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Effect of heat treatment on the wettability of white ash and soft maple by water

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Abstract Heat treatment of wood has attracted a lot of attention both in Europe and recently in North America as an environmentally-friendly wood-protection method. The untreated wood is hydrophilic (high affinity for water). During the heat treatment, wood becomes more and more hydrophobic (low affinity for water) with increasing heat treatment temperature. As a result, it becomes more resistant to biological attacks. Furthermore, it becomes dimensionally more stable compared to untreated wood. Its hardness increases. As the wood becomes more hydrophobic, its wettability by water decreases. The effect of heat treatment is different for each species. Studying the wetting characteristics of heat treated wood gives a good indication of the heat treatment effects on certain wood properties which are related to its degree of hydrophobic character. The aim of this work was to study the characteristics of dynamic wetting process for two different heat-treated North American wood species white ash (*Fraxinus americana*) and soft maple (*Acer rubrum*). Contact angle measurements before and after heat treatment showed a significant increase in wood hydrophobicity. Advancing contact angles of a water drop were in all cases higher for heat-treated wood than for untreated wood.

Einfluss der Wärmebehandlung auf die Benetzbarkeit von Weißesche und Rot-Ahorn mit Wasser

Zusammenfassung Die Wärmebehandlung von Holz als umweltfreundliche Holzschutzmethode stößt in Europa und seit kurzem auch in Nordamerika auf zunehmendes Interesse. Unbehandeltes Holz ist hydrophil, d.h. es nimmt leicht Wasser auf. Während der Wärmebehandlung wird Holz mit steigender Temperatur zunehmend hydrophob, d.h. Wasser abweisend, und infolgedessen gegenüber einem biologischen Befall resistenter. Auch ist es im Vergleich zu unbehandeltem Holz dimensionsstabiler und die Härte nimmt zu. Da das Holz zunehmend hydrophob wird, nimmt die Benetzbarkeit durch Wasser ab. Der Einfluss einer Wärmebehandlung hängt von der Holzart ab. Die Untersuchung der Benetzungseigenschaften von behandeltem Holz ist ein guter Anhaltspunkt für den Einfluss der Wärmebehandlung auf verschiedene Holzeigenschaften, die vom Grad der Hydrophobie abhängen. Ziel dieser Arbeit ist es, die Wirkung eines dynamischen Benetzungsverfahrens auf die zwei wärmebehandelten nordamerikanischen Holzarten Weißesche (*Fraxinus americana*) und Rot-Ahorn (*Acer rubrum*) zu untersuchen. Die Messung der Kontaktwinkel vor und nach der Wärmebehandlung zeigt einen signifikanten Anstieg der Hydrophobie von Holz. Die Kontaktwinkel eines Wassertropfens waren bei behandeltem Holz größer als bei unbehandeltem Holz.

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1 Introduction

Preservation of wood using a heat-treatment process is one of the alternatives to the protection of wood using chemicals. In the heat-treatment process, wood is heated to temperatures of 160–250 °C, usually above 200 °C depending on the species used and the desired material properties. This causes various changes in the structure of wood. First, hemicelluloses start to degrade since it has the lowest molecular weight among these wood polymers. Hemicelluloses degradation results in the reduction of OH bonds and the formation of O-acetyl groups. With the subsequent cross-link formation between the wood fibers, wood becomes more hydrophobic. The reduction in water absorption causes a decrease in swelling and shrinking of wood leading to improved dimensional stability. This was observed by Stamm as early as 1940's and 1950's (Stamm et al. 1946, Stamm 1956). Weiland and Guyonnet (2003) investigated the chemical modifications, the dimensional stability and the resistance against fungal degradation, and observed a formation of new ether linkage in addition to the acidic hydrolysis reactions. Hinterstoisser et al. (2003) studied the chemical changes occurring in thermally modified beech wood and observed the hemicelluloses degradation. Homan et al. (2000) found that the durability, the hygroscopicity, the dimensional stability and the UV-resistance of spruce and pine improved but their mechanical properties deteriorated by thermal modification. Pavlo and Niemz (2003) found that high temperature darkened the color, improved the dimensional stability but deteriorated the mechanical properties of spruce wood. The improvement of the dimensional stability was explained with decreasing hemicelluloses content, consequently, decreasing hygroscopic behaviour of wood. The link between the dimensional stability and the degradation of hemicelluloses was also reported by Duchez et al. (2001).

Suitable temperature, nutrients, oxygen, and moisture are required for mold formation (Robbins and Morrel 2006). The degradation of hemicelluloses reduces the water absorption by wood and the available nutrient for mold; therefore, wood becomes more bio-durable. There are also changes in lignin and cellulose at these temperatures. Lignin softens and blocks the cell pores contributing to the reduction in water absorption (Rowell et al. 2000). Hakkou et al. (2005) reported that the cellulose crystallinity first decreases between 100–160 °C due to the loss of residual water; however, it increases at temperatures higher than 200 °C because of the reactions taking place at these temperatures.

As explained above, the hygroscopicity of heat-treated wood is reduced and its dimensional stability and biodurability are improved. The heat-treated wood becomes more hydrophobic compared to the untreated wood and this might cause problems during varnish or paint deposition. Two important surface properties are wettability and surface free energy which determine if a liquid (water, paint, glue) will adhere to the surface. Quality of wetting is influenced by many factors including wood macroscopic characteristics (e.g., porosity, surface roughness, moisture content, fiber orientation, etc.). Various techniques exist for the measurement of wood wettability (Walinder and Johansson 2001, Walinder and Strom 2001, Shi et al. 1997). The most well-known and widely used method is the sessile drop technique (Neumann and Spelt 1996).

The contact angle can be determined directly from the image of the drop recorded during a wetting experiment using the sessile drop technique. There are different methods of image analysis. The drop-shape method is used during this work. In this method, a mathematical expression is fitted to the drop shape and the contact angles are determined by determining the slope of the tangent to the drop at the triple point (Woodward 2007). The surface tension can be calculated from the sessile-drop data using an empirical relationship given by Dorsey (1928).

The wood is expected to become more hydrophobic with increasing heat-treatment temperature; consequently, the contact angle will increase due to the chemical changes taking place. Hakkou et al. (2005) found that the hydrophobicity of beech wood increases during the heat treatment at temperatures between 130–160 °C. They suggest that the change in wettability might be due to the modification of conformational arrangement of wood biopolymers as a result of residual water or plasticization of lignin. Petrissans et al. (2003) found that the decrease in wettability, consequently, increase in hydrophobicity of spruce poplar, beech, and pine was more significant with heat treatment compared to that of chemical treatment. Gerardin et al. (2007) used contact angles to evaluate the surface energies of heat-treated pine and beech wood and related hydrophobic behavior of wood to hemicelluloses degradation. Rodrıguez-Valverde et al. (2002) measured the contact angle of the wood/water system on non-ideal surfaces using the axially symmetric drop-shape analysis and found that this technique gave accurate results. Most of these studies were conducted on European species. To the authors' knowledge, there isn't any reported study on the wettability of North American species (Casilla et al. 1981).

In this work the dynamic wettability by water of two heat-treated North American wood species (white ash and soft maple) was studied using sessile drop technique. The results are compared with those of the untreated species.

2 Materials and methods

The heat treatment experiments were carried out in a thermogravimetric analyzer. Wood samples of white ash (*Fraxinus americana*) and soft maple (*Acer rubrum*) with dimensions 0.035 m × 0.035 m × 0.20 m were heat-treated. They are North American hardwood species widely used by the industry. The experiments were carried out under a gas atmosphere without the presence of oxygen. The gas was composed of nitrogen mixed with small amounts of carbon dioxide and water vapor. The last two components represent the combustion products of the gas burners used in the industrial wood treatment furnaces. The humidity of the gas was kept around 100 g/m^3. The samples which were suspended from a balance into a tube furnace were first heated to about 120 °C at a heating rate of 20 °C/h, and this temperature was kept constant for half an hour in order to reduce the moisture content of wood. Then, they were heated with the same heating rate until the maximum heat treatment temperature was reached. The samples were kept at the maximum temperature for one hour before being cooled down with water spray. During the experiments, the weight of the sample was monitored continuously using an electronic balance (Mettler Toledo AG285) with an accuracy of ±0.001 g, and the weight data was taken at 60-second intervals with an automatic data acquisition system (Keithley 2700). The temperatures at predetermined positions within the sample were measured every 60 seconds by means of five T-type thermocouples which were connected to the data acquisition system. The accuracy of the thermocouples is 3.8%. The details of the experimental system are given elsewhere (Kocaefe et al. 2007).

For the wetting measurements, the sizes of wood samples were 0.02 m × 0.02 m × 0.02 m. These samples were sanded with 120-grit sandpaper. The moisture content of the wood samples depends on whether they were heat-treated or not, and on the humidity of the air. If equilibrium moisture content is not reached, the moisture content of wood changes with time. For the heat treated samples, it also depends on the process parameters of the thermal treatment. Consequently, all the samples were oven dried overnight at 105 °C, and kept in a desiccator in order to equalize their initial moisture contents prior to the wetting experiments as suggested by other researchers (Kazayawoko et al. 1997). A "First Ten Angstroms FTA 200" system was used to determine the contact angle and surface tension. The measurement technique is based on rapid video capture of images and automatic image analysis. The accuracy is ±1 mN/m for surface tension and ±3° for contact angle measurements.

The experiment set-up as shown in Fig. 1 consists of a stereo microscope, a CCD video camera connected to a computer for image storage and processing, a digital stroboscope for illumination, a syringe for holding liquid samples and the substrate. Drops of 5 µl volume, formed automatically using a syringe and a pump, were placed on a substrate surface at room temperature. When droplets have such a small volume, the effect of the gravimetric deformation can be neglected compared to that of the surface tension (Woodward 2007). However, the contact angles were measured directly from the captured images which include all the effects. The image of a droplet was captured using a video-microscope system. The drop was observed from fibber (axial) direction with the exception of the tests where the effects of radial and tangential directions on the contact angle were studied. The variation of the contact angle was higher in axial direction compared to those of the other two directions. Images were analysed with FTA 32 Video 2.0 software which identifies the baseline of the drops (contact line with the solid). The contact angles between the tangent to the contour of the droplet at triple point and the baseline were determined on both sides of the drop. The use of a strobe as illumination source enabled the acquisition of high-speed image capture with a standard CCD video camera. The microscope magnification was adjusted to the maximum with which it was possible to capture the final diameter of the drop at the end of a given time period. The video camera viewed the spreading of the drop from an angle which was a few degrees above the impact plane. This made it possible to view whole plane and to improve the image resolution. Three tests were performed for each set of experimental conditions in order to take into account the non homogeneous nature of wood.

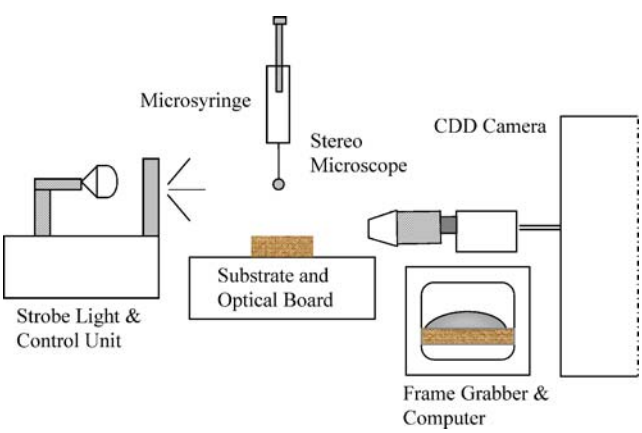


Fig. 1 Schematic of experimental set-up for wetting measurements
Abb. 1 Versuchsaufbau zur Messung der Ausbreitung des Tropfens

3 Results and discussion

The wettability of the solid by a liquid is given by the contact angle or wetting tension which is defined as the surface tension multiplied by the cosine of contact angle. The surface tension can be calculated from the sessile-drop data using empirical relationship (Dorsey 1928).

The aim of this project was to study the effect of the heat treatment on the contact angle, consequently, on the wetting properties of wood. The axial direction was chosen for a comparative study since the variation of the contact angle is most pronounced in this direction. However, the effect of the direction (radial and tangential) on the contact angle was also studied.

Figures 2 and 3 show the contact angle vs. time data for soft maple and white ash, respectively, in the axial direction (direction of the fibers). In these figures, the contact angle evolution with time is given for an untreated sample as well as for samples heat-treated at different maximum temperatures (205 °C, 210 °C, and 215 °C). As can be seen in both figures, the heat treatment increases the hydrophobic behavior of both species; consequently, the contact angles of

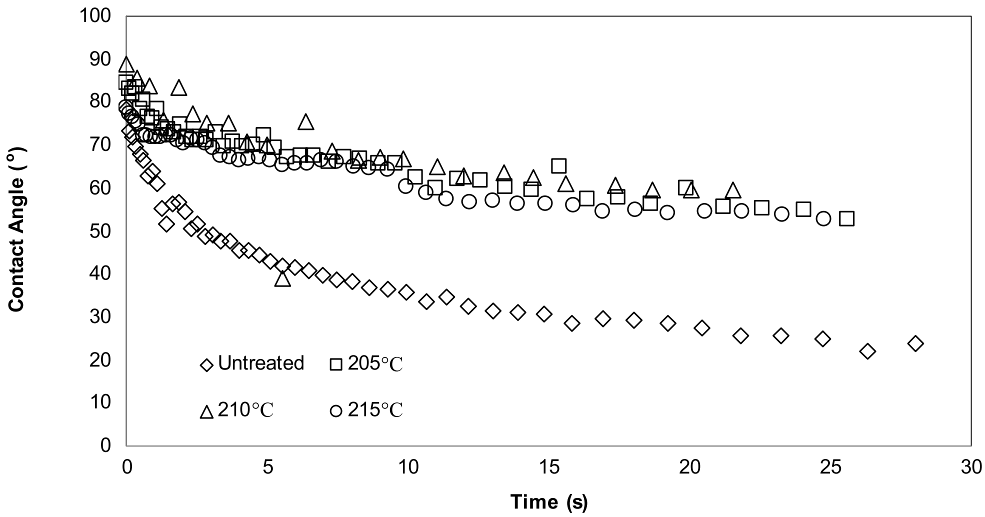


Fig. 2 Effect of maximum heat treatment temperature on contact angle vs. time data for soft maple in the axial direction
Abb. 2 Einfluss der max. Temperatur auf den Kontaktwinkel in axialer Richtung bei Rot-Ahorn in Abhängigkeit der Zeit

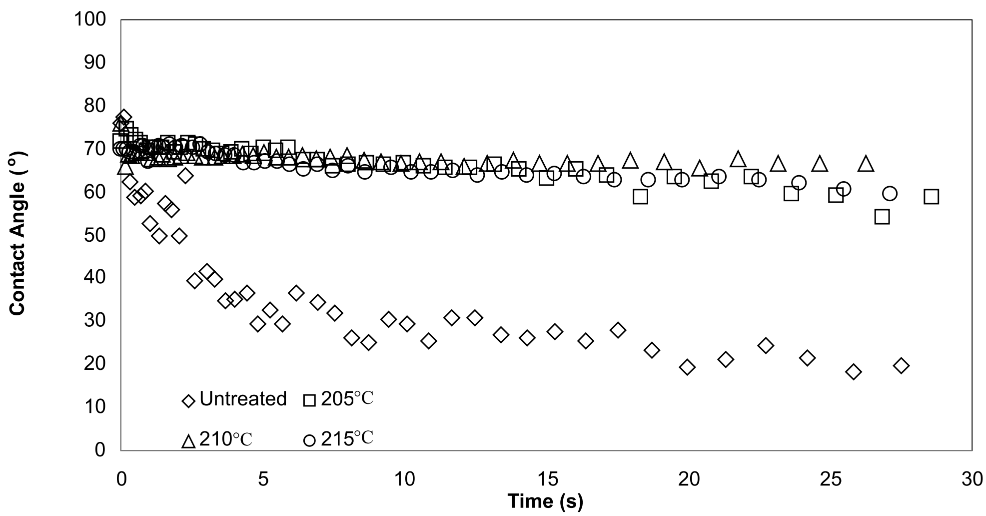


Fig. 3 Effect of maximum heat treatment temperature on contact angle vs. time data for white ash in the axial direction
Abb. 3 Einfluss der max. Temperatur auf den Kontaktwinkel in axialer Richtung bei Weißesche in Abhängigkeit der Zeit

heat-treated wood are greater than those of untreated wood of the same species. This shows that the heat treatment decreases the wettability of wood by water. The contact angles do not seem to change significantly with the maximum heat-treatment temperature within the temperature range studied. The trends observed for both species studied were found to be very similar. Therefore, results are presented for one of the species to demonstrate each point of the discussion below.

As it is well known, wood is anisotropic and its properties are different in radial, tangential, and axial directions. This difference is seen clearly from the measured contact angles. The variation of contact angles with time in three directions is given for untreated and heat-treated (the maximum heat treatment temperature: 205 °C) samples of white ash in Fig. 4. When wood is untreated, the contact angles are greatest in the axial direction compared to those measured in the radial and tangential directions. The differences between the contact angles in radial and tangential directions are not significant. When ash is heat treated, even though there is some effect in the other two directions, the biggest influence of the heat treatment on contact angle is observed in the axial direction. For this reason, all the results are given for the axial direction in this work.

The change in volume of the sessile drop with respect to its initial volume as a function of time is presented for white ash in Fig. 5. The greatest change in the drop volume is observed for untreated wood. In this case, the drop volume is decreased substantially during the experiment showing that the water is absorbed by the wood. The quantity of water absorbed decreased for the heat-treated wood indicating a more hydrophobic behavior compared to the untreated wood. This volume variation has a direct influence on the contact angle measurements. If it is assumed that the wetted surface remains constant, the contact angle can be underestimated. In order to see the actual effect of heat treatment on the contact angle, consequently on wetting, the contact angles measured four seconds after the drop was placed on

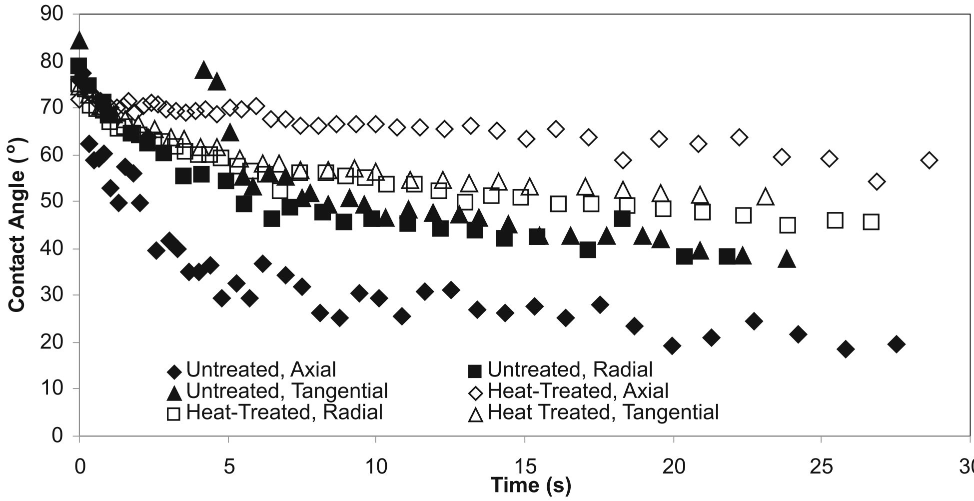


Fig. 4 Effect of direction on the contact angle for white ash heat treated at 205 °C (Maximum Heat Treatment Temperature = 205 °C)
Abb. 4 Kontaktwinkel von Weißesche, die bei 205 °C wärmebehandelt wurde, in Abhängigkeit der Zeit, getrennt nach den drei Hauptrichtungen des Holzes

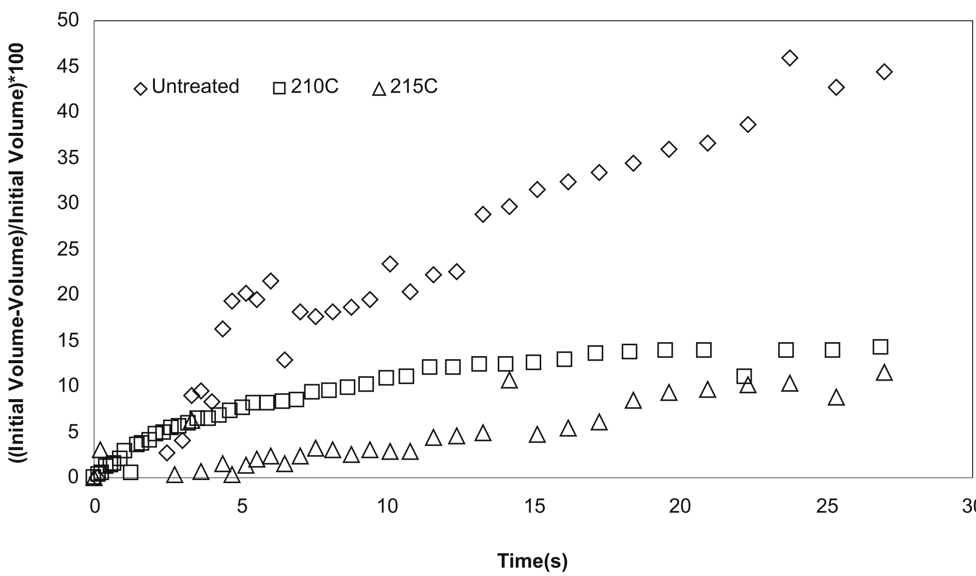


Fig. 5 Change in volume of the drop relative to the initial volume with respect to time for white ash
Abb. 5 Relative Volumenänderung des Tropfens bei Weißesche in Abhängigkeit der Zeit

wood surface are compared in Fig. 6 for the untreated and the treated wood. In this period, the change in volume is not significant (see Fig. 5). Once again it can be seen, that the wettability of wood is reduced with heat treatment and that the two species studied behave in a similar manner.

From the dimensions of the sessile drop, the surface tension between water and air at 20 °C was calculated and the result of this calculation is presented for soft maple in Fig. 7a. The surface tension was found to be 0.0728 (N/m) using the data obtained for both species investigated. This is also the value reported in the literature (Perry and Green 1999). This agreement validates both the contact angle measurements and the utilization of the empirical equation in surface tension calculations (Dorsey 1928). Then, the wetting tension was calculated as a function of time and is shown in Fig. 7b for soft maple. As discussed previously, the wetting tension also gives an indication of the level of wettability. A decrease is observed in the wetting tension with the heat treatment, again showing that the heat-treated wood is wetted less by water compared to the untreated wood.

As mentioned previously, there are no studies on the wetting of heat-treated North American species reported in the literature. Hakkou et al. (2005) studied the wetting of heat-treated European species. They found that the contact angles changed significantly around the glass transition temperature of wood. At higher temperatures, they did not see any significant change in wetting properties. This is in agreement with the results of this study. The temperature range investigated was higher than the glass transition temperature of the species studied. It was observed that the contact angles of the untreated and the heat-treated wood were very different but no significant contact angle change was observed for the wood samples heat-treated at different temperatures.

Fig. 6 Comparison of contact angles measured at 4 seconds in axial direction for untreated and heat-treated soft maple and white ash
Abb. 6 Vergleich der nach vier Sekunden in axialer Richtung gemessenen Kontaktwinkel behandelter und unbehandelter Proben von Weißesche und Rot-Ahorn

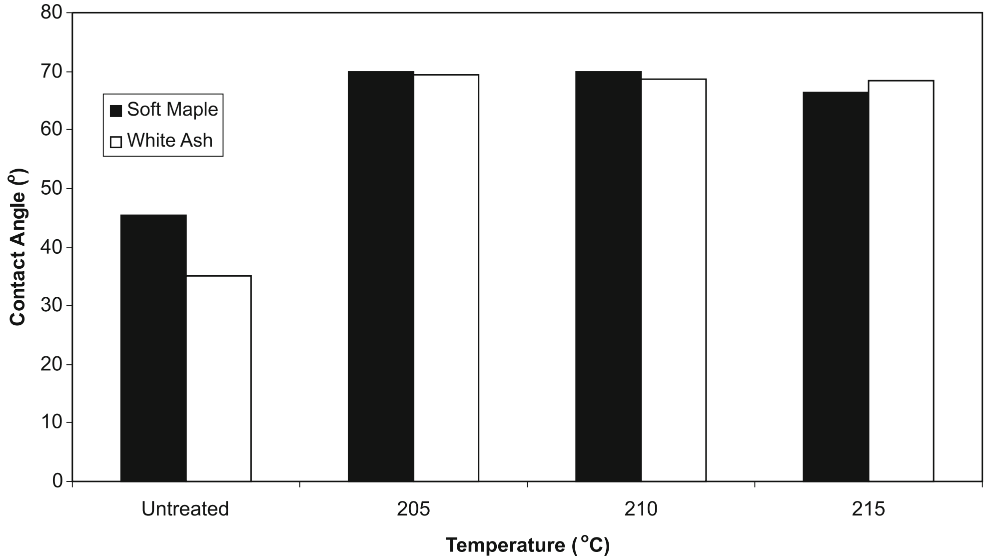
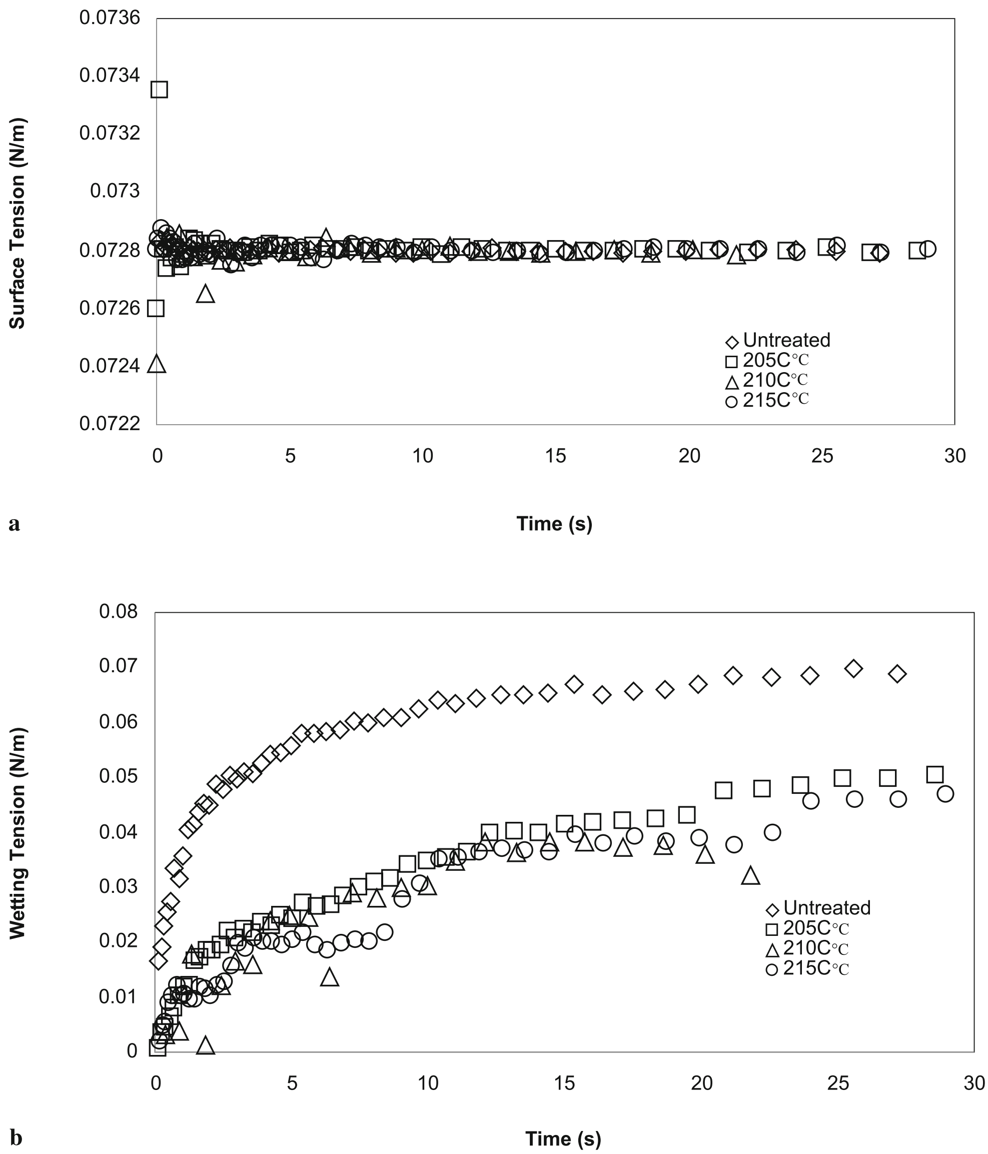


Fig. 7 Calculated surface tension (**a**) and wetting tension (**b**) for soft maple
Abb. 7 Berechnete Oberflächenspannung (**a**) und Benetzungspannung (**b**) bei Rot-Ahorn



4 Conclusion

Heat treatment of North American white ash and soft maple increased the contact angle between wood and water indicating a decrease in wood wettability. It is observed that this increase is more significant in the axial direction compared to the increase in the radial and tangential directions for both species. The contact angles in the radial and tangential directions were found to be similar.

Sessile drop method was found to be a reliable method for contact angle measurements. The surface tensions were calculated from the geometric dimensions of the drops which were obtained using the image analysis. The calculated surface tension is in good agreement with the value reported in the literature.

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