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INTERFACE SCIENCE

Chemical modification and wetting of medium density fibreboard produced from heat-treated fibres

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Abstract The objectives of this study were to investigate the effect of heat treatment of fibres on the advancing and receding contact angles and wicking of panels by the Wilhelmy plate method; to verify the possible relationships between wetting properties and water absorption of the panels; and to determine the surface composition of heat-treated fibres by X-ray photoelectron spectroscopy (XPS). Fibres were treated at 150 and 180 °C for 15, 30 and 60 min. Our results showed that the treatment increased contact angles and decreased water absorption. Wicking was reduced by about 70% for the 150 °C group and 80% for the 180 °C group. XPS analysis demonstrated a slight decrease of the O/C ratio and changes of the C1/C2 ratio following treatment.

Introduction

Heat-treated wood, known as retified or torrified wood, has been studied and used in Europe where various processes were patented. Wood treated at temperatures above 150 °C undergoes changes in its physical and chemical properties [11]. This treatment improves water repellency and increases the dimensional stability of wood [17]. A recent work performed by Garcia and co-authors demonstrated that medium density fibreboard (MDF) prepared from heat-treated fibres has reduced hydrophilic properties [5]. Similar results were found for particleboards produced from heat-treated chips in a two-stage heat treatment process between 165 and 185 °C [1].

Nonetheless, the Wood Handbook of the USDA Forest Products Laboratory states that high temperature causes inactivation of wood surfaces [3]. This generates adhesion problems due to the reduced penetration and cohesive strength of the adhesives. The surface chemical composition of yellow poplar (*Liriodendron tulipifera* L.) and southern pine (*Pinus taeda* L.) following high temperature drying was determined by X-ray photoelectron spectroscopy (XPS). The results revealed that wood drying at temperatures between 160 and 180 °C causes modifications in surface composition [15]. For yellow poplar, the O/C ratio remained constant up to a drying temperature of 150 °C and decreased for temperatures of 175 and 200 °C. For southern pine, the effect of high temperature drying was more significant, showing a lower O/C ratio than yellow poplar. In the latter case, the O/C ratio remained constant up to a drying temperature of 100 °C and decreased for temperatures of 150, 175 and 200 °C. Generally, the O/C ratio decreased, and the C1/C2 ratio increased when wood was exposed to drying temperatures of 200 °C [15]. Wood surfaces can present three or four peaks of C1s carbon components. The C1s line consists of several subunits where C–C, C–H, C–O, C=O, O–C–O and O=C–O linkages can be differentiated [20]. Most of the C1 carbon (C–C, C–H) can be attributed to aliphatic and

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aromatic carbons of lignin and extractives, the C2 carbon (C–O) to primary and secondary alcohols of lignin and extractives, the C3 carbon (C=O, O–C–O) to aliphatic and aromatic ethers in lignin and extractives—but also to carbonyl groups (in esters, aldehydes, ketones or carboxylics) in lignin and extractives—and the C4 carbon (O=C–O) to esters and carboxylic acids in lignin and extractives [8]. XPS was used also to characterize the chemical changes of beech wood after heat-treatment at 240 °C [10]. The results showed a decrease of the O/C ratio and a decrease of the C2 carbon associated with an increase of the C1 carbon [10]. On the other hand, another study on heat-treated waferboards at 240 °C did not demonstrate changes in the chemical composition [7]. Thus, the authors concluded that the main impact of heat treatment is not chemical but rather physical modifications. In fact, heating can deteriorate the physical conditions of the wood surfaces by migration of extractives to the wood surface where they physically block adhesive contact with wood by irreversibly closing the micropores of cell walls, among other factors [3]. Therefore, physical and chemical changes of wood surfaces interfere with wetting, flow, penetration and consequently adhesion strength of the adhesive.

Contact angle analysis is widely used to measure the surface wetting characteristics of solid materials and also to determine the gluing and coating properties of wood surfaces [12]. The Wilhelmy plate method has been used by several authors for this purpose [6, 16, 18–19]. However, only a few authors measured the wetting of chemically modified wood. Some wood species—pine (*Pinus sylvestris* L.), spruce (*Picea abies* (L.) Karst), beech (*Fagus sylvatica* L.) and poplar (*Populus nigra* L.)—were heat-treated at 240 °C for 8 h under nitrogen by the HTT Thermique (French Society) process in an industrial oven of 16 m^3 capacity [12]. The advancing contact angle increased between 16.2 and 85.8° depending on the wood species, i.e. the wood became less hydrophilic [12]. In another study, the contact angle of yellow poplar and southern pine were measured by the sessile drop technique following a temperature increase from 50 to 200 °C during drying [15]. For both species, the contact angle of the water drop increased with drying temperature. For yellow poplar, the contact angle increased from 59.5 to 77.5 while for southern pine it increased from 83.6 to 98.9° for drying temperatures of 50 and 200 °C, respectively. The surface of southern pine was less hydrophilic than the surface of yellow poplar probably due to the higher concentration of hydrophobic extractives in southern pine [15].

The objectives of the present study were (1) to investigate the effect of fibre heat treatment on the advancing and receding contact angles and wicking of MDF panels by the Wilhelmy plate method; (2) to verify the possible relationships between these properties and water absorption after water soaking of MDF panels produced from heat-treated fibres; and (3) to determine the surface composition of heat-treated fibres by XPS.

Material and methods

Fibre production and heat treatment

Wood chips, sawdust and shavings were supplied by Uniboard Canada Inc., MDF La-Baie, Ville-de-la-Baie, Québec, Canada. The raw material was composed of 90% softwood fibres—black spruce (*Picea mariana* (Mill.) BPS), balsam fir (*Abies balsamea* (L.) Mill.) and jack pine (*Pinus banksiana* Lamb.)—and 10% white birch (*Betula papyrifera* Marshall) fibres. The chips were refined with a pressurized disc refiner and dryer available at Forintek Canada Corp., Eastern Laboratory, located in Québec City, Québec, Canada. The refining conditions of fibres were 5 min of retention time and 9 bar of steam pressure. The fibres were treated at a variety of high temperature settings under continuous vacuum (98 kPa) for different time periods. The fibres were heat treated at 150 and 180 °C for time periods of 15, 30 and 60 min. The heat treatment was performed in a 50 × 45 cm ISOTEMP® vacuum oven, model 285A from Fisher Scientific. The initial moisture content of the fibres was between 5 and 6%. The temperature considered in this study represents the temperature of the fibres which was measured by a thermocouple located within the fibre container. The fibre initial temperature was about 25 °C, the final temperature 40 °C and the average speed of increasing temperature about 1.5 °C min^{-1}. However, it is important to mention that the temperature increase rate was not linear. The final moisture content of the fibres after the treatment was of about 1%.

MDF panels preparation

MDF panels measuring 350 × 250 × 11 mm^3 with a target panel density of 770 kg m^{-3} were manufactured using a 600 × 600 mm^2 Becker and van Hüllen™ hot press available at the Département des sciences du bois et de la forêt, Université Laval, Québec City, Québec, Canada. The initial fibre moisture content was 5%. Water was added to the fibres to obtain a mat moisture content of 14%. The panels were bonded with a commercial liquid urea-formaldehyde (UF) resin from Dynea Canada Ltd., Ste-Thérèse, Québec, Canada with a solid resin content of 14% (based on the oven-dry weight of the fibres). The resin was catalyzed with a 30% NH_4Cl solution, added until a pH of 7.0 was reached. The panels were hot-pressed at a press platen temperature of 200 °C for a press closing time of 105 s with a curing time of 180 s and a press opening time of

60 s resulting in a total press cycle of 345 s. The panels were conditioned at 20 ± 3 °C and 65 ± 1% RH for approximately one-week before testing.

The three factors chosen in the experimental design were treatment type (control and heat treatment), fibre temperature (150 and 180 °C) and treatment time (15, 30 and 60 min). The six treatment combinations of temperature and time, together with the control, were replicated two times, which resulted in a total of 14 panels.

Measurement of MDF panels wettability by the Wilhelmy plate method

Samples of 36 × 11 × 3.5 mm^3 (length × width × thickness) were cut in the MDF panel length direction, with width corresponding to panel thickness. Contact angle and wicking measurements were performed by the Wilhelmy plate method using a Tensiometer K14 with a KRÜSS Processor. This technique consisted of hanging up a MDF sample on an electronic balance which measured the apparent change of sample weight during immersion in, and withdrawal from a liquid of known surface tension with controlled immersion depth and speed as illustrated in Fig. 1. The liquid probe employed for the measurements was distilled water at 20 °C with a surface tension of 72.80 mN m^{-1} and a density of 998 kg m^{-3}. In our measurements, we applied an immersion speed of 4.5 mm min^{-1} and an immersion depth of 2 mm. Before contact angle measurements, a balance calibration was realized with Wilhelmy platinum metallic plate. The weight increase or force F was automatically recorded and contact angles were determined from the plots "force vs. depth" [16] (Fig. 2).

Wicking is instantaneous absorption of a liquid through a fibre by capillarity action. Wicking was determined from the final force or weight of the absorbed liquid during the wetting test as described in a previous work realized by Garcia and co-authors [4] (Fig. 2). Four samples were cut from each of the two panels produced for each of the seven treatments resulting in a total of 56 wettability measurements.

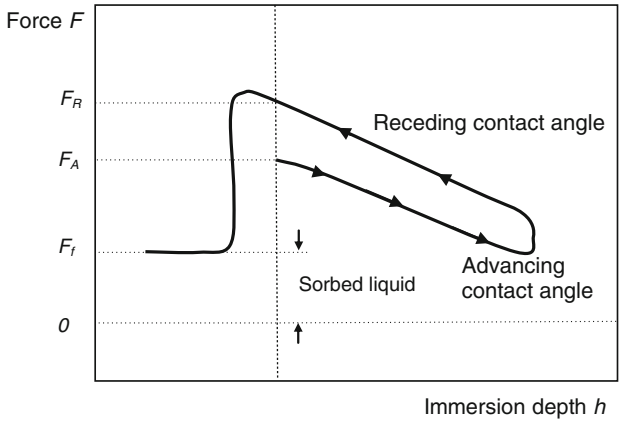

Fig. 2 The Wilhelmy plate method illustrated by a schematic plot of the force F versus immersion depth h. F_A and F_R: force obtained by linear regression of advancing and receding curves, respectively. F_f: final force or weight of the absorbed liquid during the test

Surface analysis of fibres by X-ray photoelectron spectroscopy (XPS)

An axis-ultra X-ray photoelectron spectrometer from KRATOS was employed to provide elemental and chemical data of untreated and heat-treated fibres of the longer heat treatment for both temperatures. Therefore, only the fibres treated at 150 °C for 60 min and at 180 °C for 60 min were compared with the untreated fibres. One sample for each of the three treatments was measured by XPS analysis. The pressure in the chamber was 10^{-8} mbar during XPS analysis. All spectra were recorded with an aluminium monochromatic source at 300 W potential and an incident angle of 30°. High resolution spectra were recorded with a nominal energy resolution of 0.5 eV (10 eV pass energy and 0.025 eV steps). These high resolution spectra were used for chemical analysis. The survey spectra used to quantitative elemental analyses of untreated and heat-treated fibres were recorded in 1 eV steps and 160 eV pass energy. The choice of only three treatments for XPS analysis was justified by the high cost of this kind of analysis. No statistical analysis was carried out because of the small number of samples.

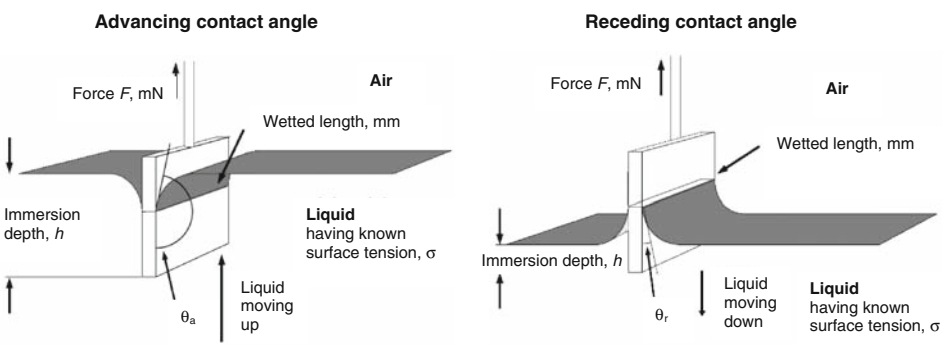

Fig. 1 Immersion in and withdrawal from a liquid to advancing and receding contact angle measurements by the Wilhelmy plate method (adapted from [9])

Results and discussion

Effect of heat treatment on the contact angles and wicking of MDF panels

Advancing and receding contact angles

Statistical analysis demonstrated a highly significant increase of the advancing (F-value = 4.57**) and receding (F-value = 15.75**) contact angles for the panels produced from heat-treated fibres at a probability level of 0.01 (Table 1). Indeed, the highest average advancing contact angle was of 85.1° for panels produced from fibres treated at 180 °C for 60 min and the lowest was of 70.5° for panels produced from untreated fibres. However, advancing contact angles for panels produced from heat-treated fibres at 150 °C for all time periods and at 180 °C for 30 and 60 min were not statistically different between themselves (Table 1). Receding contact angles increased more than advancing contact angles following heat treatment as shown in Fig. 3. Receding contact angles increased by 41.9 to 53.6° while advancing contact angle increased by 5.7 to 14.6° depending on the heat treatment conditions (Table 1). For receding contact angles, the panels produced from fibres treated at 150 °C showed an increase as a function of heating time. Nonetheless, for heat-treated fibres at 180 °C, the heating time did not affect the receding contact angles (Table 1).

Figure 4a and c present the relationship between water absorption after 2 h water soaking and advancing and receding contact angles, respectively. Figure 4b and d show the relationship between water absorption after 24 h water soaking and advancing and receding contact angles, respectively. Our results agree with results of water absorption after water soaking found by Garcia et al. [5] which demonstrated a decrease of water absorption and thickness swelling of MDF panels produced from heat-treated fibres in the same conditions. Water absorption was reduced by 50 to 90% and by 25 to 66% after 2 and 24 h water soaking, respectively [5]. The results indicate increased contact angles—especially for receding contact angles, and decreased water absorption—mainly after 2 h water soaking following fibre heat treatment which reduces the hydrophilic properties of MDF panels (Fig. 4a–d). Since increased contact angles characterize more hydrophobic materials, the heat treatment used here increases the water repellency of fibre surfaces, which may improve the dimensional stability of MDF panels. On the other hand, this could cause problems for the adhesion and coating of panel surfaces if a hydrophilic surface is required.

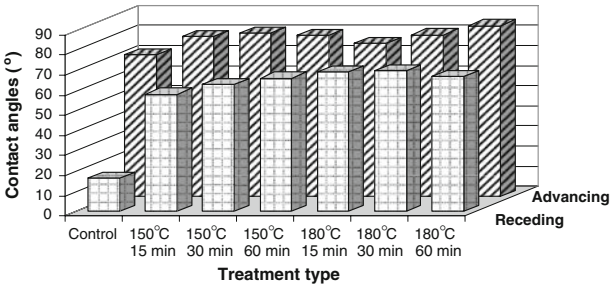

Fig. 3 Relationship between the advancing and receding contact angles of medium density fibreboards and type of heat treatment

The results of advancing contact angles can be compared with those found by Pétrissans et al. [12] for solid wood treated at 240 °C for 8 h under nitrogen which revealed an important increase of advancing contact angles with the heat treatment. The advancing contact angle values found by Pétrissans et al. [12] varied between zero and 26.5° before heat treatment and between 42.2 and 88.9° after heat treatment as a function of species. However, our results presented a lower variation between panels produced from untreated and heat-treated fibres than those

Table 1 Contact angles and wicking of medium density fibreboards produced from heat-treated fibres obtained by the Wilhelmy plate method

Treatment	Advancing CA (°)		Receding CA (°)		Wicking (g)	
	Means	LSM	Means	LSM	Means	LSM
Control	70.5 (3.6)	C	16.5 (13.3)	E	7.89×10^{-2} (0.0082)	A
150 °C, 15 min	79.8 (8.8)	AB	58.4 (4.9)	D	2.44×10^{-2} (0.0013)	B
150 °C, 30 min	81.3 (4.9)	A	63.1 (4.0)	CD	2.28×10^{-2} (0.0013)	C
150 °C, 60 min	80.4 (5.4)	AB	66.3 (4.6)	BC	2.39×10^{-2} (0.0021)	BC
180 °C, 15 min	76.2 (8.0)	BC	69.6 (4.4)	AB	1.65×10^{-2} (0.0012)	D
180 °C, 30 min	80.6 (5.9)	AB	70.1 (3.3)	A	1.57×10^{-2} (0.0007)	D
180 °C, 60 min	85.1 (11.4)	A	67.2 (8.6)	AB	1.43×10^{-2} (0.0033)	E
F-value	4.57**		15.75**		54.33**	

Advancing CA, advancing contact angle; Receding CA, receding contact angle; LSM, least squares means; Means designated with the same capital letter are not statistically different. Standard deviation is given in brackets

** Significant at 0.01 probability level

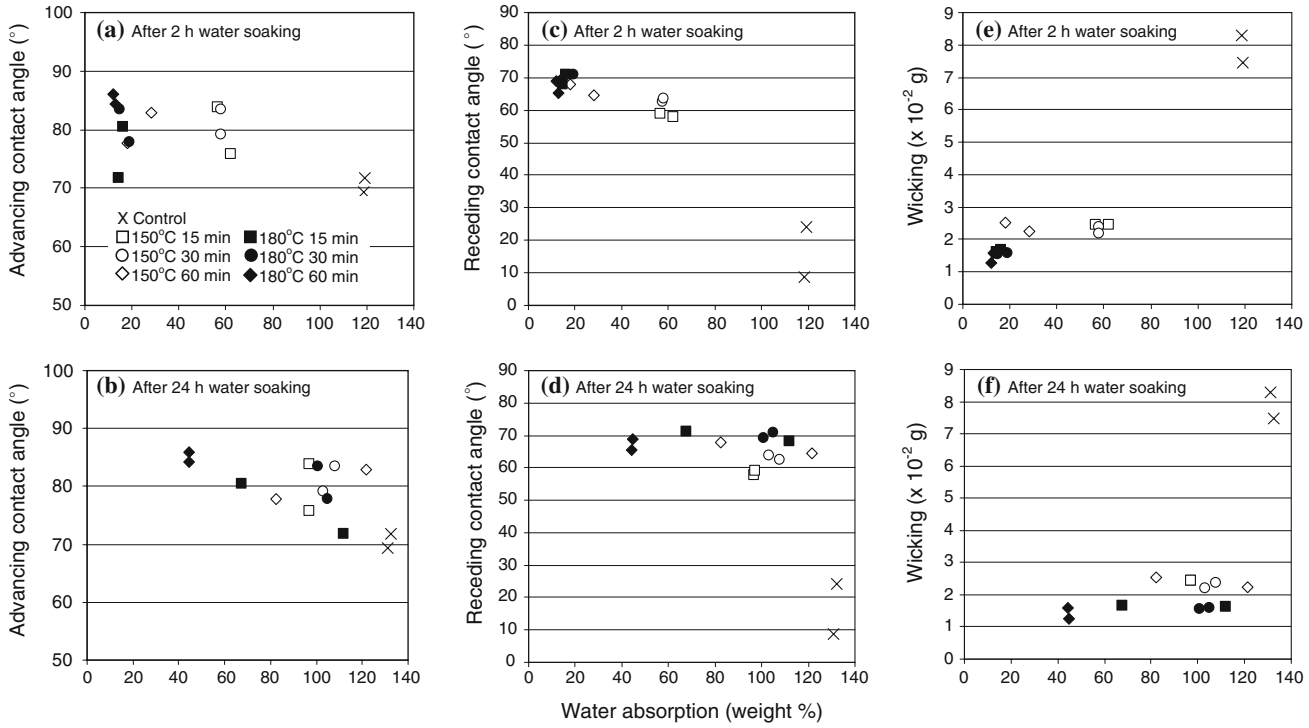

Fig. 4 (**a**) and (**b**) Relationship between advancing contact angle and water absorption after 2 and 24 h water soaking, respectively. (**c**) and (**d**) Relationship between receding contact angle and water absorption after 2 and 24 h water soaking, respectively. (**e**) and (**f**) Relationship between wicking and water absorption after 2 and 24 h water soaking, respectively

found by Pétrissans et al. [12] for untreated and heat-treated wood. This can be explained by the lower treatment temperatures used in our study and also by the fact that the hot pressing process is also a heat treatment. Therefore, even the untreated fibres were given a heat treatment due to the hot pressing. The advancing contact angle values for the panels obtained in our study are similar to those found by Sernek et al. [15] for southern pine following high temperature drying (from 50 to 200 °C).

For receding contact angles, the literature reports values equal to zero for solid wood [12, 19]. Our results revealed values different from zero, which can involve a dewetting phenomenon of MDF panel surfaces. However, this phenomenon is not well known and more investigation is required about it.

Wicking

The heat treatment revealed a highly significant effect (F-value = 54.33**) on the wicking of the panels at a probability level of 0.01 (Table 1). In fact, the heat treatment caused a reduction of wicking by about 70% within the 150 °C group and 80% within the 180 °C group (Fig. 5). Contact angle measurements demonstrated that fibre surfaces are less hydrophilic following treatment. Therefore, the fibres absorb less water by capillarity especially when they are treated at higher temperatures.

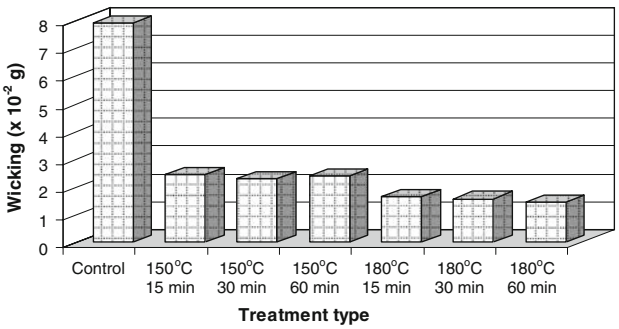

Fig. 5 Relationship between the wicking of medium density fibreboards and type of heat treatment

Figure 4e and f present the relationship between wicking and water absorption after 2 and 24 h water soaking, respectively. Figure 4e illustrates that wicking increases with water absorption after 2 h water soaking and the panels become less and less hydrophilic with the increase of temperature and time of the heat treatment. Figure 4f shows that water absorption after 24 h decreases gradually with the increase of temperature and time of the fibre heat treatment while wicking is lower for panels produced from heat-treated fibres and higher for control panels. Panels made from fibres treated at 180 °C for 15 and 30 min have similar water absorption than at 150 °C for all time periods (Fig. 4f). Panels produced from fibres treated at 180 °C for 60 min have the lowest wicking and water absorption after

24 h water soaking while the untreated panels have the highest wicking and water absorption after 24 h water soaking (Fig. 4f). The last results suggest that heat treatment modifies fibre surfaces—due to decrease in wicking—and subsequently and gradually the bulk of fibres which absorbs most of the water—due to gradual decrease of water absorption after 24 h water soaking with the increase of temperature and time of the heat treatment. Moreover, they also show that the wicking test which measures surface characteristics cannot replace the standard water absorption test (with longer water immersion time) to determine the dimensional stability of the panels—because the wicking test does not measure the modification occurred in whole cell wall thickness of the fibres while water absorption does. Our results agree with the results obtained by Garcia et al. [5] for water absorption after water soaking of MDF panels produced from heat-treated fibres in the same conditions of temperature and time.

Effect of heat treatment on the surface composition of MDF fibres

According to several authors [2, 13–14], the hydrophobic properties of the heat-treated fibre surfaces can be explained principally by the hemicelluloses degradation—the most hydrophilic polymer of wood—and by chemical modifications on the wood composition occurring during the treatment. The XPS analysis allows to identify the functional groups and the elemental composition of the surface of the heat-treated fibres which are analyzed to a depth of about 10 nm. The results of elemental analysis represent the apparent concentrations in atomic percentage of carbon (C), oxygen (O), nitrogen (N) and calcium (Ca) (Table 2). These concentrations are qualified as apparent because they are calculated under the hypothesis that the sample is homogeneous which is not the case for wood fibres. The wood fibres are also partly made up of hydrogen atoms but they are not detectable by the XPS analyses. The results reveal a weak modification of the elemental composition of fibres following heat treatment. The oxygen to carbon ratio (O/C ratio) demonstrates a slight decrease with the increase of temperature of treatment suggesting a modification of surface composition of the fibres (Table 2). However, the number of elemental analysis in our study did not allow statistical analysis. Therefore, we could not determine if these results are statistically different. Nevertheless, even minor modification of fibre surface composition has a significant impact on the wetting properties of MDF as shown in the results of contact angles and wicking (Table 1). Our results are in agreement with those found by Sernek et al. [15] in which a decrease of the O/C ratio of yellow poplar and southern pinewood with an increase of drying temperature from 156 to 187 °C is reported.

The chemical analysis of carbon compounds, C1s spectra, indicates the presence of four peaks of carbon atoms for untreated and heat-treated fibres as illustrated in Fig. 6. The chemical analyses indicate a slight difference or no change in the chemical composition of carbon compounds. The C1/C2 ratio obtained for wood fibre

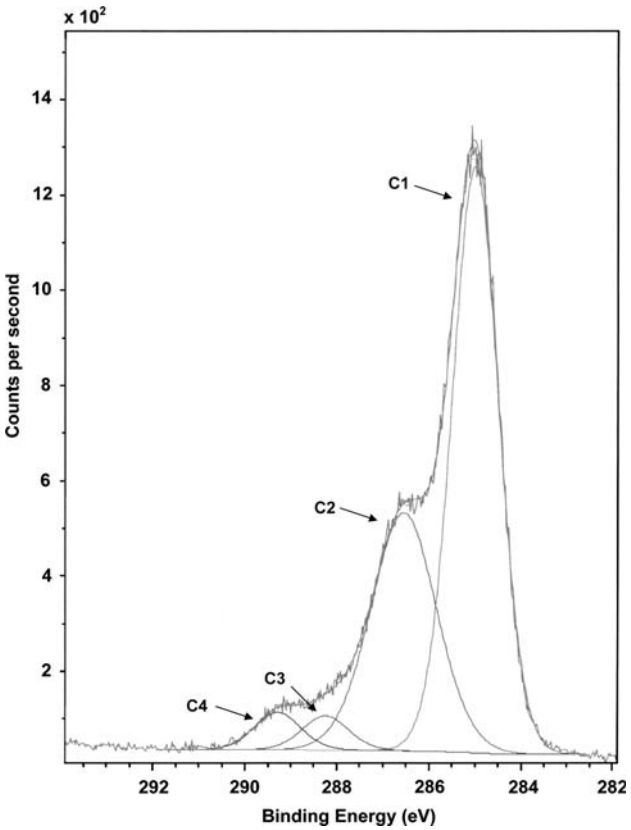

Fig. 6 Curve fits of carbon C1s peaks of untreated fibres

Table 2 Surface composition of heat-treated fibres determined by XPS

Treatment	Elements (%)				Carbon components C1s (%)				Binding energy (eV)				Ratios	
	C	O	N	Ca	C1	C2	C3	C4	C1	C2	C3	C4	O/C	C1/C2
Control	80.7	19.1	0.2	0.0	59.0	33.8	3.4	3.8	285	286.6	288.2	289.3	0.237	1.75
150 °C, 60 min	81.2	18.8	0.0	0.0	50.4	43.7	2.8	3.1	285	286.4	288.4	289.4	0.232	1.15
180 °C, 60 min	81.1	18.5	0.3	0.1	53.6	39.2	4.0	3.2	285	286.5	288.3	289.4	0.228	1.37

decreased with the heat treatment when compared with the untreated fibre (Table 2). However, when the two heat treatments are compared, the C1/C2 ratio increased when the temperature increased from 150 to 180 °C. The inconsistence of the latter results can be explained by the heterogeneity of the fibres due to the mix between hardwood (white birch) and softwood species (black spruce, balsam fir and jack pine) and by the heterogeneity of the heat treatment due to the temperature gradient within the vacuum oven. Statistical analysis could not be performed due to the lack of samples. Therefore, we could not determine if these results were statistically different. Sernek et al. [15] found an increase of the C1/C2 ratio of yellow poplar for drying temperatures higher than 156 °C but no significant differences were found in the C1/C2 ratio of southern pine for the same drying temperature. Moreover, their results showed that the C1/C2 ratios obtained for yellow poplar were lower than those obtained for southern pine. The same authors explained the decrease of O/C ratio and the increase of C1/C2 ratio on the heat-treated wood surface by the migration of extractives and the deposition of hydrocarbonaceous particles on fibre surfaces. The increase of the C1/C2 ratio following heat treatment can also be explained by the reduction of hydroxyl groups which are responsible for water absorption by cell wall polymers thus C1 increase in percentage is due to thermal degradation of hemicelluloses.

Conclusions

The results found in the present study allow to draw the following conclusions:

1. The heat treatment presented a highly significant effect on the advancing and receding contact angles and the wicking of MDF panels at a probability level of 0.01. Receding contact angle increased by 41.9 to 53.6° while advancing contact angle increased by 5.7 to 14.6° depending on the heat treatment conditions. The results also showed a reduction of wicking by about 70% within the 150 °C group and 80% within the 180 °C group.
2. The relationship between contact angles and wicking versus water absorption demonstrated a decrease of contact angles and an increase of wicking with the increase of water absorption.
3. The results obtained from contact angles and wicking experiments prove that heat treatment modifies fibre surfaces resulting in less hydrophilic panels. These changes increase water repellency nevertheless they could be a problem for adhesion and coating of MDF surfaces when hydrophilic surfaces are required. More investigations are needed on the coating of heat-treated surfaces.
4. XPS analyses suggest a slight modification of the surface composition of heat-treated fibres. The results reveal a slight decrease of the O/C ratio.
5. The C1/C2 ratio of heat-treated fibres decreases when compared to untreated fibres and slightly increases when fibres treated at 150 and at 180 °C are compared. However, statistical analysis could not be performed because of the low number of samples.

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