Effect of Different Boiling Treatments on Physical Properties of Cork from *Quercus variabilis*

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Effects of different boiling treatments were evaluated relative to various physical properties of cork from *Quercus variabilis* before and after treatment, including volume, density, hardness, compression resilience ratio, and color. The boiling water treatment decreased the density, hardness, and lightness of cork. Water absorption amount of cork boiled at 100 °C for 30 min to180 min increased from 28.85% to 52.50%, and expansion in the radial direction was 15.4% to 19.5%. The total color difference (Δ*E**) of cork gradually increased with increased boiling time. The values of the compression resilience ratio of all corks after a pressure release at 24 h were >80%. Cork samples boiled at 100 °C for 60 min, and then dried under different temperatures (140 °C to 240 °C), had volume expansion between 35.6% and 65.3%. With increased drying temperature, the Δ*E** of cork increased. Cork boiled at 100 °C for 60 min followed by microwave irradiation of different times (2 min to 8 min) had volume expansion of 39.7% to 54.5%. Microwave treatment had little influence on cork color. The sodium hydroxide solution boiling treatment decreased cork lightness, while the hydrogen peroxide-treated cork lightness increased with the increasing of solution concentration, and Δ*E** slightly increased.

Keywords: Quercus variabilis; Cork; boiling treatments; Physical properties

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INTRODUCTION

Cork is a natural, renewable, and recyclable material that is obtained mainly from the cork oak (Silva *et al.* 2005). It is known to produce the stoppers in wine bottles, and the main production in the world is concentrated in Portugal (Teixeira and Pereira 2010; Pereira 2015). Cork has many unique properties, such as low density, low acoustic impedance, thermal and electrical insulation, very low permeability to liquid and gas, and more that contribute to its use in a much broader scope of traditional and innovative applications (Fortes 1993; Faria *et al.* 2011; Fonseca *et al.* 2013).

In China, cork mainly comes from a specific species of oak, *Quercus variabilis* (Lei *et al.* 2013). Because of cork's quality and process technology, most of the raw materials of cork are treated by a series of sorting, boiling, and drying procedures, and then they are processed into granulates in Chinese factories. Boiling treatment removes dirt in the cork, causes volume expansion and reduces the unit weight of cork, and changes the physical and mechanical properties of the cork, which is one of the most important cork pretreatment processes in China. The cork planks after boiling are processed into particles with different sizes, which are used for the production of agglomerated products such as boards, wall coverings, floorings, shoe leathers, insoles, insulated panels, and so on (Song *et al.* 2011; Song *et al.* 2016; Zhao *et al.* 2014).

The boiling treatment for *Quercus suber* cork has been extensively studied in European countries (Pereira 2013; Gil 2015). The cork used for stoppers was subjected to a boiling operation before processing. The cork planks were immersed in boiling water in large tanks for approximately 1h. Various parameters related to the boiling treatment were investigated, including water temperature, time, cork quality, and the kinetics of air-drying (Heredia *et al.* 2004; Biencinto *et al.* 2014; Knapic *et al.* 2016). The boiling treatment of cork causes the attenuation of its cell-wall corrugations and gives rise to an expansion of 10% to 15% in the radial direction and 5% to 7% in the direction perpendicular to the radial direction (Rosa *et al.*1990). Water boiling on cork resulted in the expansion of all growth rings in the radial direction and the porosity coefficient of cork reduced by half (Cumbre *et al.* 2000).

The boiling water treatment causes the cork planks to flatten and facilitates the subsequent cutting processes. However, the boiling treatment research of cork from *Q. variabilis* is very rare. A new study on *Q. variabilis* cork has shown that boiling water treatment leads to volume expansion of about 25% to 27%, and causes an approximate 20% density decrease (Yuan *et al.* 2017).

In this study, the cork from *Q. variabilis* was subjected to four different treatments, including boiling water treatment with different duration, boiling water treatment followed by drying processing at different temperatures, boiling water treatment and then microwave processing, and chemical treatments. The objectives of this work were to investigate the effect of different treatments on the physical properties (including volume, density, hardness, color, *etc.*) of the *Q. variabilis* cork and to provide the basic data that could contribute to the best processing of *Q. variabilis* cork as raw-material.

EXPERIMENTAL

Materials

Reproduction cork from *Q. variabilis* was obtained from Qinba Mountain, located in the southwest portion of the Shaanxi province of China. Cork samples, containing 15 to 20 complete annual growth rings, were collected in August of 2015. They were air-dried in the laboratory and the moisture content was approximately 6%.

The samples were cut from the 30 planks of reproduction cork and were trimmed in the form of cubes with edges parallel to the three principal directions in the tree (Leite and Pereira 2017). The three sections of samples were ground flat and cleaned with compressed air. The samples for hardness and color testing were 30 mm × 30 mm × > 6 mm (axial × tangential × radial). The samples for linear dimension, volume, density, water or solution absorption, and compression resilience testing were 16 mm × 16 mm × > 6 mm (axial × tangential × radial). The tests of parameters, including water or solution absorption amount, volume, density, hardness, compression resilience, and color, were repeated 30 times. Four types of boiling treatments for the cork were studied under normal atmospheric pressure.

Methods

Boiling treatment of cork

A boiling water treatment with different durations followed methods previously described by Yuan *et al.* (2017). The boiling water treatment at approximately 100 °C was operated using a water bath kettle. The durations of the boiling operation were 30 min, 60 min, 120 min, and 180 min. The samples were weighed immediately after boiling, then oven-dried at 60 °C, and finally equilibrated in the laboratory atmosphere until the moisture content of the specimens was consistent with their initial value. Then, the linear dimensions, volume, density, hardness, and colorimetric parameters of the treated samples were determined and compared with their initial values.

To obtain the larger volume expansion, cork samples were boiled at approximately 100 °C for 60 min. Then, the samples were immediately dried in an oven. The drying temperatures were 140 °C, 180 °C, 210 °C, and 240 °C. When the mass of boiled samples had been reduced to its un-boiled value, the drying treatment at each temperature condition ended. Finally, the samples were equilibrated with the laboratory atmosphere. The changes in volume, density, hardness, and color were calculated.

Cork samples boiled at approximately 100 °C for 60 min were immediately submitted to microwave treatment (G80F23CN2P-B5, Galanz Inc., Guangdong, China). The radiation power was 500 watts. The duration of microwave treatments were 2 min, 4 min, 6 min, and 8 min. Then, the samples were equilibrated and the changes in volume, density, hardness, and color were calculated.

Sodium hydroxide and hydrogen peroxide were selected for the chemical boiling treatments of cork samples. The concentrations of sodium hydroxide solution were 0.1%, 0.3% and 0.5%, respectively. Three concentrations (3%, 5%, and 7%) of hydrogen peroxide solution were used for the boiling treatment of cork. To reduce the solvent evaporation and play a better role of a solvent, cork specimens were boiled for 60 min at 75 °C in different concentrations of solutions, and the container was properly sealed during the boiling treatment. After the freeze-drying and equalization treatment, the moisture content of the samples was reduced to the initial value. The various determinations were made, the same as with the boiling water treatment.

Basic parameters testing

The linear dimensions (including radial, axial, and tangential) of the cork cubes before and after the four different boiling treatments were measured by the Vernier caliper. The volume of the samples after boiling treatments was measured through the displacement method. The density before and after the four different boiling treatments was calculated by the sample's mass divided by its corresponding volume. Three types of hardness value (H_0, H_i, and H_e) of the cork samples were measured using the XHS Shore A hardness test (Liaoning Yingkou Inc., China). The variable H_0 represented the initial hardness of cork (HA), H_i represented the hardness measured immediately after the boiling treatment (HA), H_e represented the hardness measured after drying and equalization with the laboratory atmosphere (HA). Each sample was measured at four different locations on the tangential section. The final hardness value was the arithmetic mean of four hardness values. The amount of water or solution absorbed by cork measured immediately after boiling treatment was calculated by Eq. 1,

$$W(\%) = (M_1\text{-}M_0)/M_0 \times 100 \quad (1)$$

where W is the amount of water or solution absorbed by cork (%), M_0 is the mass of untreated cork samples (g), and M_1 is the mass measured immediately after boiling treatments with different durations or solvent treatments with different concentration (g).

Compression resilience testing

The cork moisture content after the boiling treatment was adjusted to the initial value. The compression resilience of corks after boiling water treatments and chemical treatments was investigated using a universal materials testing machine (CMT5504, SANS Inc., Shenzhen, China). The compression load was parallel to the radial direction in the oak tree. Approximately 50% compression of radial direction was done at a crosshead speed of 5 mm/min, and then the loading was removed. The dimension recovery after compression was determined by measuring the residual amount of compression in the squeezing direction immediately at 15 min and 24 h after pressure release. The compression resilience ratio was calculated by Eq. 2,

$$R(\%) = (l_2 - l_1)/l_1 \times 100 \tag{2}$$

where R is the compression resilience ratio (%), l_1 is the thickness of samples compressed into half (mm), and l_2 is the thickness of samples at 15 min or 24 h after pressure release (mm).

Color determination

The color changes of cork before and after the boiling treatments were characterized according to the Commission Internationale d'Eclairage $L^*a^*b^*$ color space (CIELAB). The colorimetric properties of the lightness index (L^*), red-green index (a^*), and yellow-blue index (b^*) were measured with the automatic colorimeter (SC-80C, Kangguang Inc., Beijing, China). Each cork sample before and after the boiling treatment was measured at three points on the tangential section. The average of the three points was the final result of each color parameter. Total color differences (ΔE^*) were expressed by Eq. 3,

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{3}$$

where ΔL^*, Δa^*, and $\Delta b^*$are the differences in the L^*, a^*, and b^* values, respectively, of each cork sample before and after each boiling treatment at different conditions. This measurement scale is as follow: L^* is the lightness index, a^* is the red-green index, and b^* is the yellow-blue index.

RESULTS AND DISCUSSION

Analysis of Boiling Water Treatment Results

Table 1 shows the results of changes in several parameters due to boiling at approximately 100 °C for different lengths of time. During the boiling treatment, water slowly permeated into cork and caused mass increase. It is apparent from Table 1 that the water absorption of cork samples increased with the boiling time. The boiling time had an obvious effect on the amount of water absorbed by cork. When the duration was increased from 30 min to 180 min at approximately100 °C, the water absorption amount of cork changed from 28.8% (the value measured immediately after the boiling) to 52.5% and had a 82% increase.

The volume and density changes of cork samples showed that the boiling water treatment led to the volume expansion and the decrease in density. When the duration of the boiling operation was 60 min, the maximum value of the volume ratio and the minimum value of the density ratio before and after boiling were 1.26 and 0.79, respectively. The calculated dimension changes in the three directions showed that the expansion of cork in the radial direction was much larger (15.4% to 19.5%) than in the non-radial directions (1.3% to 3.7%), *i.e.*, the axial and tangential directions.

In this study, the boiling water treatment caused a volume expansion and a softening and internal stress release of the cork, thus increasing the flexibility of the cork. Boiling water diffused into the cork and caused the partial straightening of the cell lateral walls, particularly in the radial direction. In the experimental conditions used, the peak value of volume change occurred in boiling after 60 min. Subsequently, the volume change maintained a high value and did not continue to increase in boiling for 120 min and 180 min. Rosa and Fortes (1989) suggested that heating cork above 250 °C in air or water could cause an almost complete straightening of cell walls. Therefore, there was only limited expansion in these research conditions. Boiling treatment for a long time caused more swelling and softening of the cork cell walls. Meanwhile, the swelling of cell walls was large and the shrinkage trend was also large during the stage of drying treatment. A long boiling water treatment dissolved some of the water extractives of cork, such as the phenolic compounds and water-soluble lignin, which decreased the mass of cork samples. The irregular change of the volume and mass of cork samples could be the reason why the density ratio of cork did not decline gradually with the prolonging of boiling time.

Table 1. Effects of Boiling Duration on Water Absorption Amount, Linear Dimension, Volume, and Density Changes of Cork

Time (min)	Water Absorption Amount after boiling(%)	Radio Dimension Ratio (R/R_0)	Axial Dimension Ratio (A/A_0)	Tangential Dimension Ratio (T/T_0)	Volume Ratio (V/V_0)	Density Ratio (ρ/ρ_0)
30	28.85±6.34	1.154±0.098	1.016±0.015	1.013±0.013	1.223±0.130	0.82±0.09
60	40.02±9.73	1.186±0.106	1.037±0.037	1.028±0.029	1.264±0.192	0.79±0.11
120	44.75±9.97	1.195±0.122	1.026±0.010	1.020±0.014	1.255±0.104	0.80±0.08
180	52.50±12.06	1.187±0.103	1.029±0.011	1.024±0.016	1.230±0.112	0.81±0.10

Note: The data are the average value ± standard deviation; R_0, A_0, and T_0 are the linear dimensions of radio, axial and tangential direction of untreated cork samples, respectively; R, A, and T are the linear dimensions of cork after different boiling treatments, respectively. V_0 and ρ_0 are the volume and density of untreated cork samples, respectively; and V and ρ are the volume and density of cork after different boiling treatment, respectively.

Table 2 shows the results of the hardness and compression resilience testing. The more time the cork had the boiling treatment, the more obviously the hardness measured immediately after the boiling treatment decreased. The combined heating and the presence of water caused a markedly softening of the cork immediately after boiling. The average hardness values measured immediately after the boiling treatment were between 46.9 HA and 52.5 HA, which were far below the initial hardness values (more than 70 HA) of untreated cork. When the moisture content after boiling was adjusted to the initial value, the hardness of the cork had a slight increase in varying degrees, which was still much smaller than the initial hardness value. Cork is a viscous-elastic material (Oliveira *et al.* 2014). The values of the compression resilience ratio of cork boiled at approximately 100 °C for different times maintained a high level, all of them after pressure release at 24 h were over 80%.

Table 2. Effects of Boiling Duration on Hardness and Compression Resilience Ratios of Cork

Time (min)	H_0(HA)	H_i (HA) (H_i/H_0)	H_e(HA) (H_e/H_0)	R_{15} (%)	R_{24} (%)
30	76.6±4.9	52.5±6.1 (0.686±0.098)	62.2± 5.0 (0.810±0.075)	82.04±3.13	84.59±2.75
60	77.8±4.6	52.0± 5.8 (0.669±0.091)	61.9± 5.4 (0.794±0.066)	77.16±4.31	81.91±4.16
120	74.2±5.4	48.1± 6.6 (0.648±0.074)	58.3± 7.4 (0.791±0.123)	76.18±5.02	81.57±3.93
180	74.4±7.6	46.9± 4.0 (0.631±0.07)	58.6± 8.1 (0.793±0.120)	77.06±4.72	81.85±4.79

Note: H_0 is the initial hardness of untreated cork; H_i, the hardness measured immediately after the boiling water treatment; H_e, the hardness after drying and equalization in the laboratory atmosphere; R_{15}, the compression resilience ratio after pressure release 15 min; and R_{24}, the compression resilience ratio after pressure release 24 h

The Analysis of Drying Treatment after Boiling

The cork samples were boiled at approximately 100 °C for 60 min, and then dried under different temperatures. The volume and density changes are shown in Table 3. Because of the high moisture content, high drying temperatures caused the water of the cork to vaporize and prompted volume expansion. The drying temperature had a marked effect on the cork expansion. As the drying temperature rose, the volume ratio increased noticeably and the density ratio therefore decreased. In the range of test temperatures (140 °C to 240 °C), the volume expansion of cork (35.6% to 65.3%) was much larger than that of cork samples boiled at approximately 100 °C for 30 min to 180 min and oven-dried at 60 °C (22.3% to 26.4%). With the increase of drying temperature, the hardness of the cork gradually decreased.

Thermogravimetric analysis from Shangguan *et al.* (2017) illustrated that the onset of decomposition temperature of cork components (suberin, lignin, and holocellulose) from *Q. variabilis* was between 180.04 °C and 191.57 °C. When the temperature of drying treatment was in excess of 200 °C, it could cause a certain extent of carbonization and mass loss of some cork samples. More issues, such as rational drying temperature and time, property changes after drying treatment, and so forth, need to be deeply studied in future.

Table 3. Effects of Drying Temperature on Volume, Density, and Hardness of Cork

Primary Processing	T(°C)	Volume Ratio (V/V_0)	Density Ratio (ρ/ρ_0)	H_e (HA) (H_e/H_0)
Boiling at About 100°C for 60 min	140	1.356±0.196	0.73±0.113	66.0±1.4 (0.854±0.035)
	180	1.552±0.116	0.60±0.111	63.9±5.8 (0.821±0.074)
	210	1.558±0.292	0.56±0.135	61.8±5.6 (0.794±0.056)
	240	1.653±0.171	0.47±0.091	50.6±5.9 (0.653±0.080)

Note: T is the drying temperature after the boiling water treatment; V_0 and ρ_0 are the volume and density of untreated cork samples; V and ρ are the volume and density of cork after different drying treatments; H_e is the hardness after drying and equalization in the laboratory atmosphere; and H_0 is the initial hardness of untreated cork.

The Analysis of Microwave Treatment After Boiling

The cork samples were boiled at approximately 100 °C for 60 min and then treated by microwave irradiation of different times. The changes of volume, density, and hardness are shown in Table 4. In the experimental conditions, the values of cork volume expansion ranged from 39.7% to 54.5% and the values of density ratio were from 0.616 to 0.701, which were also superior to volume and density changes of cork boiled at 100 °C for different times. Microwave irradiation quickly heated the internal moisture of cork and made it form high steam pressure, which obviously caused volume expansion and density decrease of cork.

The hardness of the cork samples was lowered to some extent after boiling water treatment followed by microwave processing. However, the hardness did not consistently decrease with increase in the duration of microwave processing.

Table 4. Effects of Microwave Treatment on Volume, Density, and Hardness of Cork

Primary Processing	t (min)	Volume Ratio (V/V_0)	Density Ratio (ρ/ρ_0)	H_e (HA) (H_e/H_0)
Boiling at About 100 °C for 60 min	2	1.467 ± 0.333	0.701 ± 0.188	64.9± 5.7 (0.890 ± 0.025)
	4	1.545 ± 0.167	0.616 ± 0.071	67.2 ± 4.6 (0.884 ± 0.021)
	6	1.507 ± 0.207	0.632 ± 0.089	68.3 ± 4.2 (0.933 ± 0.048)
	8	1.397 ± 0.106	0.681 ± 0.049	68.7 ± 6.8 (0.919 ± 0.094)

Note: t is the duration of microwave irradiation after the boiling water treatment; V_0 and ρ_0 are the volume and density of untreated cork samples; V and ρ are the volume and density of cork after microwave treatment; H_e is the hardness after microwave and equalization treatment in the laboratory atmosphere; and H_0 is the initial hardness of untreated cork.

The Analysis of Chemical Boiling Treatment Results

Tables 5 and 6 summarize the results of two types of chemical boiling treatments at 75 °C for 60 min in different concentration conditions. The amount of solution absorbed by the cork samples increased with the increase of the two types of solvent concentrations. In the experimental conditions used, the chemical boiling treatments of sodium hydroxide and hydrogen peroxide with different concentrations caused an increase in cork volume, and a decrease in density and hardness of cork. Just like the boiling water treatment, the linear expansion in the radial direction was larger than that in the non-radial directions. The radial expansion of the cork treated with the sodium hydroxide solution was in the range of 8.4% to 10.7%, and the non-radial expansion was from 0.5% to 1%. Correspondingly, the radial expansion of the cork treated with the hydrogen peroxide solution was from 15.2% to 22.0%, and the non-radial expansion was from 2.1% to 3.6%.

With increasing of concentration of hydrogen peroxide, the volume expansion of cork was larger, and the hardness decreased substantially. The ratio of hardness of cork treated with the 7% hydrogen peroxide solution had fallen to 0.694. All values of the compression resilience ratio after pressure release at 15 min had already exceeded 80%.

Table 5. Effects of Chemical Boiling Treatment on Solution Absorption Amount, Linear Dimension, Volume, and Density Changes of Cork

Solvent Type	Concentration (%)	Solution Absorption Amount after Chemical Treatment (%)	Radio Dimension Ratio (R/R_0)	Axial Dimension Ratio (A/A_0)	Tangential Dimension Ratio (T/T_0)	Volume Ratio (V/V_0)	Density Ratio (ρ/ρ_0)
NaOH (sodium hydroxide)	0.1	35.98±9.37	1.084±0.059	1.006±0.006	1.006±0.009	1.097±0.787	0.91±0.06
	0.3	40.30±12.11	1.103±0.046	1.005±0.005	1.008±0.041	1.117±0.068	0.90±0.05
	0.5	43.82±10.08	1.107±0.069	1.007±0.060	1.010±0.009	1.126±0.080	0.89±0.06
H_2O_2 (hydrogen peroxide)	3	22.93±5.52	1.152±0.095	1.021±0.010	1.027±0.024	1.208±0.157	0.84±0.10
	5	28.35±8.64	1.188±0.118	1.035±0.020	1.036±0.022	1.274±0.618	0.80±0.10
	7	30.94±7.59	1.220±0.125	1.023±0.014	1.035±0.026	1.292±0.180	0.79±0.11

Note: R_0, A_0, and T_0 are the linear dimensions of radio, axial and tangential direction of untreated cork samples, respectively; R, A, and T are the linear dimensions of cork after different chemical treatments, respectively. V_0 and ρ_0 are the volume and density of untreated cork samples; and V and ρ are the volume and density of the cork after different chemical treatments.

Table 6. Effects of Different Chemical Boiling Treatments on the Hardness and Compression Resilience Ratio of Cork

Solvent Type	Concentration (%)	H_0(HA)	H_e (HA) (H_e/H_0)	R_{15} (%)	R_{24} (%)
NaOH sodium hydroxide	0.1	71.2±6.0	64.5±5.0 (0.910±0.084)	81.12±2.92	86.11±2.94
	0.3	73.9±5.4	62.9±4.7 (0.852±0.045)	79.03±5.52	83.49±5.05
	0.5	74.3±5.7	61.1±3.9 (0.824±0.046)	79.23±3.70	82.92±3.91
H_2O_2 hydrogen peroxide	3	76.5±2.9	54.1±4.1 (0.709±0.065)	80.91±3.16	83.37±3.49
	5	73.8±3.9	53.9±4.7 (0.732±0.073)	83.36±3.94	87.61±3.66
	7	75.7±3.7	52.5±5.1 (0.694±0.056)	82.56±4.03	87.46±3.64

Note: H_e is the hardness after freeze-drying and equalization treatment; H_0 is the initial hardness of untreated cork; R_{15} and R_{24} are the compression resilience ratio after pressure removal at 15 min and 24 h.

The Analysis of Color Variation

The summary of the CIELAB color parameters of cork after the boiling water treatment at approximately 100 °C for different times is shown in Table 7. Boiling water treatment caused the decrease of cork lightness. With the increase of boiling time, the lightness index difference (ΔL^*) continued to increase. The parameters of red-green index difference (Δa^*) and yellow-blue index difference (Δb^*) had less change with boiling time. The change of lightness was the main reason that the total color difference (ΔE^*) of cork, before and after boiling treatment, gradually increased with the extending boiling time.

Table 8 shows the color changes of cork samples, which were boiled at approximately 100 °C for 60 min and then underwent a drying treatment at different temperatures. Compared with their untreated cork, boiling and then drying treatment caused the obvious decrease of cork lightness. With the increase of drying temperature, the ΔL^* continued to increase and the ΔE^* of cork progressively increased. The Δa^* and Δb^* had less change.

Table 9 shows the color changes of cork samples, which were boiled at approximately 100 °C for 60 min and then underwent microwave treatment with different durations. The ΔL^* of cork ranged from -12.98 to -13.69. The ΔE^* of cork ranged from 13.79 to 14.92. Compared with the ΔL^* (-13.76) and ΔE^* (14.27) of cork boiled at approximately 100 °C for 60 min (Table 7), it was found that microwave treatment had little influence on surface color of cork in the experimental conditions.

Table 10 shows the results of color parameters of cork before and after the chemical boiling treatment at 75 °C for 60 min. The two types of chemical treatments had different results. Compared with their untreated samples, the lightness of the corks boiled in the sodium hydroxide solution decreased obviously, and the ΔE^* increased. After the cork was treated with hydrogen peroxide solution, the lightness increased with the concentration increase and the ΔE^* had a slight increase. Two kinds of solvents had little effect on the parameters of Δa^* and Δb^* of cork.

According to the National Bureau of Standards (NBS) rating system, when the value of ΔE^* is more than 12.0, the color change is substantial, *i.e.*, the color changes to the other color. When the value of ΔE^* is in the 6.0 to 12.0 range, the color change is "much", *i.e.*, the color has an extremely marked change (Koksal and Dikbas 2008; Jiang and Fu 2017). In this study, the values of ΔE^* of cork after boiling water treatment at approximately 100 °C for 30 min to180 min were more than 12.87, and the values of ΔE^* of cork treated with the sodium hydroxide solution were more than 21.66 and the values of ΔE^* of cork treated by drying treatment at different temperatures were all over 14.64; therefore, the color change of the cork was substantial. The color change of cork treated with the hydrogen peroxide solution was much (ΔE^*, 6.56 to 10.50). As the value of ΔL^* increased, the cork treated with hydrogen peroxide became bright and was total different from that treated with other boiling treatments. Some pictures of the cork treated with the four different boiling treatments are shown in Fig. 1.

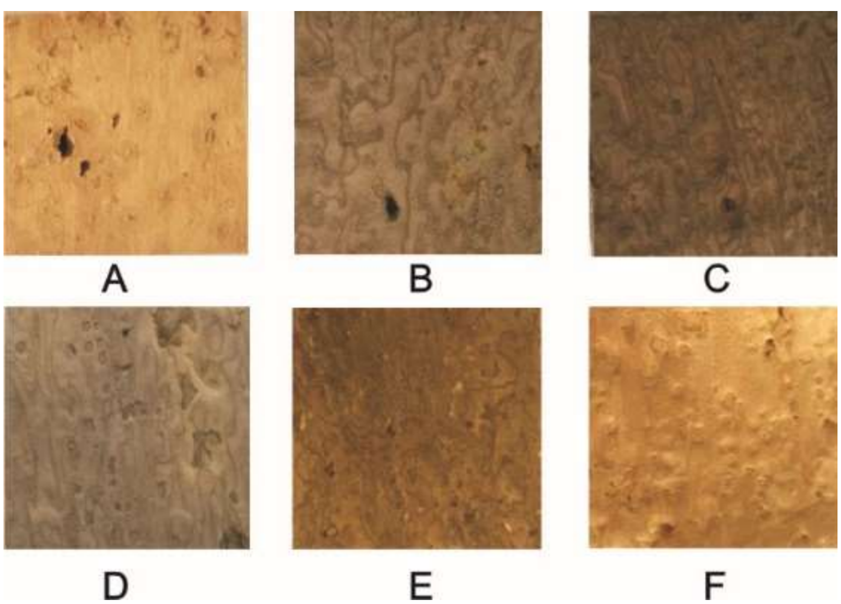

Fig. 1. Color change of corks after the different boiling treatments, (A) untreated cork, (B) cork boiled at approximately100 °C for 3 h, (C) cork boiled at approximately 100 °C for 1 h and then dried at 240 °C, (D) cork boiled at approximately100 °C for 1 h and then made microwave treatment for 8 min, (E) cork boiled at 75 °C for 1 h with 0.5% sodium hydroxide solution, (F) cork boiled at 75 °C for 1 h with 7% hydrogen peroxide solution

Table 7. Effects of Boiling Duration Treatment on Color Difference Between Treated Cork and Untreated Cork

Time/min	Δ*L**	Δ*a**	Δ*b**	Δ*E**
30	-11.89±4.80	-0.19±1.96	-4.37±1.57	12.87±4.89
60	-13.76±2.54	-0.21±1.50	-2.13±2.67	14.27±2.42
120	-15.16±3.51	-2.14±1.55	0.66±2.34	15.61±3.31
180	-17.74±2.38	-1.91±1.98	0.74±2.84	18.17±2.47

Note: Δ*L* is the lightness index difference; Δ*a* is the red-green index difference; Δ*b* is the yellow-blue index difference; and Δ*E* is the total color difference. (the same below)

Table 8. Effects of Drying Duration Treatment on Color Difference Between Treated Cork and Untreated Cork

Primary Processing	*T*(°C)	Δ*L**	Δ*a**	Δ*b**	Δ*E**
Boiling at About 100 °C for 60 min	140	-13.82±1.54	-0.14±0.67	-3.25±1.25	14.64±1.68
	180	-16.17±1.30	-0.18±0.99	-5.73±0.63	17.82±1.24
	210	-28.43±1.72	-1.08±0.80	-5.19±2.54	29.09±1.49
	240	-34.03±1.68	-3.19±0.88	-5.48±2.88	34.95±1.64

Table 9. Effects of Microwave Duration Treatment on Color Difference Between Treated Cork and Untreated Cork

Primary Processing	*t* (min)	Δ*L**	Δ*a**	Δ*b**	Δ*E**
Boiling at About 100 °C for 60 min	2	-13.39±3.30	0.94±0.43	-4.39±0.55	14.52±3.09
	4	-12.98±2.58	-0.76±0.58	-3.97±0.79	13.79±1.76
	6	-13.69±1.55	0.39±0.59	-3.78±1.03	14.43±1.75
	8	-13.64±3.73	-0.81±0.46	-4.27±1.48	14.92±3.45

Table 10. Effects of Chemical Boiling Treatment on Color Difference Between Treated Cork and Untreated Cork

Type	Concentration (%)	Δ*L**	Δ*a**	Δ*b**	Δ*E**
NaOH (sodium hydroxide)	0.1	-21.86±3.33	1.31±1.52	0.26±1.45	22.00±3.31
	0.3	-21.82±3.36	0.32±0.96	1.98±1.51	21.97±3.42
	0.5	-21.25±2.81	1.57±1.42	3.15±1.71	21.66±2.77
H_2O_2 (hydrogen peroxide)	3	4.74±2.25	-0.95±1.10	3.95±0.96	6.56±1.69
	5	5.41±3.09	-2.14±1.23	3.42±0.71	7.32±1.73
	7	9.35±2.16	-2.92±1.07	3.34±0.91	10.50±1.78

The Comparative Analysis of Four Different Treatments

In the experimental conditions used, four different treatments for cork samples caused volume expansion, density decrease, hardness changes, and color changes. Because of the differences of experimental condition, function mechanism and cork samples, the effects of four boiling treatments were different.

Drying processing at high temperatures and microwave processing after the boiling operation obviously promoted cork expansion and large decrease in density. The presence of moisture in cork was crucial for the expansion to occur. Hence, the process of this two treatments included three stages. The first stage was raising the moisture content of cork, followed by the drying processing or microwave processing, and finally the stage of cooling and equilibration. The humidity value of cork before drying or microwave treatment was one of the key parameters.

In the testing range, four boiling treatments had different effects on cork color. Hydrogen peroxide solution had bleaching function and caused lightness increase of cork. Other treatments resulted in the lightness decrease in various extent. Hydrogen peroxide could decompose to radicals (HO, HOO, *etc*.), which had chemistry activity and could cause pigment decomposition of cork (Lui and Cui 2013). During boiling water or sodium hydroxide or high temperature drying treatments, there were many factors that could cause color variation of cork, such as the changes of cork composition, medium conditions, etc. The boiling water treatment could solubilize some tannins of cork, which was a influence factor of cork color and also could brought a brown color to the waste water in the boiling operation (Rosa and Fortes 1990). The color change of cork during the boiling treatments is a complex process that needs more research for clarification.

Boiling treatment is an important process in the industry of *Q. variabilis* cork, which should be selected according to the purpose of cork products. Compared with the *Q. suber* cork, the research on boiling process of *Q. variabilis* cork has rarely been reported. The effect of different boiling treatments on basic physical parameters (volume, density, hardness, color, etc.) of *Q. variabilis* cork had been studied in this research, which on other properties, such as mechanical properties, microstructure, permeability, component analysis of boiling filtrates, *etc*., also need to be deeply studied.

CONCLUSIONS

1. In this research, when the duration of boiling water treatments changed from 30 min to 180 min at 100 °C, the amount of cork water absorption increased from 28.85% to 52.50%. The expansion of cork in the radial direction was 15.4% to 19.5% and the non-radial expansion only had 1.3% to 3.7%. The hardness and lightness of cork noticeably decreased after the boiling treatment. The total color difference (ΔE^*) of cork gradually increased with the extension of the boiling time. The values of compression resilience ratio of all corks after pressure release at 24 h were over 80%.
2. As the drying temperature rose, the volume change ratio of cork noticeably increased and the density change ratio obviously decreased. In the range of test temperatures, the volume expansion of cork was between 35.6% and 65.3%.
3. In the experimental conditions, microwave irradiation caused the volume expansion and density decrease of cork. It had little influence on surface color of cork.
4. Chemical boiling treatments of sodium hydroxide and hydrogen peroxide with different concentrations all caused cork expansion and decreases of density and hardness. However, the sodium hydroxide solution treatment led to an obvious decrease of cork lightness. The lightness of cork treated with the hydrogen peroxide solution increased with the concentration increase, and the total color difference experienced a slight increase.

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