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Effect of hot pressing densification on the cellular structure of black agglomerated cork board

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Samples of black cork agglomerate boards were observed by scanning electron microscopy, prior and after different densifications. These boards were densified under conditions previously defined, and were observed in two directions, parallel and perpendicular to the compression axis. The relationship between the average cell wall distance and the compression applied was studied and it was found that the maximum densification is achieved with a pressure of ca. 3 MPa. Some aspects of the influence of densification treatments on the chemical composition of the material were also broached.

Einfluß der Verdichtung durch Heißpressen auf die Zellstruktur von Korkplatten

Proben von Korkplatten wurden vor und nach verschiedenen Verdichtungsprozessen im Rasterelektronenmikroskop untersucht. Die Beobachtungen erfolgten in zwei Ebenen, parallel und senkrecht zur Verdichtungsrichtung. Dabei wurde das Verhältnis der durchschnittlichen Zellwandabstände zum Preßdruck ermittelt. Maximale Verdichtung erfolgte bei einem Druck von ca. 3 MPa. Mögliche Auswirkungen der Verdichtungsbedingungen auf die chemische Zusammensetzung werden ebenfalls diskutiert.

1 Introduction

Current commercial black cork agglomerate (expanded or steam-backed), also called pure cork board or insulation cork board, is exclusively made of cork. These agglomerates are manufactured mainly with granules from cork strippings (virgin cork) obtained from pruned branches of the cork oak tree (*Quercus suber* L.). After grinding and partial cleaning of the cork strips, the granules, usually in the range 5–20 mm, are placed into an autoclave, undergo light compression (precompression), and after steaming at 300–350°C and 30–60 KPa, the particles are self-bonded (and expanded) without the use of adhesives. This process usually originates agglomerates in block form, which upon cooling are cut into boards (Gil 1988).

Although such cork agglomerate is produced with the lowest quality types of cork, it has very good properties for some applications, e.g. accoustical, thermal and vibration insulation, shock and sound absorber, and is a completely natural product.

The usual manufacturing process allows for the production of boards with densities of 80 to 300 $kg.m^{-3}$, depending on the range of applications. Nevertheless, this superior limit of density is also a limit for other applications which need a higher physico-mechanical strength. In order to achieve higher densities, a process was developed for the densification of black agglomerated cork boards following the usual manufacturing process. This new process, which also produces smoother surfaces, is based on heating of the boards (optional) prior to hot pressing, under pressure, temperature and time conditions such that irreversible densification is achieved (Gil, unpublished data).

The purpose of this paper is to discuss some aspects of the transformations brought about in the structure and chemical composition of the black cork agglomerate through the densification process on the basis of scanning electron microscopy observations and chemical extraction.

2 Materials and methods

Specimens of black agglomerated cork boards with a nominal size of 1000 × 1000 × 50 mm were cut by half and compressed in a hot plate press under conditions summarized in Table 1. Another board type (number 6) to be considered was the normal black agglomerated cork board.

From these densified (1–5) and non-densified (6) samples, small specimens with approximate dimensions of 15 × 15 × 20 mm were cut, placed into a rotating device, and then cut with razor blades. Their surfaces were coated with a gold film and scanning electron microscopy observations and photographs were made. Measurements of the cell wall distances were made directly on the SEM photographs. The microscope had an X-ray analyser, and the photographs were taken at the most representative cell regions. The observation codes on the photographs are indicated in the example of Fig. 1.

The specimens were observed in two directions, parallel (board's surface) and perpendicular (board's thickness) to the compression axis, except the non densified specimen, which was observed only in one direction since cork granules are distributed at random.

For chemical analysis, four samples were taken from the same group of cork boards (1000 × 1000 × 50 mm) made from the same raw material. Each of these samples was cut by half in two

Table 1. Densification conditions of the cork boards.

Board type	1	2	3	4	5
Previous heating temperature (°C)	180	180	180	180	180
Previous heating time (min)	70	70	70	70	70
Pressure (KPa)	98	196	294	1471	2942
Compression temperature (°C)	230	230	230	230	230
Compression time (min)	10	10	10	5	5

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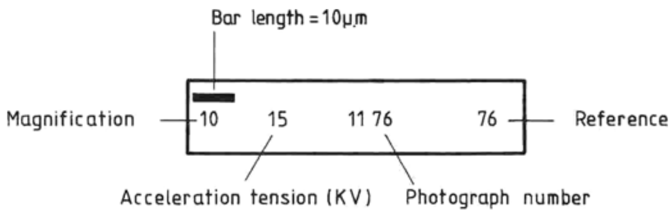

Fig. 1. Micrographs codes (Figs. 3–10)
Bild 1. Erläuterung des Codes der Bilder 3–10

specimens, and a specimen of each board was submitted to one of the different steps of densification:

A – Normal black agglomerated cork board
B – Black agglomerated cork board after over heating (heating time = 70 min; heating temperature = 180°C)
C – Black agglomerated cork board after hot pressing (pressing time = 20 min; pressing temperature = 230°C; pressure = 294 KPa)
D – Black agglomerated cork board after oven heating and hot pressing (heating time = 70 min; heating temperature = 180°C; pressing time = 10min; pressing temperature = 230°C; pressure = 294 KPa).

For extraction, these boards were prepared by mill grinding to a granule size lower than 2 mm and the granulated products subject to the following chemical treatments:

1 – Water extraction, in soxhlet, during 12 hours.
2 – Ethyl acetate extraction, in soxhlet, during 5 hours.

The solvent and extraction conditions were according to the literature (Pereira, 1979 Pes 1976). The extracted materials were gravimetrically determined. Five extractions were made in each case and the average value was calculated.

3
Results and discussion

Cork structure has already been described (e.g. Gibson 1988; Pereira et al. 1987), but its cellular arrangement must be referred for comparison with the microphotographs.

The typical cork cell has a poligonal form with six faces, in a honey-comb type arrangement. In the radial and sections, the cells have a rectangular shape and are arranged parallel to the radial direction (Fig. 2). The expanded cork cells of black cork agglomerate have a "prism" height of 35–50 μm and a base area of (6–10) $\times 10^{-6}$ cm^2 (Pereira et al. 1989).

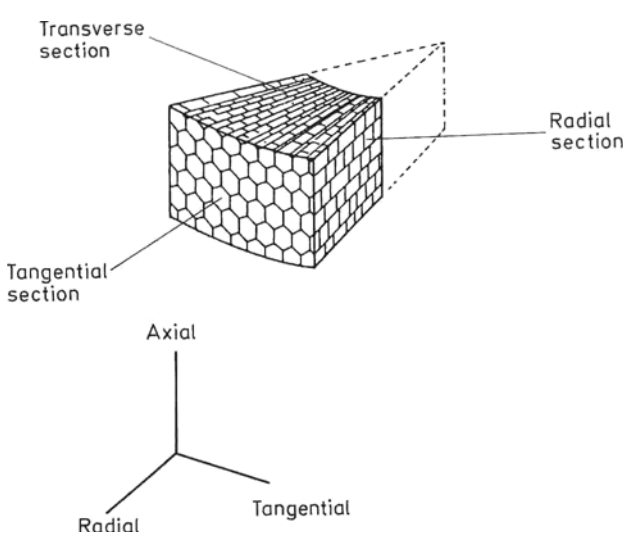

Fig. 2. Diagram of cork structure showing axis system and cork cells
Bild 2. Schematische Skizze der Korkstruktur

The SEM observations of the agglomerates specimens, the most representative ones, are summarized in Figs. 3–10. The distribution at random of the cork granules in the black cork agglomerate is well demonstrated by Fig. 3 and 4. Figure 3 represents an observation of usual black agglomerated corkboard, showing the radial or transverse section, with a "brick-layered"-type arrangement of cells. Figure 4 shows other region of the same observation, with cork cells of the tangential section having a "honey-comb"-type arrangement. The Figs. 5–10 show different aspects of the cork cells in black cork agglomerate after different

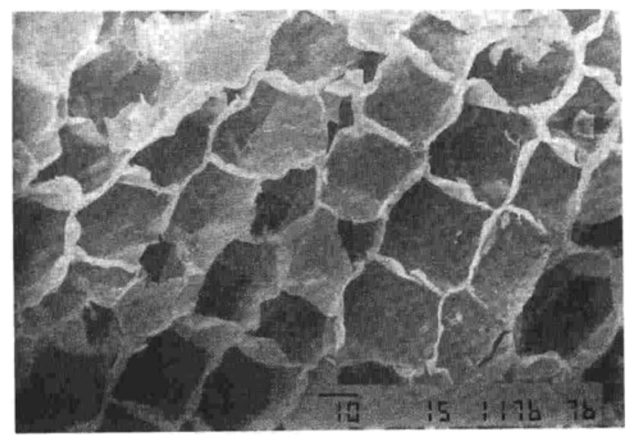

Fig. 3. Detail of normal black cork agglomerates
Bild 3. Detailansicht einer unbehandelten Korkplatte

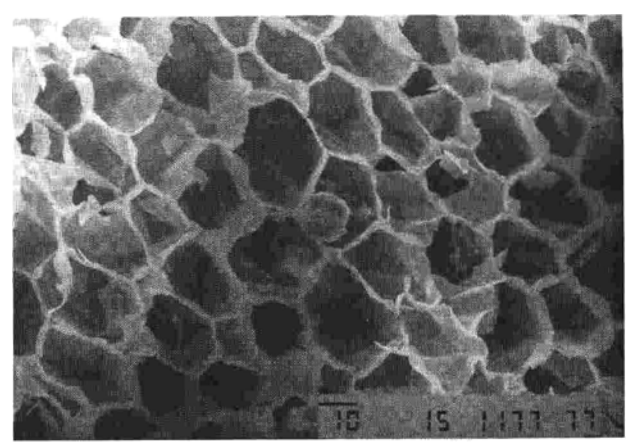

Fig. 4. Different section from the same specimen (Fig. 3) of normal black cork agglomerate
Bild 4. Eine andere Stelle der unbehandelten Korkplatte aus Bild 3

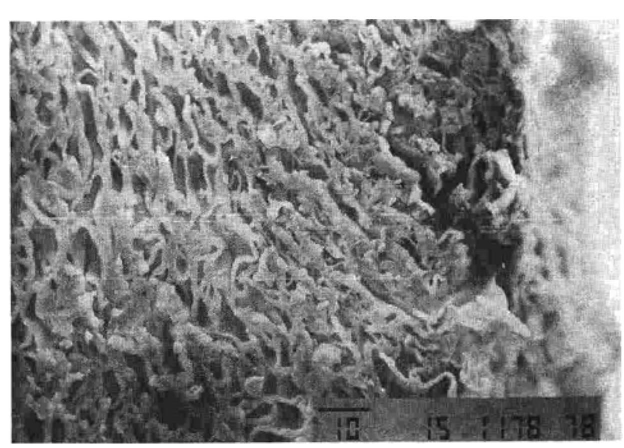

Fig. 5. Aspect of cork cells from densified cork board (98 KPa) seen in direction perpendicular to the compression axis
Bild 5. Korkzelle nach Verdichtung mit 98 KPa. Beobachtung senskrecht zur Druckachse

compression conditions. In Fig. 5, the observation is perpendicular to the compression axis and show the very corrugated cells near the side of the board type 1. An observation of board type 2 is shown in Fig. 6, in a half thickness region (of the densified board), where the compactness is lower than in the board's surface. At the center of this figure a grey mass is observed of what is attributed to be an exudation of cell walls materials, and at its center, the white particle was identified as potassium chloride. A top observation of the cells of the board's surface (type 3) is shown by Fig. 7, demonstrating a total smashing of these cells, contributing to the surface's smoothness, unlike the normal black cork agglomerate, with a surface obtained by cut. With greater amplification, Fig. 8 shows the cork cells of a board type 4 in a half thickness region (side center), not much different from board type 3 near the surface. In Fig. 9 the same board is observed in the same direction but near its surface, where the cell walls are totally joined, and several proportions of exudated material are observed. An observation perpendicular to the compression axis of a board type 5, not represented, shows that even in its half thickness zone, the cell walls are completely joined, similar to Fig. 9. In some regions, it is even impossible to differentiate the cell walls, possibly occurring their interpenetration. Figure 10 represents an observation parallel to the compression axis of the densified board type 5, being very difficult to differentiate the cell walls. Some of the white particles were identified as calcium compounds.

The average cell wall distances were calculated as the mean of ten measurements made on the microphotographs for each case, considering the different amplifications. This average cell wall distances were related with the pressure of densification, and the values are summarized in Table 2. For normal black cork agglomerate (pressure 0 KPa), these ten measurements were made for cells of each of the directions (axial, radial or tangential) and an average of all these measurements was then calculat

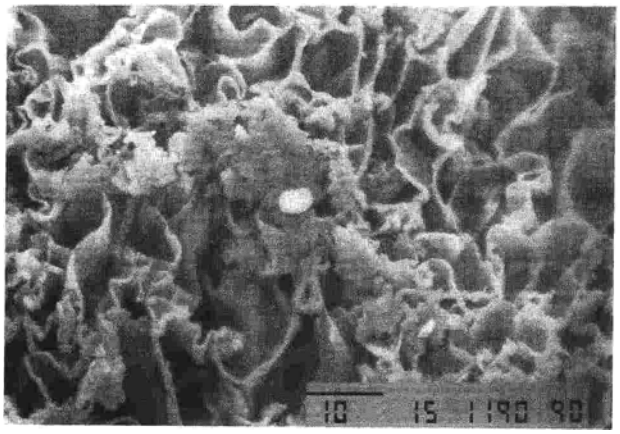

Fig. 6. Densified cork board (196 KPa). Observation perpendicular to the compression axis, in half thickness zone
Bild 6. Korkzellen nach Verdichtung mit 196 KPa. Beobachtung senkrecht zur Druckachse, etwa in Plattenmitte

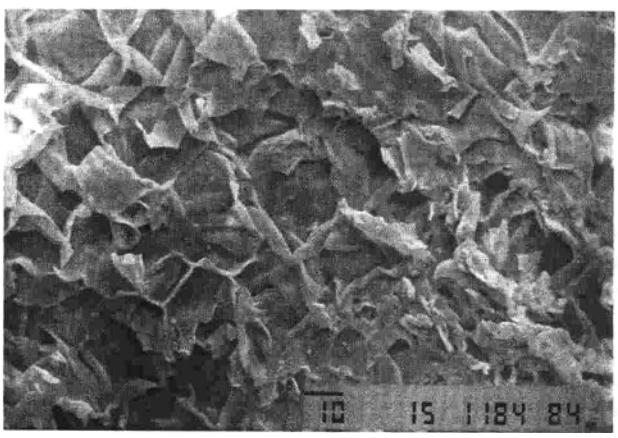

Fig. 7. Cork cells on the surface (direction parallel to the compression axis) of densified cork board (294 KPa).
Bild 7. Korkzellen an der Oberfläche einer mit 294 KPa verdichteten Korkplatte. Die Beobachtung erfolgt in Richtung der Druckachse

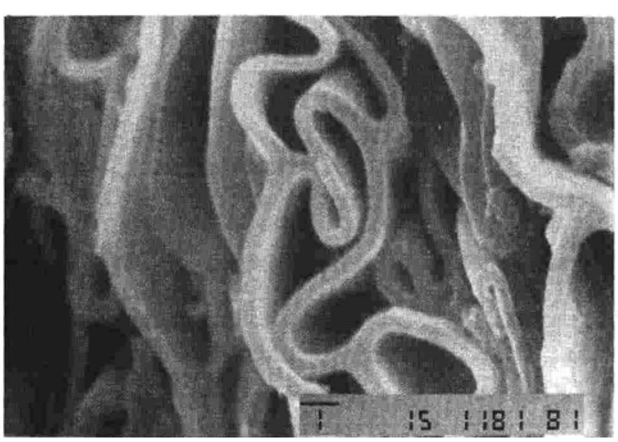

Fig. 8. Aspect of cork cells (direction perpendicular to the compression axis) of densified cork board (1471 KPa)
Bild 8. Aufnahme von Korkzellen nach Verdichtung mit (1471 KPa). Die Beobachtung erfolgt senkrecht zur Druckachse

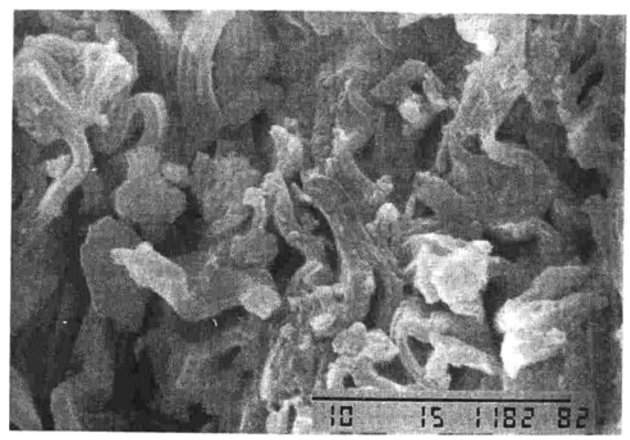

Fig. 9. Other aspect of cork cells in a direction perpendicular to the compression axis of a densified cork board (1471 KPa)
Bild 9. Ansicht eines gröberen Bereichs der Probe aus Bild 8.

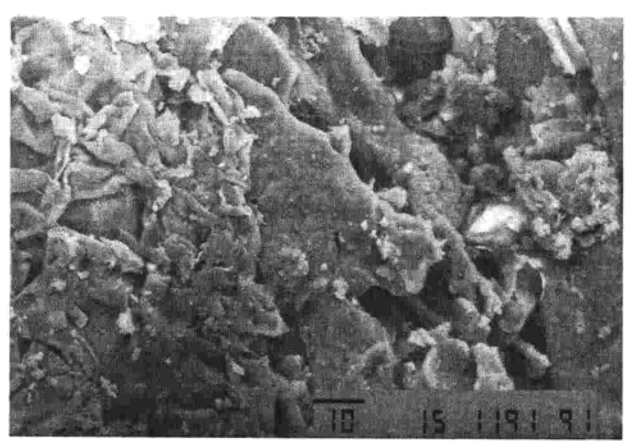

Fig. 10. Observation parallel to the compression axis (surface) of densified black cork agglomerate (2942 KPa)
Bild 10. Oberfläche einer Korkplatte (parallel zur Druckachse) nach Verdichtung mit 2942 KPa

Table 2. Change of average cell wall distance with pressure (densification).

Pressure (KPa)	0	98	196	294	1471	2942
Av. cell wall distances (μm)	38.0	3.1	1.6	0.6	0.5	0.0

ed. The value obtained (38 μm) is greater than the refered by other authors (Fortes 1989).

With these results and the SEM observations, the conclusion is that with pressures greater than about 3 MPa it is very difficult to achieve a decrease in thickness (densification) for the boards, and that there is not a great change of densification for pressures between about 0,3 and 1,5 MPa. Thus, these values of pressure (0,3 and 3 MPa) should be a reference. The first one corresponds to a considerable state of densification, with a relatively low pressure value, and the second corresponds to a state near the maximum densification, and related to the first by a factor of ten, which may facilitate further comparisons.

According to the observations, the densified boards type 5, as they have not spaces between cell walls, should have a density similar to the cell wall density, which is refered to be 1200 kg.m^{-3} (Fortes 1989). However, its value is about 760 kg.m^{-3}. There are several possible explications for this fact. Macroscopically, the original black agglomerated cork boards have an important fraction of impurities, mainly coal, due to the carbonization of some wood chips which became attached in the barking process. This materials has a density much lower than the cell wall density and it does not allow a perfect contact between the granules and their external cell walls in a surrounding region, decreasing the overall density. In second place, the value of density of the cell walls is related to the cells of normal cork after extraction of the tree, and not the cells of cork from black cork agglomerate, which undergo a steambacking process. Thus, according to other authors (Pereira et al. 1989), and now confirmed, while for non-treated cork the cell walls have an average thickness of 1 μm, for the black cork agglomerate this value is about 0,2–0,5 μm. This fact is due to the cell wall straightening (increase of cell volume) and to the loss of some extractives, which also may cause a change in density. The third hypothesis is that the pressure of about 3 MPa is not enough to eliminate all the space between cell walls in all the mass of the boards and even that the material swells lightly in a medium-long term.

The influence of densification treatments on the chemical composition of the densified materials is important to know since some changes may occur, when relatively high temperatures are used (for an organic cellular material), and because these components work as natural binding agents.

Some authors mentioned that in black cork agglomerate the binding agents are the waxes and/or tannins components of cork (Pereira et al. 1989). Other authors refered that the chemical analysis of this type of cork board suggests that its mass loss related to the original raw cork is mainly due to the thermic degradation of the polysacharides and waxes (Rosa et al. 1988).

Table 3. Tannin and wax content of black cork agglomerate after several steps of densification.

Densification step	Tannins (%w/w)	Waxes (%w/w)
A	0,78	5,91
B	0,75	3,01
C	0,85	7,40
D	0,84	5,47

The first step was to study quantitatively the tannin and wax fraction, for several steps of the densification process. The extraction results (average) are summarized in Table 3.

The boards of step C and D, after compression, showed a higher tannin content than the others, which may be related with the degradation of some cell walls, due to the effects of heat and pressure, that facilitate the extraction. This value for tannin content is much lower than the mentioned for the original cork (about 6%) but it is concordant with the manufacture process of steam-backing of the black cork agglomerate, which produces an extraction of these and other compounds.

The content of waxes is also greater after compression, perhaps by the same reason. Other explication is that these treatments may fluidify these components, facilitating their exudation from the cell walls and granules and consequently their extraction. In step B (only heating), the low value may be due to the volatilization of some waxy compounds, what is also verified between C and D.

Another possible reason for the greater content of some component groups could be related with the counting of other products resulting from the degradation of other components of other groups, usually non-extractable (lignin, suberin, cellulose). Anyway, the fact of the tannin and the wax content be greater for densified boards, expecting that both work as binding agents, is a positive aspect, since it should improve the binding of the particles and/or the cell walls, improving the densification results and the physico-mechanical behaviour of the densified boards.

4 Conclusions

The maximum densification of black agglomerated cork board (no distance between cell walls) under the conditions of these study, is achieved with a pressure of ca. 3 MPa. For lower pressures greater cell wall distance is observed but this distance is small in the cells near the board's surface, growing for the center cells. Hot pressing densification produces the exudation of some cell wall materials which helps the cell wall binding, rendering the densification process irreversible. This process releases some of the cell walls components, namely the waxy compounds.

5 References

Fortes, M. A. (1989): A Cortiça (The cork). In Portuguese. Rev. Colóquio/Ciências, 4: 35–60

Gibson, L.; Ashby, M. (1988): Cellular Solids-Structure and Properties. Pergamon Press

Gil, L. (1988): Cortiça-Tecnologia de Processamento e Constituição Ouímica. (Cork-Processing Technology and Chemical Composition). In Portuguese. DTIQ/LNETI, No 3

Pereira, H.; Ferreira, M.; Faria, M. (1979): Química da cortiça. I-Estudos de extracçäo com água. (Cork chemistry.I-Studies of water extraction). In Portuguese. Bol. Inst. Prod. Flor. (Cortiça), 485: 296–300

Pereira, H.; Rosa, M. E.; Fortes, M. A. (1987): The cellular structure of cork from *Quercus suber L.* IAWA Bull., 8: 213–218

Pereira, H.; Ferreira, E. (1989). Scanning Electron Microscopy Observations of Insulation Cork Agglomerates. Mat. Sci. Eng., A111: 237–240

Pes, A.; Lissia, F. (1976): Extracção de cera e de ácidos gordos da cortiça. (Extraction of wax and fatty acids from cork). In Portuguese. Bol. Inst. Prod. Flor. (Cortiça), 452: 135–140

Rosa, M. E.; Fortes, M. A. (1988): Thermogravimetric analysis of cork. J. Mat. Sci. Letters, 7: 1064–1065