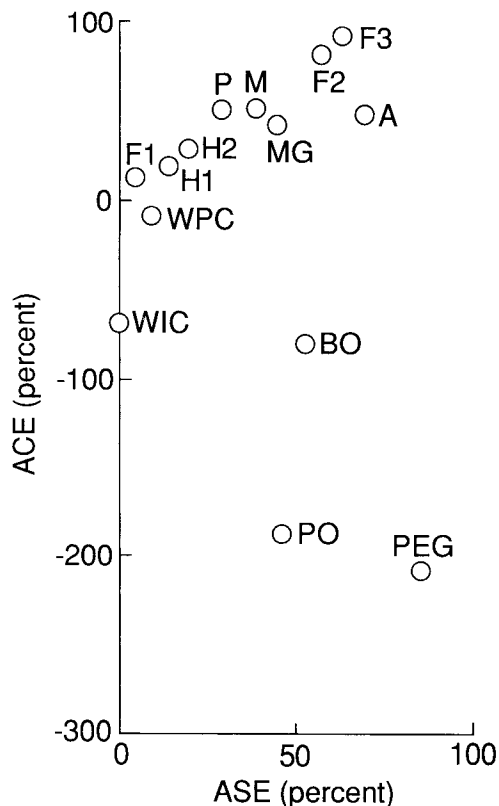


FIG. 5. Anti-creep efficiency (ACE) compared to anti-swelling efficiency (ASE). See legends to Figs. 3 and 4 for treatment abbreviations.

The PEG treatment resulted in an excellent ASE value, but the ACE value was negative and the loss in strength was drastic (except for the higher maximum strain). Like PEG, the WIC treatment is a type II-7 treatment because the molecule involved is a salt that is extremely water-reactive. The WIC treatment has similar drawbacks to those of PEG, although the drawbacks are not as pronounced in the case of WIC; moreover, the WIC treatment did not yield a high ASE value (Fig. 4). Although the chief purpose of WIC treatment is fireproofing, in the future it may be useful to combine WIC with other treatments for other applications.

Although most of the phenol resin in treatment P is not supposed to react with the molecular constituents and thus it should act as a pure bulking agent of the type II-8, a small proportion of linkages of type II-5 may be ex-

pected. The hydrophobic nature of the bulking agent resulted in a good ACE value for a quite modest ASE value (Fig. 4). Strength properties were increased, but the material became more brittle. For the WPC, the low ASE value shows that only a small proportion of the MMA penetrated into the cell wall (Fig. 3); therefore, this treatment is closer to a III-0 type than to a III-8 type. Thus, the enhancement of mechanical properties is mainly due to the fact that the polymer fills the lumens and supports a part of the mechanical load in parallel with the cell walls. Neither ASE nor ACE can be affected unless the cell wall is modified at the molecular level.

The ACE and ASE values obtained by the various treatments are compared in Fig. 5. As shown by the figure, ACE could often be predicted from ASE, but this was not generally the case. Pattern 6 and pattern 7 chemical treatments (Fig. 2) are the exception. In the case of these types of treatments, the bulking agent is hydrophilic, and no crosslinking occurs to prevent the molecular movements resulting from the combined action of stress and water.

CONCLUSIONS

The effect of chemical treatments on mechanosorptive creep of wood has been characterized by a factor named anti-creep efficiency (ACE), analogous to anti-swelling efficiency (ASE), that quantifies the ability of the treatment to reduce load-free moisture expansion. Modification of the cell wall at the molecular level (and not filling of cell-wall cavities alone) is required to affect either moisture expansion or mechanosorptive creep. Depending on the type of treatment, this can be obtained through molecular crosslinking, bulking, or a combination of these. In the case of treatments that induce crosslinking (patterns 1 to 4 of Fig. 2), a good correlation can be expected between ASE and ACE, as shown by the contrast between pattern 1 (high ASE and ACE values) and pattern 2 (low ASE and ACE values). The bulking effect alone (patterns 5 to 8) may induce high ASE values but negative ACE val-

ues. This occurs in patterns 6 and 7, where the bulking agent is hydrophilic. The best example is PEG treatment, which resulted in the highest ASE value and the lowest ACE value of all the treatments.

These results have important practical consequences. For example, the use of epoxides should be avoided in the case of load-bearing structural members, although the plasticizing action of epoxides may be an advantage for other applications, and these chemicals also increase the sorption capacity of wood. It is a difficult task from both a theoretical and practical point of view to establish a comprehensive typology of chemically modified wood. The use of the ACE factor should be seen as one attempt to widen the concept of dimensional stabilization to all types of dimensional change in wood.

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