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Temperature-induced structural and chemical changes in cork from *Quercus cerris*

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ABSTRACT

The effects of temperature on anatomical and chemical characteristics of *Quercus cerris* cork were examined. Cork samples were subjected to isothermal air heating between 150 °C and 400 °C and analyzed for mass loss, cellular structure and chemical composition.

The thermal decomposition of *Q. cerris* cork is similar to that of *Q. suber* cork. Cork is thermally stable below 200 °C and after that degradation depended on temperature and heating time with increasing mass loss, i.e. 3% at 200 °C 10 min and 46% at 350 °C 60 min. With temperature and starting at 200 °C, cells expanded, cell wall thickness was reduced and corrugations were lost.

Extractives degraded at lower temperatures, although aliphatic extractives were found to be more stable. Suberin from *Q. cerris* was more heat resistant than *Q. suber* suberin, while lignin showed similar resistance.

These results provide a basis for studies on the production of *Q. cerris* bark expanded cork agglomerates for insulation purposes.

1. Introduction

Cork is a cellular material of biological origin contained in tree barks that has been used as an heat insulator since early antiquity. In plant anatomy cork is also named phellem. Its remarkable insulation properties arise from the anatomical and chemical characteristics of the cork cells: the small, non-communicating (at micrometer or higher levels) and air filled cells give cork a low density of about 0.14–0.17 g cm^{-3} and a low heat transfer coefficient of approximately 0.040–0.045 W/mK (Pereira, 2007).

Today, most cork used for thermal insulation, i.e. by the construction industry, is in the form of expanded cork agglomerates. These are cork-only materials, composed by cork granules that are thermally self-bonded without addition of synthetic adhesives at temperatures of about 300–350 °C (Pereira and Ferreira, 1989). The thermal properties of expanded cork agglomerates are comparable with those of synthetic commercial foams but with significant advantages regarding durability and thermal stability.

Cork is also used in composites as adhesive-bonded agglomerates, that are applied for flooring and surfacing, and in special combinations, i.e. with fire proof minerals to reinforce its properties for harsher temperature conditions such as in ablative insulators for space vehicles.

In either case, the thermal behaviour of cork is an important aspect. Temperature-induced structural and chemical changes occur that may affect the material's properties and its behaviour in use. Upon heating the cork cells expand and cell wall thickness decrease (Rosa and Pereira, 1994). Mass loss is relatively small until 200 °C but increases with temperature and exposure time until complete carbonization at approximately 450 °C (Pereira, 1992). The cell wall components have different thermal stabilities, with lignin and suberin being the most resistant while extractives and hemicelluloses are more heat sensitive (Bento et al., 1992; Pereira, 1992).

All the studies made until now on the thermal behaviour of cork have used cork from the cork oak (*Quercus suber*) which is the only cork material that is produced and processed commercially at significant scale (Pereira, 2007). However other tree species contain cork in their barks and may therefore be envisaged as potential producers of this type of raw material.

This is the case of the Turkish oak (*Quercus cerris*), an important tree species in Eastern Europe and Minor Asia, that has a substantial content of cork tissues in its thick bark, especially the var. *cerris* that includes large, albeit not continuous, regions of cork that are clearly visible to the naked eye (Şen et al., 2010).

Recent studies on *Q. cerris* cork have shown that its chemical and anatomical properties are close to those of *Q. suber* cork (Şen et al., 2010, 2011a). This triggered the interest to use *Q. cerris* cork as an insulating material, as suggested already a few decades ago (Telgeren, 1976), but no further development occurred and the bark of *Q. cerris* is still left unused.

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In this study, the effects of temperature on the chemical and structural properties of *Q. cerris* cork were examined. Mass loss and the change in chemical composition and cellular structure were followed for different treatment times in the temperature range of 150–400 °C using granulated cork material obtained by grinding and fractioning of *Q. cerris* bark. The aim is to obtain the information basis for the potential production of expanded cork agglomerates for insulation purposes using *Q. cerris* barks as the cork raw-material source.

2. Materials and methods

2.1. Samples

Bark samples were collected from *Q. cerris* var. *cerris* mature trees with 70–80 years of age, in the Andırın district of Kahramanmaraş, located in the south-eastern part of Turkey. The samples were dried in the open air and stored at room temperature prior to granulation with an industry-type hammer mill (screen dimensions: 3 mm × 25 mm).

The granulated samples were sieved with a Retsch Analytical Sieve Shaker AS 200. The granulometric fraction above 2 mm was taken and purified by suspending in water for a short time for separation of the cork granules (floating layer) from the phloem (sedimenting material).

This material was dried at 60 °C for 3 days prior to a further visual inspection that was made to separate manually any apparent residual phloem particles from the cork sample. The resulting cork fraction was used in the subsequent heat treatments.

2.2. Heating treatment

Isothermal treatment in air in a temperature controlled furnace was made using 2 g samples at temperatures from 150 °C to 400 °C, and with treatment times from 5 to 90 min. Mass loss was determined gravimetrically after each treatment. Six replicated samples were separately tested for each set of experimental conditions. The mass loss repeatability of treatments was on average 0.85.

2.3. Chemical summative analyses

The heat-treated cork samples and one untreated control sample were ground and sieved to separate the 40–60 mesh size fractions that were used in chemical analyses. Chemical summative composition included determination of extractives, suberin, klason and acid soluble lignin.

Extractives were determined by successive Soxtec extractions of 2 g samples with dichloromethane, ethanol and water during 1.5 h with each solvent. The solvents were recovered and the extractives content determined from mass of residue after drying at 105 °C and reported in percent of original samples. Duplicate determinations were made in all cases and the results are the mean value.

Suberin content was determined in extractive-free material by use of methanolysis for depolymerization. A 1.5 g aliquot of extractive-free material was refluxed with 100 ml of a 3% methanolic solution of $NaOCH_3$ in CH_3OH during 3 h. The sample was filtrated and washed with methanol. The filtrate and the residue were refluxed with 100 ml CH_3OH for 15 min and filtrated again. The combined filtrates were acidified to pH 6 with 2 M H_2SO_4 and evaporated to dryness. The residues were suspended in 50 ml water and the alcoholysis products recovered with dichloromethane in three successive extractions, each with 50 ml dichloromethane. The combined extracts were dried over anhydrous sodium sulphate (Na_2SO_4), and the solvent was evaporated to dryness (Pereira, 1988). Suberin extracts were quantified gravimetrically, and results were expressed in percent of cork dry weight. These include the fatty acid and fatty alcohol monomers of suberin.

Table 1
Chemical composition (in % of sample dry mass) of cork of *Quercus cerris* after 10 min treatments at different temperatures and their corresponding mass loss (in % of untreated material, mean and standard deviation).

	Untreated	250 °C	300 °C	350 °C
Mass loss	–	13.4 ± 2.2	26.2 ± 3.2	47.9 ± 3.0
Extractives				
Total	7.01	4.98	3.84	2.54
Dichloromethane	2.50	3.08	2.82	1.82
Ethanol	3.48	1.69	0.86	0.52
Water	1.03	0.21	0.16	0.20
Suberin	11.84	19.36	22.63	11.39
Lignin				
Total	32.34	51.96	70.51	80.28
Klason	29.44	49.71	69.01	78.61
Acid soluble	2.90	2.25	1.50	1.66

Klason lignin and acid soluble lignin, and carbohydrate contents were determined on the extracted and desuberinised materials. Sulphuric acid (72%, 3.0 ml) was added to 0.35 g of an extracted and desuberinised sample, and the mixture was placed in a water bath at 30 °C for 1 h after which the sample was diluted to a concentration of 3% H_2SO_4 and hydrolysed for 1 h at 120 °C. The sample was vacuum-filtered through a crucible and washed with boiling purified water. Acid soluble lignin was determined on the combined filtrate by measuring the absorbance at 206 nm using a UV/VIS spectrophotometer. Klason lignin was determined by the mass of residue after drying at 105 °C. Measurements were reported in percent of the original sample and Klason lignin and acid soluble lignin were combined to give the total lignin content.

2.4. SEM observations

Cork granules of the heat treated samples were separated and cut with a sharp knife to obtain a plain surface. The samples were vacuum-dried and gold was vapour-sprayed making up an approximately 450 A thick coating. The surfaces were observed in an electron scanning microscope Hitachi S-2400 at magnifications ranging from 50 to 1000×, and the images were recorded in digital format. The cell measurements were made on the images using image analysis software (Leica Qwin Plus) by measuring the radial total width and the lumen width in the radial and tangential directions in early cork and late cork cells. Cell wall thickness was calculated by difference of cell width and lumen width. A total of 120 cells was measured in each sample.

3. Results and discussion

The cork material that was fractionated from the bulk granulates of *Q. cerris* bark, showed a summative chemical composition (Table 1) that can be compared to the composition of "pure" cork and phloem tissues separated previously from *Q. cerris* bark (Şen et al., 2010). The results show that the obtained crude cork granulate is not fully made up of cork tissue and still contains a substantial proportion of phloemic material. This can be seen in the differences in the content in extractives and suberin which were lower than those of pure cork, i.e. suberin content in the granulate was 11.8% (Table 1) and in pure cork is 28.5%.

Although this was not the aim of this work, the result of this fractionation process confirms that it will be feasible from a practical point of view to separate a cork-enriched fraction from the other bark components after the grinding of *Q. cerris* whole bark using air or water fractionation. In fact any industrial use of the *Q. cerris* cork has to pass through a bulk grinding of the bark and

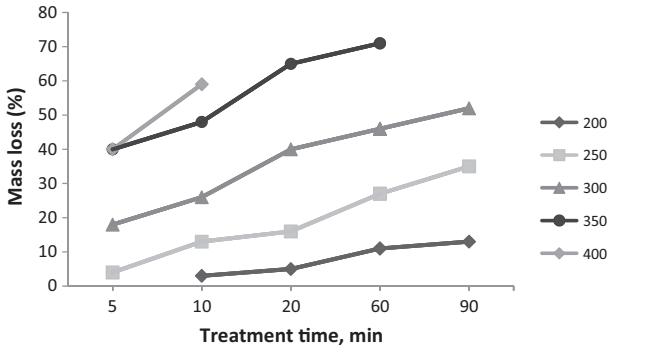

Fig. 1. Variation of mass loss of cork granules from *Quercus cerris* upon air heating at different temperatures and treatment times.

its fractioning. However further developments on the fractionating procedure might improve the purity of the cork fraction.

3.1. Mass loss

Fig. 1 summarizes the results for the mass loss for the temperature range 200–400 °C. At 150 °C mass loss was negligible representing only 3% after 90 min treatment. At 200 °C the effect was also small for short treatments, e.g. 3% mass loss occurred after 10 min, but became significant with longer treatment times e.g. 11% and 13% mass loss were recorded after 60 and 90 min respectively. At higher temperatures mass loss occurred for shorter treatment times. For instance, at 250 °C 13% mass loss occurred after 10 min, while at 300 °C and 350 °C, after 5 min, mass losses of 18% and 40% were already recorded.

With increasing temperature, the mass loss became larger. Approximately 50% of mass loss occurred after 90 min at 300 °C and after 10 min at 350 °C. At 350 °C the mass loss was rapid and attained very large values, e.g. 65% in 20 min and 71% in 60 min of treatment. At 400 °C, already 59% of the cork mass was lost during the first 10 min of treatment.

The thermal degradation of *Q. cerris* cork showed a similar decomposition pattern to that of *Q. suber* cork, where the extent of degradation depended on the temperature and time of exposure (Pereira, 1992). During the process, and in an extent determined by the conditions, it was found that the cells underwent expansion and cell walls became thinner as a result of the chemical degradation of cell wall components and overall mass loss.The mass loss values due to the thermal degradation by volatilization of *Q. cerris* cork were found to be in agreement with those reported for *Q. suber* cork (Pereira, 1992; Rosa and Fortes, 1988). The cork is thermally stable below 200 °C and loss of material starts at this temperature and increases with time of exposure to temperature. The rate of mass loss increased significantly with temperature (Fig. 1).

3.2. Structural changes

In the mildest conditions of heating, corresponding to small mass losses, the structural features of the cork tissue were maintained. For instance, at 200 °C for short treatment times with mass loss of about 3% no differences were observed between untreated and heat treated cork samples. The radial structural arrangement was maintained; the cork cells preserved their dimensions and showed corrugations of cell walls (Fig. 2).

With increasing treatment time and temperature, and along with increased mass loss, clear effects were observed on the cellular organization and cell dimensions (Figs. 3–7).

Upon heating, the cork cells expanded (Fig. 3). The effect was first noticed in the increased dimensions in the radial direction, together with straightening of cell walls and disappearance of corrugations.

Cells enlarged in the radial direction in conjunction with mass loss, i.e. for samples treated 10 min at 200 °C and 350 °C, the radial dimensions in earlycork were respectively 26.2 μm and 37.6 μm, and in latecork 11.6 μm and 21.3 μm respectively (Fig. 4). The tangential cell width remained relatively constant until 60 min treatment at 300 °C but enlarged for harsher conditions.

As a result of the heavy cell enlargement, the cells appear inflated and with stretched cell walls and the overall structure lost somewhat its clear radial alignment of cell rows in the radial and transverse sections which became more similar to the typical honeycomb arrangement of the tangential section. Fig. 5 shows fully expanded cells in a sample where the cell volume was increased approximately by a factor of 2 corresponding to a sample heat treated 10 min at 350 °C.

Physical damage of the cell walls started at approximately 40% mass loss e.g. 300 °C and 60 min, and increased at higher temperatures and for longer treatment times. The cell walls were torn and cracks were formed (Fig. 8).

The loss of material resulted into a significant reduction of the cell wall thickness (Fig. 6). *Q. cerris* cork cells have a wall thickness of 2.5 μm in the earlycork region (Şen et al., 2011b) that was reduced steadily with increasing intensity of the thermal treatment starting at 1.7 μm for 3% mass loss and reaching 0.6 μm for about 50% mass loss.

In latecork cell wall thickness was approximately 1.9 μm until 10% mass loss and decreased subsequently to 1.2 μm (Fig. 7). The temperature-induced effect of cell wall stretching due to expansion of cell volume also contributed to the decrease of cell wall thickness, as seen in Fig. 5.

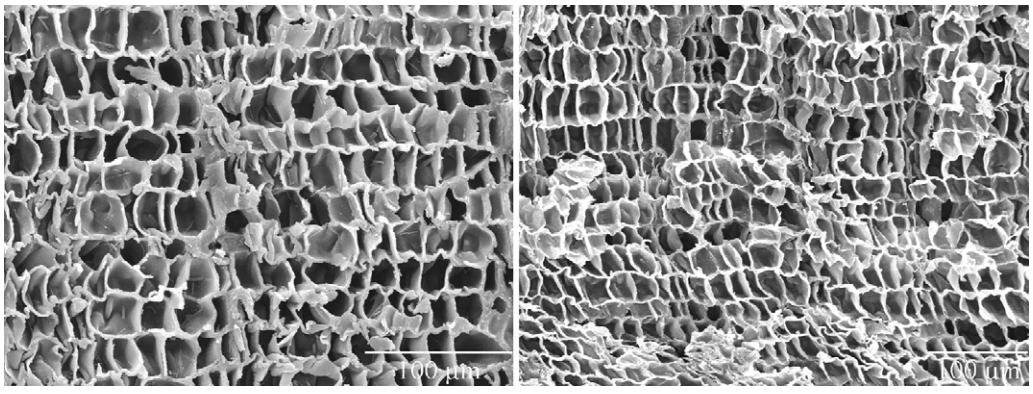

Fig. 2. SEM photographs of the transverse section of untreated *Q. cerris* cork (left) and of heat treated sample during 10 min at 200 °C (right) showing similar radial arrangement of cell rows and cell corrugations.

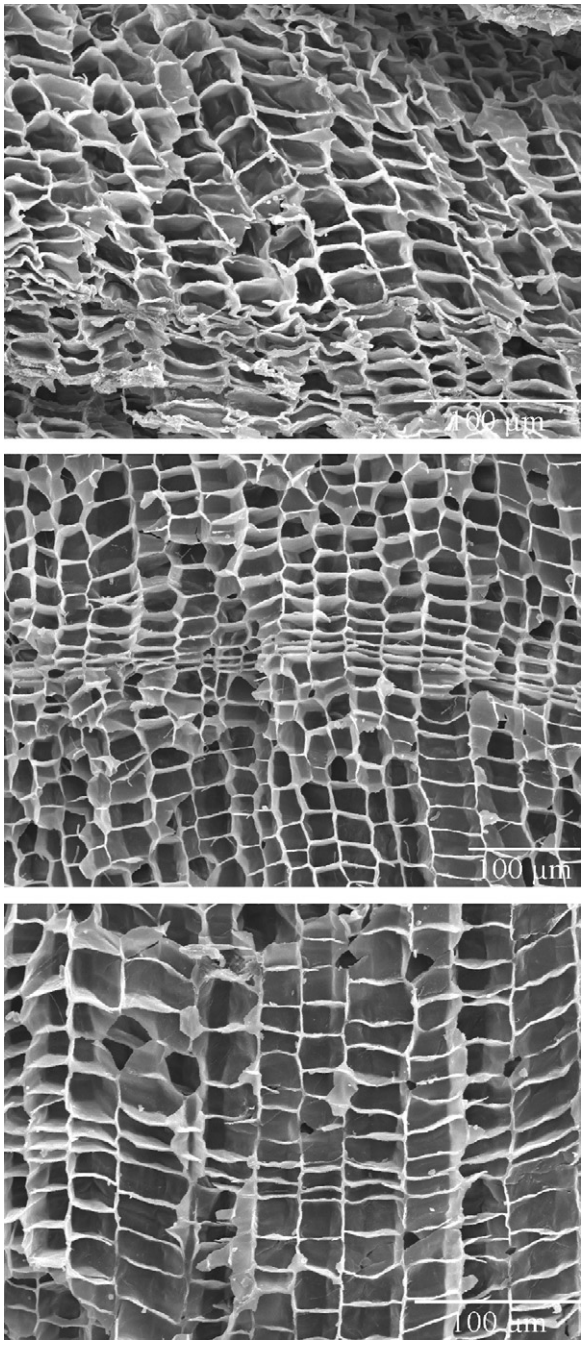

Fig. 3. SEM photographs of the transverse section of *Q. cerris* cork samples that were heat treated during 60 min at 200 °C (top), 250 °C (middle) and 300 °C (bottom) showing the progressive expansion of cell dimensions and the disappearance of cell corrugations.

The SEM observations showed clearly that the cellular structure of cork was altered with the heat treatment, although only for exposures above 10 min at 200 °C (Figs. 2 and 3). The cells expanded, the cell walls straightened loosing the corrugations that were found in the original cork as described by Şen et al. (2011b).

The same effect was observed for the cork of *Q. suber* for which prior studies showed also a cell volume expansion leading to smaller densities in heat-treated cork especially in the cases of cork with many corrugations such as virgin cork in comparison with reproduction cork (Pereira, 1992; Pereira and Ferreira, 1989; Rosa and Fortes, 1988). In *Q. cerris* cork the highest cell

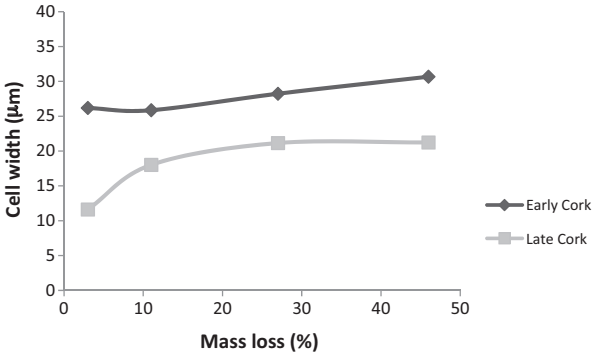

Fig. 4. Variation of cell dimensions width in the radial direction in earlycork and latecork of *Q. cerris* cork with mass loss during heat treatment.

expansion occurred at 350 °C while it occurred at 300 °C in *Q. suber* cork (Pereira, 1992).

3.3. Thermochemical degradation

The summative chemical composition of the heat treated cork samples is summarized in Tables 1–3.

Extractives were the most heat sensible compounds. Starting at 7.0% in untreated cork, extractives were rapidly lost with heating and represented only 0.7% in the sample treated 60 min at 350 °C. Approximately 50% of the extractives were lost in the first 60 min of treatment at 200 °C (Table 2). In relation to the different types of extractives, some difference in degradation rate was found: the non-polar extractives soluble in dichloromethane were comparatively more heat stable than the more polar compounds, as can be seen by the composition of samples treated at 200 °C (Table 2). The explanation may derive from their chemical composition because they are aliphatic extractives composed of *n*-alkanes, fatty acids identical to suberin monomers, fatty alcohols and friedelin and the fact that extractives also include heat sensitive carbohydrates in addition to phenolics (Şen et al., 2010).

Suberin was relatively resistant to thermal degradation until 250 °C, and therefore the heat treated samples showed a higher suberin content than the untreated sample (Table 1). Suberin content only decreased for the 350 °C treated samples, to which corresponded over 50% mass loss (Table 1). For instance the untreated sample contained 11.8% of suberin, while a heat treated sample 60 min at 250 °C contained 22.4% suberin. The results are in agreement with the findings obtained for *Q. suber* cork although in this case suberin content decreased already after 200 °C. Another

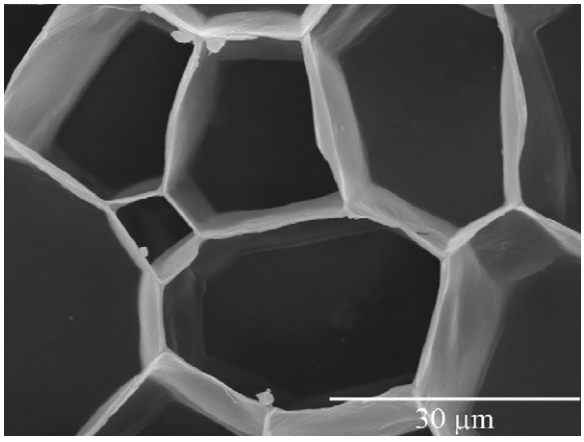

Fig. 5. Expanded cork cells of *Q. cerris*, as observed in the tangential section, after 10 min at 350 °C.

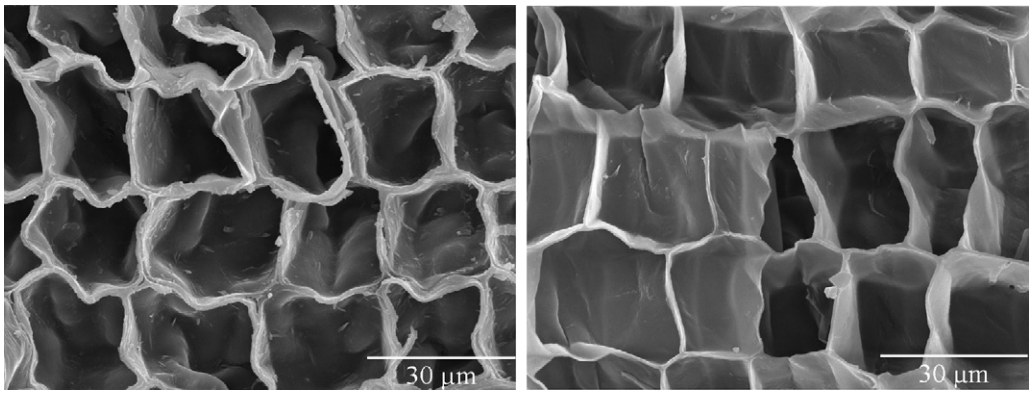

Fig. 6. Comparison of cell wall thickness of heat treated *Q. cerris* cork samples 10 min at 200 °C (left) and 60 min at 300 °C (right).

interesting difference of *Q. cerris* cork is that at 300 °C and higher temperatures, more suberin remained in the samples than in *Q. suber* cork: at 300 °C, 6.7% and 14.2%, and at 350 °C 1.1% and 2.8% for *Q. suber* and *Q. cerris* cork respectively (Pereira, 1992). This may be the result of differences in the monomeric composition of suberin of both corks: *Q. cerris* cork suberin was found to be composed mainly of ω-hydroxyacids and, contrary to *Q. suber* cork, the α–ω diacids content was found to be much smaller (Pereira, 2007; Şen et al., 2010).

Lignin content increased with temperature in all the heat treated samples and was the most heat resistant component, especially the acid insoluble lignin (Table 3). In the heat treated samples with large thermal degradation, the acid insoluble material determined as lignin was by far the dominant component e.g. 85% in the sample treated 60 min at 350 °C (Table 2).

Lignin content is slightly higher in *Q. cerris* cork (28%) as compared to *Q. suber* cork (21–23%) (Pereira, 1988). In the present study lignin content was found to be higher (32%), because of the phloemic inclusions. Lignin content increased with temperature: at 250 °C lignin content reached two times the value of untreated samples and at 300 °C and 350 °C lignin represented 80–85% of the sample. The results are in agreement with those obtained with *Q. suber* cork (Pereira, 1992). These high values of lignin should be taken with care since they do not represent lignin with its original chemical composition structure but rather a transformed lignin that underwent heat-induced chemical alteration. Lignin in *Q. suber* cork was found to be decomposed at temperatures of approximately 250–350 °C (Neto et al., 1995). The lignin determined after heating treatments should therefore be regarded as a transformed lignin (Pereira, 1992).

Table 2
Chemical composition (in % of sample dry mass) of cork of *Q. cerris* after 60 min treatment at different temperatures, and their corresponding mass loss (in % of untreated material, mean and standard deviation).

	Untreated	200 °C	250 °C	300 °C	350 °C
Mass loss	–	11.2 ± 0.9	26.5 ± 5.0	46.0 ± 2.0	71.1 ± 5.9
Extractives					
Total	7.01	3.64	2.21	1.80	0.70
Dichloromethane	2.50	1.48	1.41	1.19	0.36
Ethanol	3.48	1.47	0.60	0.34	0.17
Water	1.03	0.69	0.20	0.26	0.17
Suberin	11.84	16.50	22.43	14.22	2.80
Lignin					
Total	32.34	51.75	75.74	86.41	86.28
Klason	29.44	48.91	74.11	84.98	84.84
Acid soluble	2.90	2.84	1.63	1.44	1.44

Table 3
Chemical composition (in % of sample dry mass) of cork of *Q. cerris* after treatment with different times at 200 °C, and their corresponding mass loss (in % of untreated material, mean and standard deviation).

	Untreated	10 min	60 min	90 min
Mass loss	–	3.5 ± 0.8	11.2 ± 0.9	13.2 ± 3.6
Extractives				
Total	7.01	6.63	3.64	2.67
Dichloromethane	2.50	2.77	1.48	1.10
Ethanol	3.48	2.41	1.47	1.04
Water	1.03	1.45	0.69	0.53
Suberin	11.84	12.60	16.50	14.35
Lignin				
Total	32.34	33.10	51.75	54.46
Klason	29.44	30.27	48.91	51.90
Acid soluble	2.90	2.83	2.84	2.57

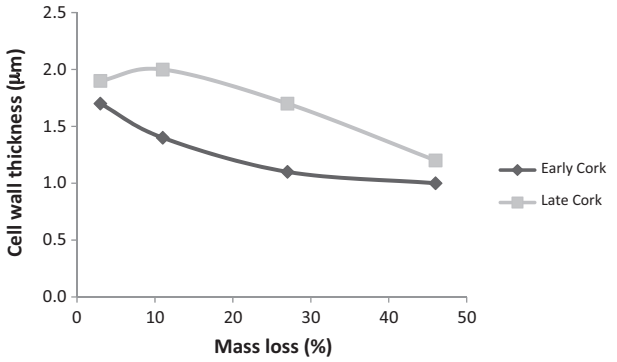

Fig. 7. Variation of cell wall thickness in earlycork and latecork of *Q. cerris* with mass loss during heat treatments.

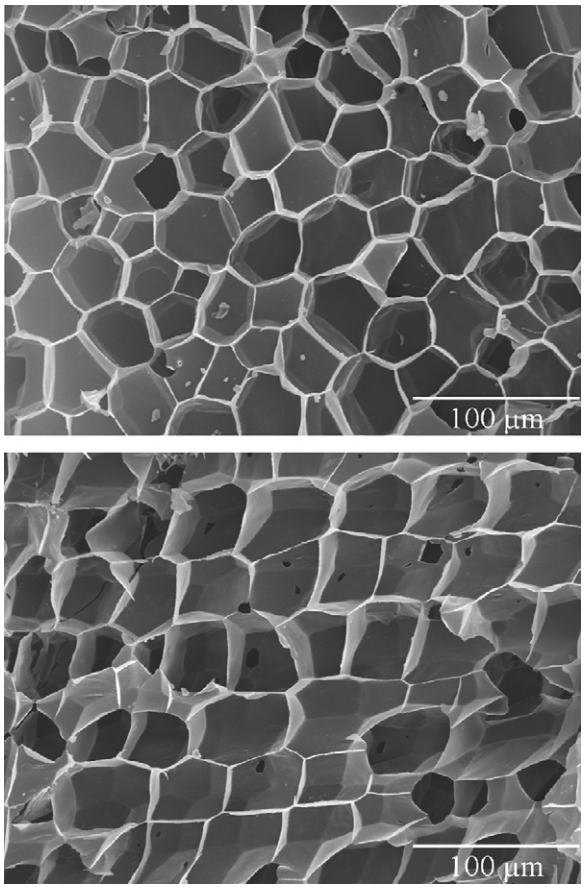

Fig. 8. Formation of cell wall rupture and cracks in the cork of *Q. cerris* as seen in the tangential section (above) and in the radial section (bottom) after 10 min at 350 °C.

Overall the results showed that cork from *Q. cerris* behaves upon heating in a way similar to the cork of *Q. suber* with cellular expansion and density decrease, and chemical changes that enhance lignin and suberin contents. Therefore this opens the possibility of using *Q. cerris* cork as a raw-material for the production of insulation agglomerates, using an autoclave thermal treatment where self-expansion and adhesion of the cork granules will result into an agglomerate, as it is done for the production of the expanded insulation agglomerates of *Q. suber* cork (Pereira and Ferreira, 1989). Improving the enrichment in cork of the granulate will increase process yields and quality of the agglomerate since the phloemic content affects adversely the self agglomeration process as shown for *Q. suber* cork (Pereira and Baptista, 1993).

4. Conclusions

The cork of *Q. cerris* showed similar temperature-induced alterations as the cork of *Q. suber*. Exposure to temperature induces thermal degradation with mass loss and chemical alteration of the cell wall with suberin and lignin as the more stable components. The structural effects included cell expansion and cell wall thickness reduction.

The higher suberin content in elevated temperatures in *Q. cerris* cork is a promising feature for its potential higher temperature stability.

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