EFFECTS OF HOT WATER TREATMENT ON THE STRUCTURE AND PROPERTIES OF CORK

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(Received July 1988)

ABSTRACT

The cork used for stoppers (reproduction cork) is subjected to a boiling operation before processing, which consists of immersing the cork boards in boiling water for approximately one hour. An experimental study of the hot water treatment was undertaken with the purpose of characterizing the alterations that it may cause in the structure, dimensions, mass and compression properties of cork.

Various parameters related to the treatment were investigated, including water temperature, time, cork quality, and the kinetics of open air-drying.

The major structural alteration due to boiling is the attenuation of cell-wall corrugations. This leads to an expansion of 10–15% in the radial direction and 5–7% in directions perpendicular to this, including the axial and tangential directions. The mass is virtually unaffected. Boiling causes a softening of cork and also a reduction of its elastic anisotropy. These and other observed changes in the stress-strain curves in compression can be explained in terms of the structural changes.

Keywords: Cork, hot water treatment of cork.

INTRODUCTION

Cork stoppers are made from planks of reproduction cork of adequate quality and thickness. This type of cork is obtained by the stripping of cork-oaks of more than 30–40 yr, after at least two previous cork strippings, which yield virgin cork and second cork, respectively (Natividade 1950). In general, the planks of reproduction cork vary in thickness from 2 to 5 cm, corresponding to a 9-yr growth period. In their natural form they are bent following the tree stem curvature, have a rough surface, and are difficult to cut.

Before processing, the planks of reproduction cork are subjected to a treatment with hot water, called, in the cork industry, the "boiling" of cork. It consists of the immersion of stacks of up to 20 planks, bound with ropes or chains, in boiling water for about 1 h. After the treatment, the planks are left in the open air to dry for a period of approximately 10–15 days, reaching an equilibrium moisture content of about 6–10%. The aim of the industrial boiling operation is to increase the flexibility of cork, promote the straightening of the planks, and improve the performance in subsequent manufacturing operations.

The research was financially supported by the Instituto de Ciência e Tecnologia dos Materiais (ICTM), Lisboa, Portugal and by the Raw Materials Programme of the Economic European Commission under contract MA 1B-0093-P(TT).

Wood and Fiber Science, 22(2), 1990, pp. 149–164

Boiling causes an expansion and changes in the cellular structure of cork, which in turn, results in alterations to mechanical properties. The hot water treatment also solubilizes some of the water extractives of cork, particularly the tannins, which give a characteristic brown color to the water used in the boiling operation. However, the conditions used allow the extraction of only a very small fraction of the water-soluble constituents (the total amount of which is around 6%), and therefore the change in the chemical composition of cork may be considered as negligible (Pereira et al. 1979).

The purpose of this study is to contribute to the characterization and understanding of the effects of the boiling operation on the structure and mechanical properties of cork. These were measured in compression tests and correlated with the observed changes in linear dimensions, density and structure. In addition, various parameters related to the boiling operation were investigated, such as the water temperature, duration of the treatment, and the subsequent drying in air.

Cork quality is mostly assessed by the volume fraction and dimensions of the radially oriented lenticular channels (usually termed pores), but also depends on the thickness of the growth rings. Narrower rings (i.e., thinner boards) correspond to larger densities (because they contain less thin-walled spring cells than thicker rings) and are associated with better cork quality. The experimental study on the effects of boiling concentrated on a good quality reproduction cork (low porosity, relatively narrow growth rings). Experiments with other types of reproduction cork were undertaken in order to assess the variability of the effects of boiling.

EXPERIMENTAL

Specimens of the various cork types investigated were prepared in the form of cubes with edges parallel to the three principal directions in the tree (radial, axial, and tangential) (Pereira et al. 1987). The specimens were cut from planks of natural, untreated reproduction cork from the south of Portugal (Alentejo). They were air-dried in the laboratory atmosphere to a constant moisture content, between 6 and 8% (measured by further drying at 100 C in an oven). Measurements of the mass and edge lengths were made for each specimen, before and immediately after the boiling operation. A number of boiled specimens were air-dried to constant mass in the laboratory atmosphere, and then measured for their dimensions and mass.

Compression tests were made at a constant crosshead speed of 2 mm/min (equivalent to a strain rate of 2×10^{-3} s^{-1}) on cubes of 16 mm of edge, up to a load of 5,000 N. The compression axis was, in different tests, parallel to each of the three principal directions. Specimens were tested in each of the following states or conditions: unboiled, immediately after boiling, and boiled plus air-dried. The cork in this last state will be termed for simplicity "boiled cork." Young's modulus was calculated from the average slope of the stress-strain curve between strains of 1% and 1.5%. Three specimens were tested for each direction and under each of the three conditions.

The cellular structure was observed in the three principal sections of unboiled and boiled specimens by scanning electron microscopy (SEM). Sections of dried specimens, cut with a razor, were coated with $\simeq$200 Å of gold for microscopic examination.

The duration of the boiling operation at 100 C was varied between 5 and 60

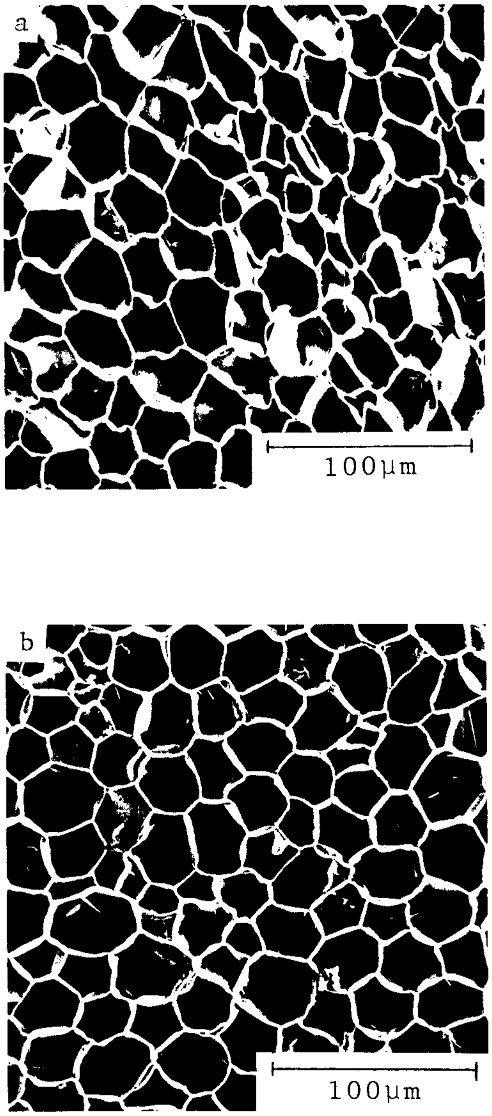

FIG. 1. Effect of boiling on the cellular structure of reproduction cork, observed in tangential sections: a) before boiling; b) after boiling.

min, and the resultant dimensional changes were measured. For each time period, twenty specimens were measured. These specimens were then left to dry in the laboratory atmosphere, and their masses were periodically measured until they reached constant values.

At this stage the specimens were subjected to a second boiling for 30 min at 100 C, and the dimensional changes were again measured upon air-drying.

The effects of the water temperature on the water uptake and dimensional changes were studied in water treatments of 30-min duration at temperatures

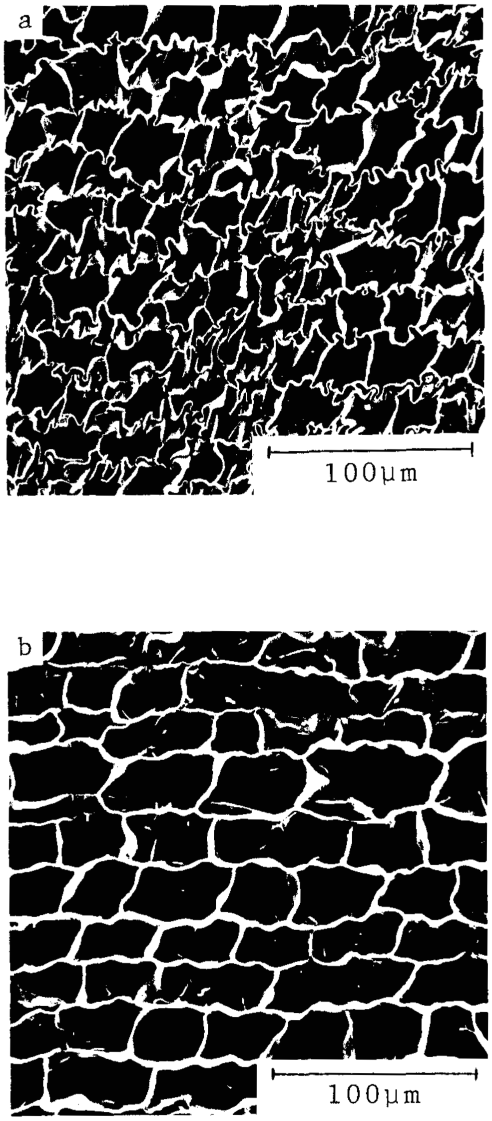

FIG. 2. Effect of boiling on the cellular structure of reproduction cork, observed in transverse sections in a region of spring cells: a) before boiling; b) after boiling. The radial direction is horizontal in the figures.

between 40 and 100 C. The specimens used in these experiments were in the form of cubes with edge dimensions of 20 mm.

Finally, boiling experiments (100 C, 45 min) were made on specimens of identical dimensions taken from cork planks of various thicknesses (and therefore with different widths of the growth rings) and of different quality classes, corresponding essentially to different porosity (i.e., different volume fractions of lenticular channels).

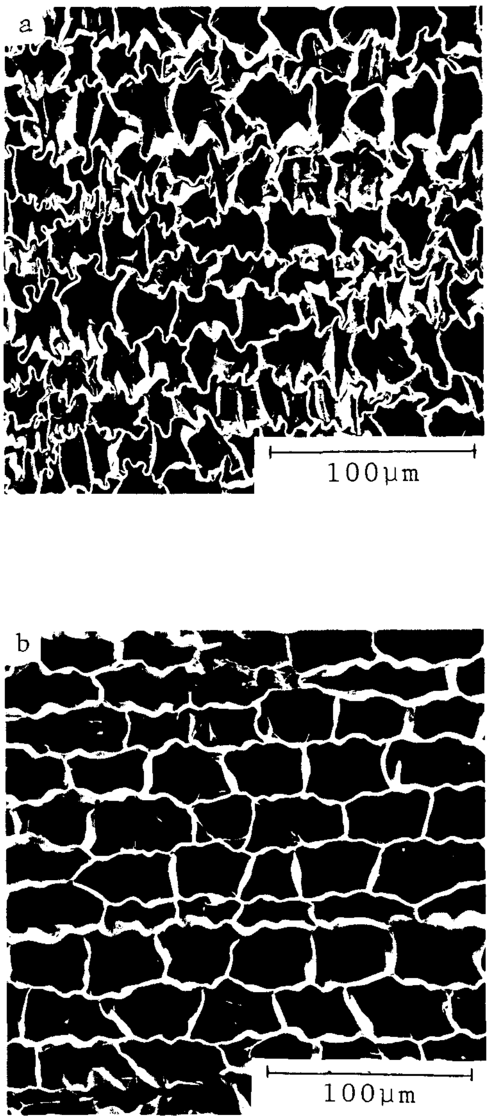

Fig. 3. Effect of boiling on the cellular structure of reproduction cork, observed in radial sections in a region of spring cells: a) before boiling; b) after boiling. The radial direction is horizontal in the figures.

RESULTS

Effect of boiling on the cellular structure of cork

The cork used in SEM observations was of good industrial quality (low porosity), with a density of 186 kg m^{-3} prior to boiling. The average width of the growth rings was about 2.5 mm (thickness of the board $\simeq 25$ mm).

The main alteration in the cellular structure caused by boiling is the attenuation of the corrugations of the lateral walls of the prismatic cells, i.e., the walls parallel

TABLE 1. *Effects of boiling duration on the dimensional, volume and density changes of boiled cork after air-drying.*

Boiling duration (min)	l/l_0			$\frac{V}{V_0}$	$\frac{\rho}{\rho_0}$
	Radial	Axial	Tangential		
5	1.082 ± 0.001	1.031 ± 0.003	1.033 ± 0.005	1.15 ± 0.01	0.87 ± 0.01
15	1.12 ± 0.01	1.050 ± 0.004	1.055 ± 0.005	1.25 ± 0.02	0.80 ± 0.01
30	1.14 ± 0.01	1.062 ± 0.004	1.060 ± 0.004	1.29 ± 0.02	0.78 ± 0.01
45	1.15 ± 0.01	1.063 ± 0.004	1.064 ± 0.004	1.30 ± 0.02	0.77 ± 0.01
60	1.15 ± 0.01	1.061 ± 0.004	1.058 ± 0.004	1.29 ± 0.02	0.78 ± 0.01

to the radial direction (Figs. 1–3). The lateral cell walls in unboiled cork are heavily corrugated, particularly in those cells that were formed in spring, which are longer and of thinner walls than those produced in autumn (Pereira et al. 1987). The bases of the cells (perpendicular to the radial direction) are in general not corrugated but are not planar. With boiling there is a general tendency for the cell walls to become more planar. The effect of cell-wall straightening obtained by boiling is more pronounced in the more heavily corrugated spring cells.

Dimensional changes; effect of boiling duration

Table 1 summarizes the results on dimensional changes due to boiling at 100 C for various times. The changes are given in terms of the ratio between the values measured in air-dried specimens, after and before boiling. The cork used in these, and following experiments, was of similar quality and density to that used to study the effect of boiling on the cellular structure. The average width of the growth rings was again ≃2.5 mm. Also shown in Table 1 are the calculated volume changes and the calculated density changes after air-drying in the laboratory atmosphere. As already mentioned, the variations of mass were negligible (less than 1%) and were not considered in the density calculations.

It is apparent from Table 1 that expansion increases with time, stabilizing when a maximum value is attained. In the experiments undertaken, no further dimensional changes occur after ≃30 min of boiling. It should be noted that the time interval for boiling equilibration depends on the geometry and dimensions of the specimens, since boiling is essentially a diffusion controlled process. Furthermore, the dimensional variations induced by boiling are anisotropic. The expansion in the radial direction is much larger (≃15%) than in the nonradial directions (≃6%) which show similar behavior.

Data on the mass change during air-drying are given in Fig. 4, which contains drying curves of cork specimens boiled for 15, 30 and 60 min at 100 C. The curves give the mass variation, in relation to the mass of unboiled cork, as a function of the time for which the specimens were left in air after boiling. The curves show that the mass of the air-dried cork is practically independent of the boiling time and nearly the same as in the unboiled condition. It was also found that the linear dimensions (and therefore the volume) change very little during drying, i.e., they keep the values reached upon boiling.

Specimens that were boiled at 100 C for different times and subsequently air-dried were submitted to a second boiling operation at 100 C for 30 min, and their dimensions after air-drying were measured. The purpose of these experiments

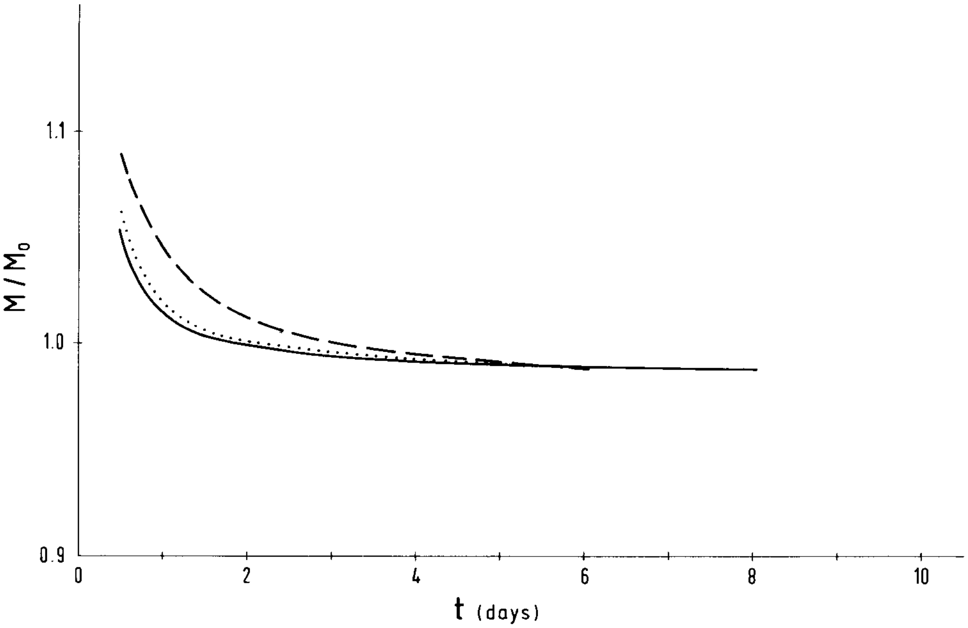

FIG. 4. Drying curves of reproduction cork for three boiling durations: 15 min (——); 30 min (···) and 60 min (– – –).

was to find whether a dimensional stabilization was achieved in the first boiling treatment. It was found that when the first boiling was long enough to give a constant expansion, no significant changes were detected following the second boiling, although a slight increase (≃2%) was detected in some specimens. On the other hand, the specimens that were first boiled for only 5 to 15 min showed further expansions on the second boiling to attain the values expected as if the times of the two boilings could be added.

Effect of boiling and of subsequent drying on the compression behavior of cork

The same cork characterized above was used in the compression tests. Figures 5–7 show average engineering stress-strain curves obtained in compression parallel to each of the three principal directions and in the following states: unboiled, immediately after boiling for 60 min and boiled (i.e., air-dried after boiling). Table 2 gives the corresponding Young's moduli, all measured at room temperature.

In unboiled cork (Fig. 5), the compression curves for the nonradial directions

TABLE 2. *Young's modulus changes of cork.*

Treatment	E (M Pa)		
	Radial	Axial	Tangential
Unboiled	8 ± 1	14 ± 1	15 ± 3
Immediately after boiling	2 ± 1	2 ± 0.3	2 ± 0.5
Boiled	6 ± 3	9 ± 2	8 ± 0.3

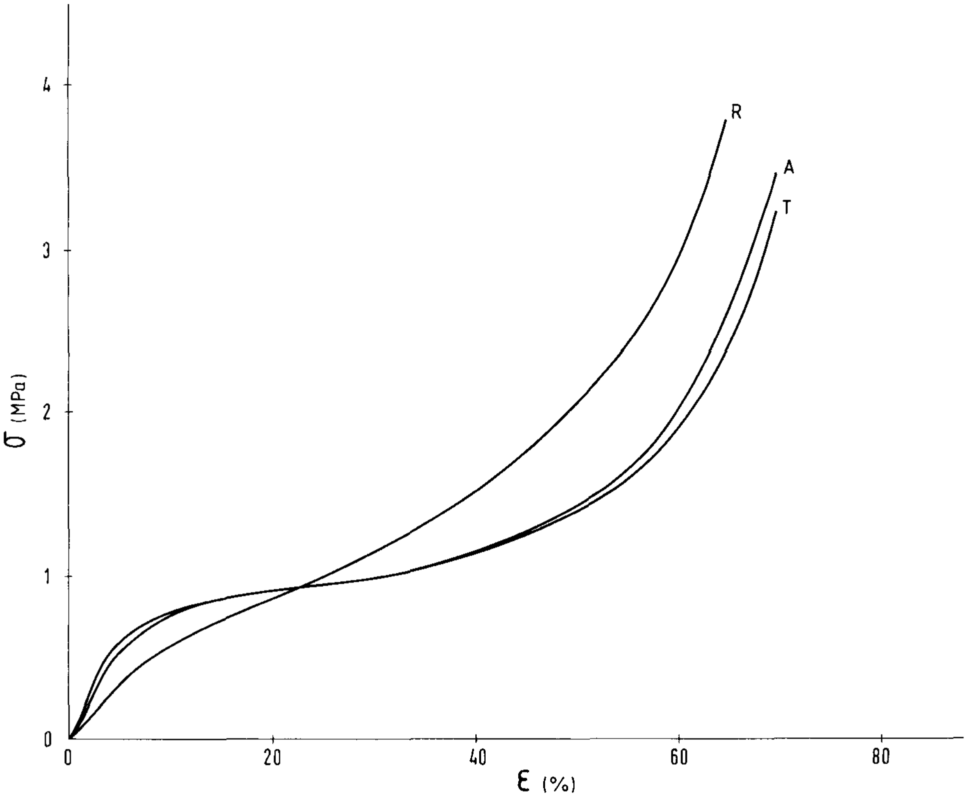

FIG. 5. Compression curves of unboiled reproduction cork, along each of the principal directions: R—radial; A—axial; T—tangential.

(axial and tangential) are nearly coincident and show a well-defined plateau region, which corresponds to the successive buckling of the cell walls (Rosa and Fortes 1988a; Gibson et al. 1981). The plateau is not well defined for compression in the radial direction, implying that there is not a well-defined yield point. The strength in this direction is below the strength in the other two directions for strains below 20%, the reverse being true for strains above 20%. In particular, the Young's modulus (Table 2) in the radial direction is approximately one half of that in the other two directions.

Immediately after boiling (Fig. 6), the compression strength and the Young's moduli are much smaller and fairly isotropic, i.e. independent of the direction of compression, although at large strains the radial direction shows larger strength.

Finally, after air-drying of the boiled specimens, the compression strength increases (Fig. 7) for all directions, with the radial direction showing the largest increase; the nonradial directions again have nearly identical behavior. The yield points are fairly well defined for the three directions, at similar yield stresses. The stress plateau is again better defined for the nonradial directions, although the slope of the compression curve for the radial direction is smaller than in untreated cork.

A clearer picture of the effect of boiling can be obtained from Fig. 8, which

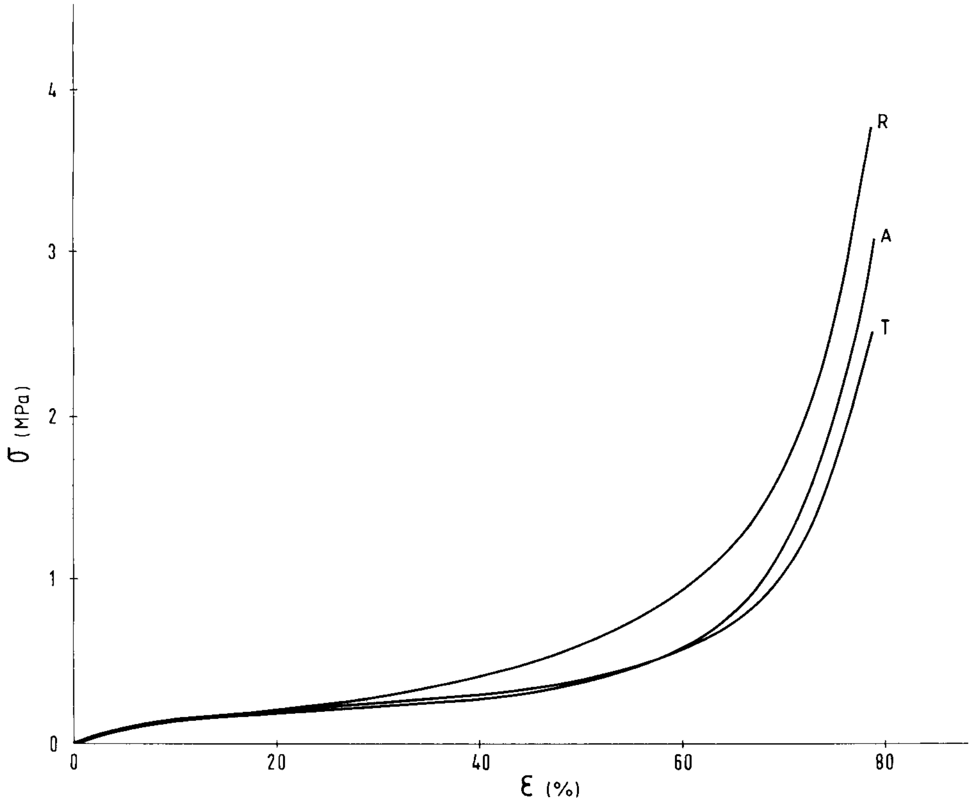

FIG. 6. Compression curves of reproduction cork immediately after boiling, along each of the principal directions: R—radial; A—axial; T—tangential.

compares the stress-strain curves under the three conditions tested, for compression in the radial direction and in a nonradial direction. It can be concluded that there is an increase in strength in the radial direction, due to boiling, for strains up to ≃30%, while for strains larger than this, boiling causes a decrease in strength. The strength in the nonradial directions is, for all strains, smaller in boiled specimens than in unboiled specimens. The reduction in the elastic anisotropy and the softening produced by boiling is apparent when Young's moduli are compared (see Table 2).

Effect of boiling temperature

Table 3 shows the effects of water temperature on the dimensional, mass and density changes measured immediately after treatments of 30 min. The anisotropy of expansion found in the previous experiments is again observed, with a larger value in the radial direction at all temperatures. Temperature has a marked effect on the rate of water uptake by cork and therefore on its expansion. At 40 C, the increase in dimensions is less than 1% and only for temperatures of 80 C or above does the expansion attain 10% and 4%, respectively, for the radial and the nonradial directions.

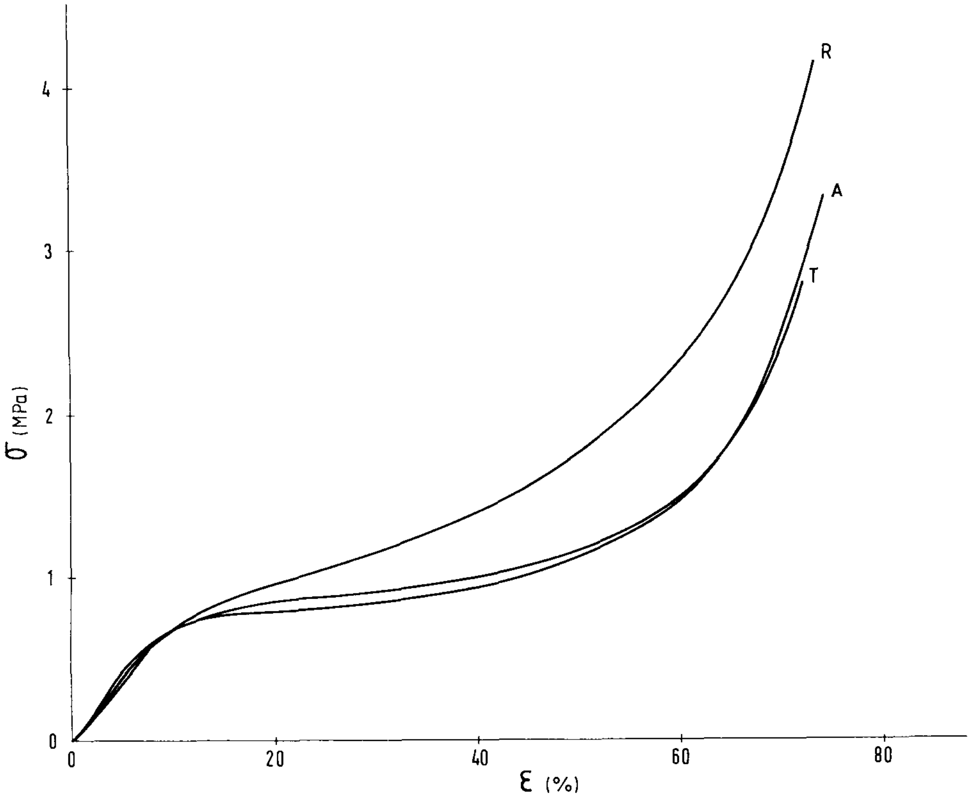

FIG. 7. Compression curves of boiled reproduction cork, along each of the principal directions: R—radial; A—axial; T—tangential.

Effect of cork type

Experiments were performed to assess the extent to which the results previously described, and obtained with a single type of cork, might be affected by the type of cork (i.e., porosity, width of growth rings). For the three types of cork tested, which include two widths of growth rings and three porosity grades, the same pattern of expansion behavior, as previously described, was observed, with a dimensional increase in the radial direction larger than that in both the axial and tangential directions. In the tangential and axial directions, expansions are typically 5–7% after 45 min at 100 C and virtually independent of the type of cork. On the other hand, the expansion in the radial direction is variable from type to type, being larger for cork from thinner boards (10–15% for cork with growth rings 2.5 mm wide and 8–9% for cork with 3.5 mm growth rings). Cork porosity also affects radial expansion particularly for thinner boards: expansion increases with decreasing porosity (15%, 11%, and 10% respectively for good, average, and low quality cork).

DISCUSSION

The main structural alteration induced in cork by boiling is the partial straightening of the cell walls. The straightening is particularly noticeable in the lateral walls, parallel to the radial direction, which are heavily corrugated in natural cork. These corrugations are due to growth stresses that arise when new cork cells are pushed against the other cells, leading to buckling of the lateral walls (Pereira et al. 1987; Rosa and Fortes 1988a). The bases of the cells (perpendicular to the radial direction) are not in general planar, but usually show little or no corrugation. Water absorption during boiling softens the cell walls, while pressure differences beween adjacent cells induce tensile stresses high enough to straighten the walls. Boiling can therefore be regarded as a stress-relieving treatment, which also eliminates the slight curvature of the cork boards. In a previous study (Rosa and Fortes 1988b, 1989) it was observed that heating cork above $\simeq$250 C in air or water vapor causes an almost complete straightening of the cell walls, which become nearly planar. At 100 C the straightening is only partial. It is more pronounced in the radial direction, which expands by as much as 15% in some cork types, compared to $\simeq$6% for the nonradial directions.

The expansion in the radial direction is entirely due to the attenuation of the corrugations in the lateral cell walls. It is easy to estimate the change in the average amplitude, a, of the corrugations, from the observed expansion in the radial direction. We assume that the undulations are circular (Fig. 9) of amplitude a and wave length λ. The arc length, s, corresponding to a wave length, λ, is, for $a \ll \lambda$, given by (Fortes and Rosa 1988).

$$s/\lambda = 1 + \frac{32}{3}\left(\frac{a}{\lambda}\right)^2 \tag{1}$$

Boiling does not change s, but alters both λ and a. The increase in length parallel to the radial direction is $\simeq$15%. This is also the average increase in λ. An estimate of the average a/λ in unboiled cork is difficult to make, but is certainly around 0.2. The average value of a after boiling is, then, from Eq. 1, around 85% of its initial value.

The larger radial expansion that is observed in cork with narrower growth rings is difficult to explain. The fraction of spring cells decreases as the width of the growth rings decreases (Natividade 1938). These cells are more corrugated than the thick-walled autumn cells, which would point to a smaller expansion in thinner boards. It is likely that the larger expansion found in thinner boards, results from the fact that the spring cell walls in them are considerably more corrugated than those in thicker boards, which is indeed observed.

The expansion in the nonradial directions is in part due to the straightening of the cell bases, which become, on average, "more perpendicular" to the radial direction. Boiling causes a slight increase in the diameter of the pores which also contributes to the nonradial expansion.

The changes in dimensions and volume are not accompanied by a pronounced mass change. The density therefore decreases on boiling to values as low as 77% of the original density, both measured in the air-dried condition. In the experimental conditions used, boiling water removes mostly phenolic compounds, e.g., tannins, the fraction of which, in cork, is very small (Pereira 1988). This is supported by chemical analysis of the water used in the industrial boiling operation (Pereira et al. 1979).

The amount of water absorbed by cork in a given time interval increases with

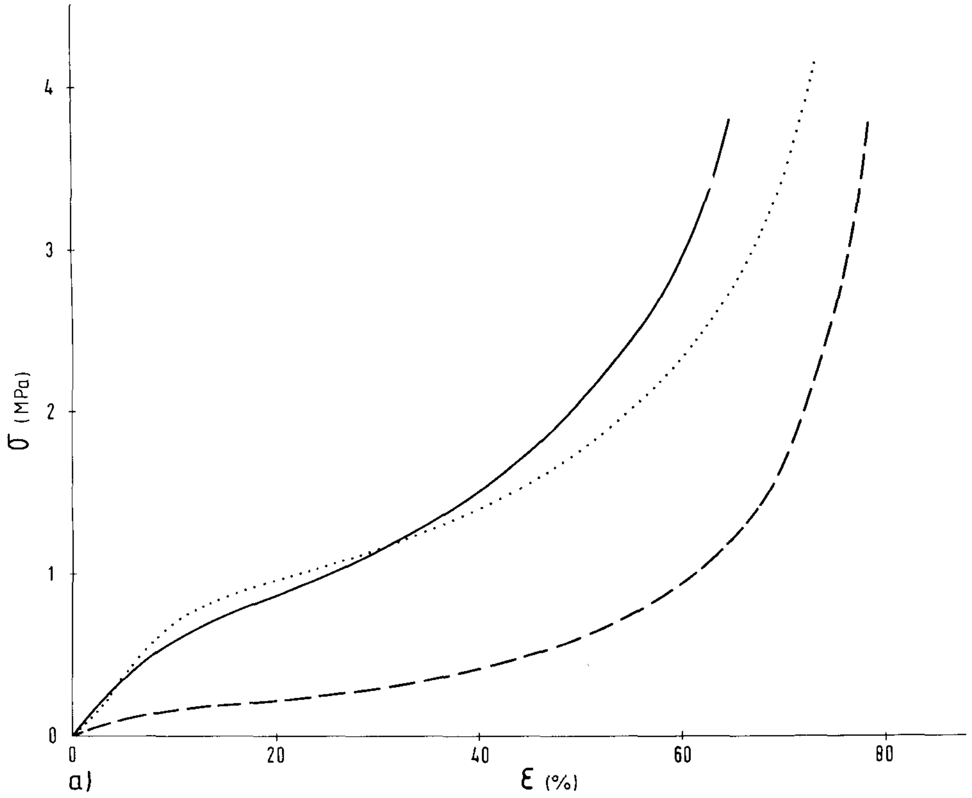

FIG. 8a. Compression curves of reproduction cork along radial direction: unboiled (——), immediately after boiling (– – –), and boiled (· · ·).

temperature. At 100 C, the moisture content changes from 6% (the value for the air equilibrated natural cork) to values around 75% after 1 h boiling. Water diffuses into cork through the cell walls and the lenticular channels. The optimum duration of the boiling treatment therefore depends on the thickness of the cork boards and on the type of cork, particularly on the volume fraction of lenticular channels. Our results suggest that 1 h at 100 C is enough to stabilize the dimensions of even the thicker boards. Direct measurement of the temperature at the center of the samples, using a thermocouple, showed that the temperature reaches 100 C after 10 min of immersion. This time interval is considerably shorter than the one (≃30 min) for stabilization of the expansion, meaning that expansion is a relatively slow process compared to heat diffusion.

The strong effect of temperature on the kinetics of the hot water treatment is a direct consequence of the fact that it is diffusion controlled. The drying of boiled cork in open air also requires diffusion, and therefore the time for air equilibration is again dependent on geometry. The results suggest that cork boards of average thickness will equilibrate after 5-8 days, when their moisture content is ≃6%, the same as in natural cork.

From the practical point of view, important changes brought about by boiling are also those that occur in the mechanical properties. Only the properties in

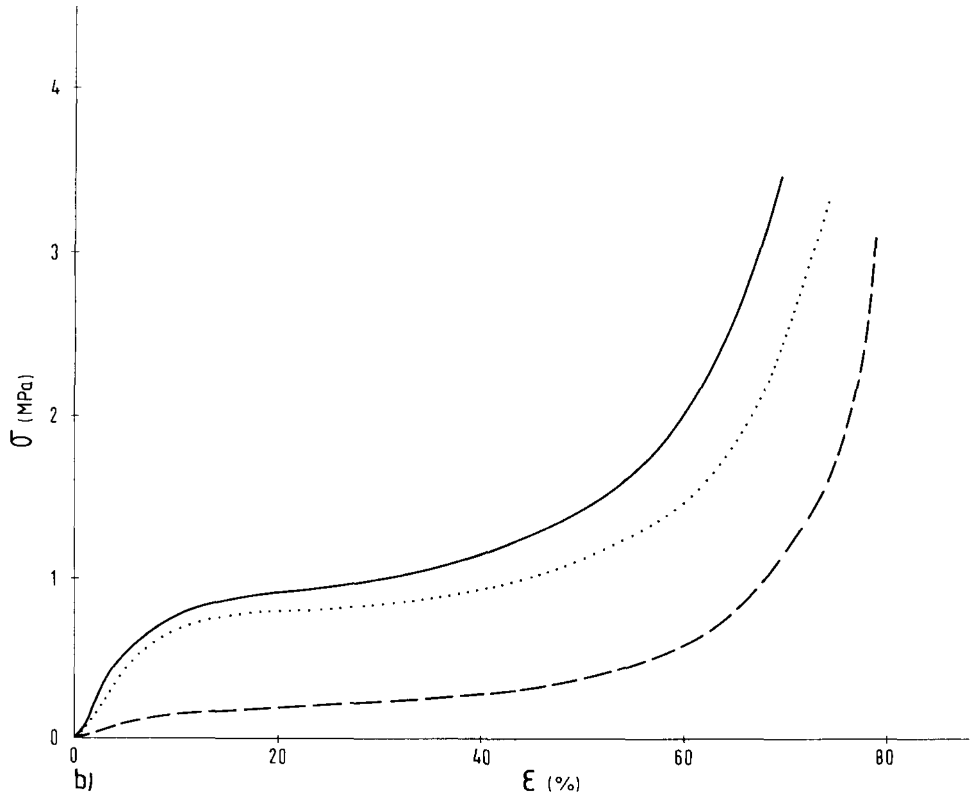

FIG. 8b. Comparison curves of reproduction cork along nonradial direction: unboiled (——), immediately after boiling (– – –), and boiled (· · ·).

compression were investigated in this study, but it is likely that beneficial changes occur in other mechanical properties, notably on the fracture toughness of cork. Investigation along this line is in progress.

The changes in the compression behavior of cork that are caused by boiling can be summarized in the following points: 1—there is a general reduction in strength; 2—there is a reduction in the anisotropy, particularly in the elastic region; 3—a sharper yield point appears in radial compression.

Immediately after boiling, cork is very soft and isotropic (the reduction in the Young's modulus is by a factor of 5–8). This large reduction in strength explains why, under boiling, the internal stresses can be, at least partly, relieved.

The stress-strain curves for compression in nonradial directions show three well-defined regions, which correspond, respectively, to the elastic bending of the cell walls, to the buckling of the cell walls which occurs progressively giving the plateau region of the curves, and finally to crushing of the cell walls which, at this stage, contact each other (Rosa and Fortes 1988a; Gibson et al. 1981). The stress-strain curves in the radial direction do not show so distinctly these three regions, particularly in unboiled cork. There is no plateau region and no well-defined yield point. In boiled cork the yield point is sharper and the compression curve is similar to those for the nonradial directions. The reason for this has to do with

TABLE 3. *Effects of water temperature on the dimensional, volume, mass and density changes of cork immediately after 30 min treatment.*

Water temperature (C)	l/l_0			$\frac{V}{V_0}$	$\frac{M}{M_0}$	$\frac{\rho}{\rho_0}$
	Radial	Axial	Tangential			
40	1.005 ± 0.004	1.003 ± 0.002	1.002 ± 0.002	1.01 ± 0.01	1.019 ± 0.004	1.01 ± 0.01
60	1.05 ± 0.01	1.012 ± 0.002	1.01 ± 0.01	1.07 ± 0.01	1.025 ± 0.006	0.96 ± 0.02
80	1.11 ± 0.01	1.04 ± 0.01	1.04 ± 0.01	1.20 ± 0.03	1.10 ± 0.01	0.92 ± 0.03
100	1.14 ± 0.01	1.051 ± 0.002	1.05 ± 0.01	1.26 ± 0.02	1.16 ± 0.01	0.92 ± 0.02

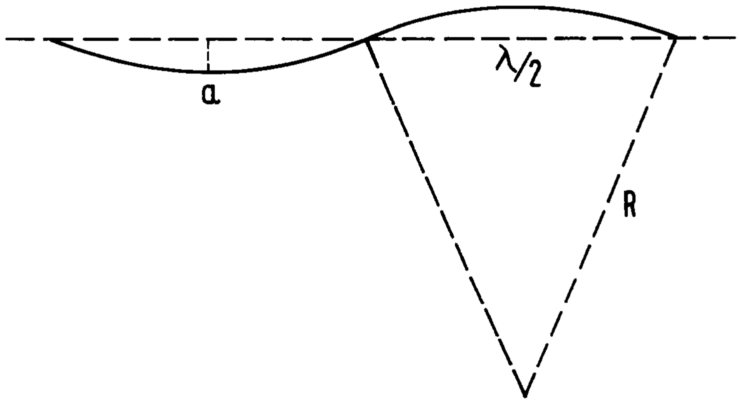

FIG. 9. Circular undulations of the lateral cell walls of cork.

the corrugations in the lateral cell walls and to its attenuation on boiling. Corrugated walls may yield without buckling, as in the folding of a concertina.

As the amplitude of the corrugations increases, the yield transition becomes less sharp and the plateau region less well defined. A similar phenomenon was observed when successive large compressions were given to boiled cork (Rosa and Fortes 1988c). After the first compression, the yield point disappears and the slope of the stress-strain curve becomes more uniform.

The effective Young's modulus, E_u, of a plate of thickness, t, and with sinusoidal undulations of amplitude, a, when loaded transversely to the undulations is given by (Gibson et al. 1981):

$$E_u = E_s\left(1 + \frac{6a^2}{t^2}\right)^{-1} \tag{2}$$

where E_s is the modulus of the material. If there are several of these walls, parallel to the direction of compression, with a volume fraction, f, the Young's modulus is:

$$E = fE_s\left(1 + \frac{6a^2}{t^2}\right)^{-1} \tag{3}$$

This is a reasonable model for the radial compression of cork. When cork is boiled, a decreases and f decreases, due to the expansion in nonradial directions; E_s is practically unchanged. Since the value of E in the radial direction is little affected by boiling, it can be concluded from Eq. 3 that the effects of decreasing f and a cancel. Since f decreases by a factor of $(1.05)^2$, it is expected that a decreases by a factor of $\simeq 1.05$. This is fairly close to the change of a calculated above from the measured radial expansion.

The changes in the nonradial compression curves, due to boiling, are more difficult to model, particularly because there may be an effect due to alteration in the size of pores. If this effect is neglected and the effect of undulations is also neglected, elastic deformation occurs by the bending of the lateral walls. Gibson et al. (1981) have shown that in this case the modulus can be related to the global density, ρ, through the equation:

$$E = 0.5E_s(\rho/\rho_s)^3 \qquad (4)$$

where ρ_s is the cell-wall density. Boiling decreases ρ by a factor of 0.77. Eq. 4 predicts a reduction in E by a factor of $\simeq 0.5$, which compares favorably with the measured change.

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