SURFACE ENERGY CHARACTERIZATION OF THERMALLY MODIFIED SPRUCE USING INVERSE GAS CHROMATOGRAPHY UNDER CYCLIC HUMIDITY CONDITIONS

*Susanna Källbom**†
PhD Student
E-mail: susanna.kallbom@byv.kth.se

Magnus Wålinder†
Professor
E-mail: magnus.walinder@byv.kth.se

Kristoffer Segerholm
Research Scientist
KTH Royal Institute of Technology
Division of Building Materials
SE-100 44 Stockholm
and
SP Technical Research Institute of Sweden
E-mail: kristoffer.segerholm@sp.se

Dennis Jones
Research Scientist
SP Technical Research Institute of Sweden
SE-114 86 Stockholm, Sweden
E-mail: dennis.jones@sp.se

(Received April 2015)

Abstract. The surface energy of unmodified and thermally modified spruce wood components was researched at dry and moist conditions using inverse gas chromatography. The results indicate a more pronounced heterogeneous nature of the thermally modified wood surfaces in terms of the dispersive (nonpolar) component of the surface energy, compared with that of the unmodified wood surfaces. The dispersive component of the surface energy of the thermally modified wood ranged between 44 and 38 mJ/m^2 corresponding to an increase in surface coverage from a low level and up to about 10%. Suggested explanations for the more distinct heterogeneity of the thermally modified wood sample are related to chemical changes of the wood substance which seem to result in certain micromorphological features observed by scanning electron microscopy as alternated fracture surfaces created in the grinding process; and also possible changes or redistribution of the wood extractives. An increase of the MC, representing a change from a dry condition of approximately 0% RH to ca 75% RH, of both the unmodified and thermally modified samples seemed to have a marginal influence on the dispersive component of the surface energy. Possible implications of the results in this study can be found in the tailoring of new compatible and durable material combinations, for example, when using thermally modified wood residuals as a component in new types of biocomposites.

Keywords: Thermally modified wood, inverse gas chromatography, humidity cycling, Norway spruce, dispersive surface energy, surface energy heterogeneity, BET-specific surface area.

---

* Corresponding author
† SWST member

Wood and Fiber Science, 47(4), 2015, pp. 410-420

INTRODUCTION

In all building material applications, there is a risk for moisture exposure which may cause in-service and durability issues for hygroscopic materials such as wood and bio-based products. A number of different means are used in industry today to modify wood to make it less hygroscopic. One approach, by far the most applied method, is thermal treatment, a wood modification process which involves heating of the wood up to temperatures of around 200°C in a near oxygen-free environment, that is, controlled pyrolysis. This leads to significant changes of the wood with respect to its chemical composition and morphology, and for wood species like spruce and pine, a significantly darker color. Such alterations give wood a number of enhanced properties, such as improved dimensional stability and resistance to decay (Hill 2006). This makes thermally modified wood suitable for outdoor applications, for example, cladding or decking. Some disadvantages are the changes in mechanical properties, such as decreased strength and a more brittle behavior compared with unmodified wood. Other critical features can be related to changes of the surface characteristics (Bryne and Wålinder 2010) which may lead to difficulties in further uses of thermally modified wood residuals in applications involving bonding processes, for example, in wood-based biocomposites.

Inverse gas chromatography (IGC) is a technique particularly useful for surface energy characterization of materials in particle, fibrous, or powder form (Lloyd et al 1989). It is a technique useful for characterization of various typical wood processing by-products. The method can be applied to determine surface free energy and acid–base characteristics (surface energetics) of modified wood which may provide insight into changes in the surface chemistry which is important for a better understanding of the interaction between the wood substance and other materials. Such information may furthermore be useful for tailoring or designing suitable and durable material combinations in, for example, wood gluing, coating and in composite applications. IGC has been used to study physicochemical properties of various particles or fibers (Dorris and Gray 1980; Ylä-Mäihäniemi et al 2008) as well as pharmaceuticals (Davies et al 2013). The method uses various known gases for evaluating their interaction with the surface of the solid material with unknown properties. The total surface energy is determined by a polar (chemical interactions) and a nonpolar (physical interactions) part. The polar part is also named the specific surface energy, or acid–base component, and the nonpolar the dispersive component of the surface energy.

IGC has also been used an analyzing method for studying surface energetics of various lignocellulosic materials, for example, wood pulp fibers, cellulose or lignin (Dorris and Gray 1980; Matuana et al 1999; Tze et al 2006), and wood particles and fibers also including their interaction with thermoplastics (Kamdem et al 1993; Tshabalala 1997; Wålinder and Gardner 2000, 2002; Peterlin et al 2010; Oporto et al 2011), cotton and linen (Csiszár and Fekete 2011) and microfibrillated cellulose and cellulose nanofibers (Siddiqui et al 2011). Historically, IGC measurements have normally been conducted at very low solute concentrations (infinite dilution) resulting in single values of the surface energy representing only high-energy sites of the surface. It is obvious that natural materials like wood and cellulosic fibers are inherently variable in both microstructure and chemical composition, including surface chemical composition, that is, they are clearly very heterogeneous materials. Newly developed IGC methods (Ylä-Mäihäniemi et al 2008) enable analyses of the surface energy distribution of heterogeneous particulate and fibrous materials. This can be obtained by letting the surface interact with different concentrations of gas probes, that is, solute concentrations at finite dilution. The acid–base characteristics may be analyzed using a series of polar acid–base probes. Such analysis has, however, been proven to be a quite complex matter, probably due to strong preferential sorption and dissolution related to the wood extractives (Wålinder and Gardner 2000).

In IGC analyses, the particulate or fibrous material studied is packed in a glass column and one gas probe at a time is injected into a stream of an inert carrying gas that passes through the sample column. The elution time of the gas is then detected by a flame ionization detector which gives a peak in a chromatogram from where the interaction between the gas probe molecule and the surface of the sample can be calculated. In state-of-the-art IGC, it is possible to regulate the conditions in the chromatograph in terms of temperature, RH and exposure time. This new generation of IGC methodology also enables analyses of the surface energy heterogeneity, which is sorption measurements at lower and higher surface coverage, representing sorption sites at higher and lower surface energy, respectively. The IGC method can also be used to determine the Brunauer, Emmet, and Teller (BET) specific surface area, by the help of one of the alkanes at finite dilution, usually octane.

The stationary phase is normally analyzed in a dry state in traditional IGC. Because wood is a hygroscopic material and in practical aspects always contains moisture, the dry state is not a realistic condition for building material applications. In this study, the new generation of IGC apparatus is applied with the possibility to condition the stationary phase at different moisture levels. This enables analyses of surface energetics of hygroscopic materials that relates to more relevant and real technical applications. The new method of cycling the humidity conditions in the chromatograph should add new knowledge for tailoring optimal interfacial properties between the thermally modified wood and various polymers, for example, for outdoor and high-humidity uses of composites. The exposure of wood components to different RH levels and the effects on the surface energy heterogeneity has not been studied before. Such an exposure will lead to potential water adsorption/absorption in the samples. Since thermally modified wood is less prone to sorb water than unmodified wood, mainly attributable to the reduced number of accessible hydroxyl groups (Hill 2006), such effects could be studied by IGC adding new valuable information regarding its sorption properties. It is also important to remember that a change of MC in the wood could result in swelling on different levels, which can lead to changes of the surface area and the surface energetics.

The objective of this paper was to apply and further develop IGC for studying the surface energy characteristics, including surface energy heterogeneity, of thermally modified spruce components exposed to humidity cycling. Such information is an important basis for developing new possible uses of thermally modified wood residuals. It should be noted that this study was restricted to include only the dispersive component of the surface energy. Research on the heterogeneity of the acid–base characteristics of wood using IGC has been very limited and this is intended to be part in future work.

MATERIALS AND METHODS

Wood Materials

Norway spruce (*Picea abies* Karst) wood components (often called wood fibers or particles), both unmodified and thermally modified, were prepared using a two-step grinding procedure, described in Segerholm et al (2012) and then sifted through a 120 mesh (<0.125 mm) screen. The thermal treatment followed procedures according to the ThermoWood® D process (Anon 2003) and had been performed before the grinding.

The length of the unmodified and the thermally modified wood components were determined using a kajaaniFiberLab™ apparatus (Metso Automation, Helsinki, Finland). Four repetitions of the length measurements were performed both for the unmodified and thermally modified components. First, about 2 g of the components were mixed with 5000 mL of water (20°C) and stirred in a tank. From the mixture, 50 mL was taken out with a pipette for each test for analysis in the kajaaniFiberLab™ apparatus. The sample dilution was drawn into a capillary (0.5×0.5 mm^2) where the components were detected and monitored by a polarized laser. A photo was taken, using a xenon lamp and a camera and then the lengths of the components were measured and calculated using image analysis software.

Scanning electron microscopy (SEM, Hitachi Tabletop Microscope TM-1000, Krefeld, Germany) was used to analyze the overall micromorphology of the wood components and to correlate the appearance to other surface properties in this study. The analysis was performed using three samples of both the unmodified and thermally modified wood components.

IGC Theory

The BET-specific surface area of, for example, solids, particulates, and fibers can be determined by physical adsorption in IGC experiments using an alkane, such as octane. The BET equation is an adsorption isotherm derived from Brunauer et al (1938):

$$\frac{1}{[n(p_0/p)-1]} = \frac{c-1}{n_m c}\left(\frac{p}{p_0}\right) + \frac{1}{n_m c} \tag{1}$$

where p_0 and p are the saturation and equilibrium pressures of the adsorbates at the adsorption temperature, n is the amount of moles adsorbed, n_m is the number of moles for monolayer adsorption and c is the sorption constant based on the heat of adsorption. By plotting the p/p_0 vs $1/n[(p_0/p)–1]$ a linear correlation can be obtained in the range of $0.05 < p/p_0 < 0.35$. The sorption isotherms should form a type II or IV curve (Brunauer et al 1938; Naderi et al n.d.). From the slope of the linear correlation, the monolayer capacity (n_m) can be obtained. The specific surface area is calculated using the following equation:

$$\mathrm{BET} = \frac{(n_m N a)}{Vm} \tag{2}$$

where N is the Avogadro's number, a is the adsorption cross section of the gas, V is the molar volume adsorbed gas and m is the adsorbent mass.

In the IGC approach, the surface property calculations are based on net retention volume (V_N), which will depend on the time of interaction between the injected gas probe and the solid surface. For each alkane, n_m is known which makes it possible to determine the surface coverage n/n_m for a specific solute concentration by the amount of moles adsorbed (n). Different surface coverages will be used together with the corresponding experimental values of the net retention volume. V_N is defined in the following equation:

$$V_N = V_r^0 - V_d^0 \tag{3}$$

where V_r^0 is the measured retention volume of the probe and V_d^0 is the measured dead volume, which is measured before the first probe injection and also after the last, using the inert gas methane. V_r^0 is obtained using the following equation:

$$V_r^0 = \frac{j}{m} F(t_r - t_0)\frac{T}{273.15} \tag{4}$$

where j is a correction factor attributable to pressure drop, m is the mass of the sample, F is the flow rate of the carrier gas, t_r is the retention time, t_0 is the retention time of methane (measuring the dead volume), and T is the temperature. Two approaches can be used to determine the dispersive component of the surface energy: the Schultz method (Schultz et al 1987) or the Dorris–Gray method (Dorris and Gray 1980). It has been suggested that the latter method is more accurate and with smaller errors than the Schultz method (Ylä-Mäihäniemi et al 2008; Shi et al 2011; Gamble et al 2012). The Dorris–Gray method is based on the free energy of adsorption of one methylene group (-CH_2) from the gas probe molecule. The dispersive component of the surface energy can be obtained from the correlation and slope of the free energy of adsorption of at least three alkanes plotted vs their carbon number. The free energy of adsorption of one CH_2 group is described as (Dorris and Gray 1980)

$$\Delta G^{CH_2} = -RT\ln\left(\frac{V_{N,n+1}}{V_{N,n}}\right) \tag{5}$$

where R is the universal gas constant, T is the temperature, V_N is the retention volume, and n is the carbon alkane number. The work of adhesion between the solid and the CH_2 group is described according to Fowkes' theory for Lifshitz-van der Waals interactions:

$$W_a^{CH_2} = 2\sqrt{\gamma_s^d \gamma_{CH_2}} \tag{6}$$

where γ_s^d is the dispersive component of the surface energy of the solid and γ_{CH_2} is the free energy of the CH_2 group. The change in free energy of adsorption of one CH_2 group can be written as

$$-\Delta G^{CH_2} = N a_{CH_2} W_a^{CH_2} \tag{7}$$

where N is the Avogadro's number and a_{CH_2} is the cross-sectional area of the CH_2 group.

Combining Eqs (6) and (7) gives the following correlation:

$$-\Delta G^{CH_2} = N a_{CH_2} \times 2\sqrt{\gamma_s^d \gamma_{CH_2}} \tag{8}$$

which leads to

$$\gamma_s^d = \frac{1}{4 \times \gamma_{CH_2}} \left(\frac{-\Delta G^{CH_2}}{N a_{CH_2}} \right)^2 \tag{9}$$

$$\gamma_s^d = \frac{\text{Slope}^2}{4 \times N^2 (a_{CH_2})^2 \times \gamma_{CH_2}} \tag{10}$$

The dispersive component of the surface energy can be obtained by plotting the free energy of adsorption vs the carbon number as can be seen in Fig 1, using Eq 10. In this study, the dispersive component of the surface energy distribution, or the dispersive surface energy heterogeneity, was obtained according to methodology presented in Ylä-Mäihäniemi et al (2008). This approach involves adsorption measurements at different surface coverages together with the corresponding experimental values of the net retention volume.

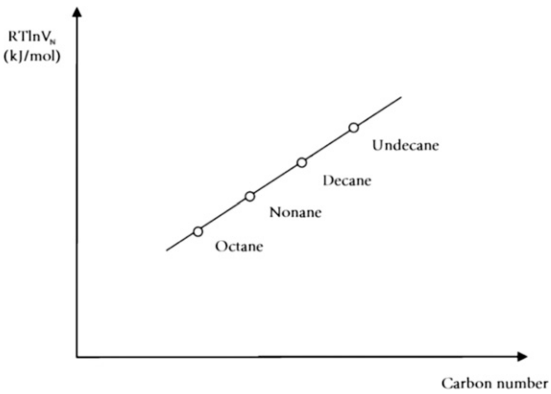


Figure 1. Example plot for determining the dispersive component of the surface energy using IGC.

IGC Measurements

The wood component samples were dried in a conventional oven at 103°C for 2 h, and then packed into 300 mm long silanized glass columns, with an inner diameter of 3 mm. The packing process was performed using a column packer provided by Surface Measurement Systems (SMS, Alperton, London, UK). The wood components were immobilized in the columns by silanized glass wool at both ends. The packing density of a sample was calculated from the mass of the wood divided by the volume of the packed sample. Both the packing density and the dry mass can be seen in Table 1.

The IGC measurements were performed on two replicate columns for each wood sample, placed in the inverse gas chromatograph, an IGC Surface Energy Analyzer developed by Surface Measurement Systems. In a preconditioning step, the sample columns were further dried at 60°C for 2 h to obtain the dry mass and to remove volatiles. Purified helium with a flow rate of 10 mL/min was used as carrier gas. The BET-specific surface area was determined at finite dilution, in the partial pressure range 5-35% using octane isotherms before each surface energy measurement. Octane, nonane, decane, and undecane were used as nonpolar probes for the surface energy analyses (Table 2). However, undecane had to be excluded from the results because of unsatisfactory interaction with the samples. After injecting a gas probe, it interacted with the sample and the retention time was determined using an SMS software. Methane was used as a reference gas probe to determine the dead volume.

The dispersive component of surface energy measurements were performed at dry and moist

Table 1. The dry mass of the wood components and the packing density of the sample columns (average) are shown.

Sample	Dry mass (mg)	Packing density (10^{-3} kg/m^3)
Unmodified	260-280	0.20 ± 0.01
Thermally modified	130-140	0.18 ± 0.01

Table 2. Properties of the nonpolar IGC probes used.

Probe	a (Å^2)[a]	γ_L^D (mJ/m^2)[b]	Supplier
n-Octane	63	21.1	Sigma-Aldrich
n-Nonane	69	22.4	Sigma-Aldrich
n-Decane	75	23.4	Sigma-Aldrich
n-Undecane	81	24.2	Sigma-Aldrich

[a] The surface area that can be occupied by one probe molecule (Liu and Rials 1998).

[b] The surface tension of the probe liquids at 25°C (Lide 1995).

conditions using the results from the BET measurements. Before the measurements in the dry condition, the samples were conditioned at 60°C for 2 h whilst for measurements at the moist condition, the samples were conditioned at 30°C between 2 and 4 h at respective RH. The thermally modified samples were exposed to three dry-moist cycles, starting with dry conditions at 30°C and 0% RH, then at a moist condition at 30°C and 75% RH. After that, the samples were also exposed to three dry–moist cycles where the moist condition was 30°C and 25% RH. The unmodified samples were exposed to one dry–moist cycle only, at 30°C, 0% RH and 75% RH, in terms of measuring the dispersive component of the surface energy. Different alkanes (Table 2) were used for measuring the dispersive component of the surface energy with a target surface coverage from 1 to 10% coverage (0.01-0.1 n/n_m) using the Dorris–Gray method; center of mass. The MC of the samples was compared with data from dynamic vapor sorption (DVS) measurements at 30°C, performed in a parallel study (Källbom et al 2015) on wood components from the same sample batch.

RESULTS AND DISCUSSION

Length Distribution

The length distribution of the unmodified and thermally modified wood components can be seen in Fig 2. In total, 37,981 unmodified components and 15,572 thermally modified components were measured. Components with length between 0.01 mm and up to 0.85 mm were observed, with the thermally modified components showing a wider distribution than the unmodified components. Higher fractions of shorter wood components (more fines) were found in the unmodified wood sample than the modified wood sample. The reason for this difference in size distribution, that is, more fines in the unmodified wood sample, is unclear but could perhaps be attributable to the pronounced electrostatic nature of the thermally modified wood component which may affect the fractionation process. However, the majority of the wood components were longer than 0.125 mm, which was the size of the sieve they were passed through. The variation in the length of the components might influence the determination of the BET-specific surface area.

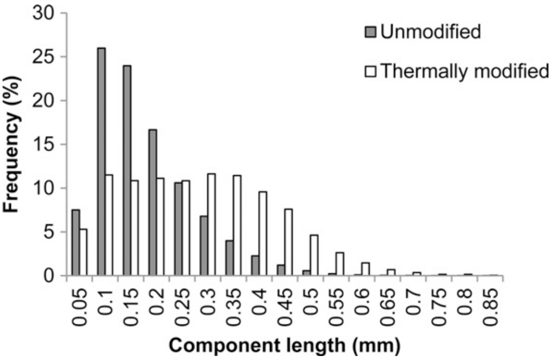
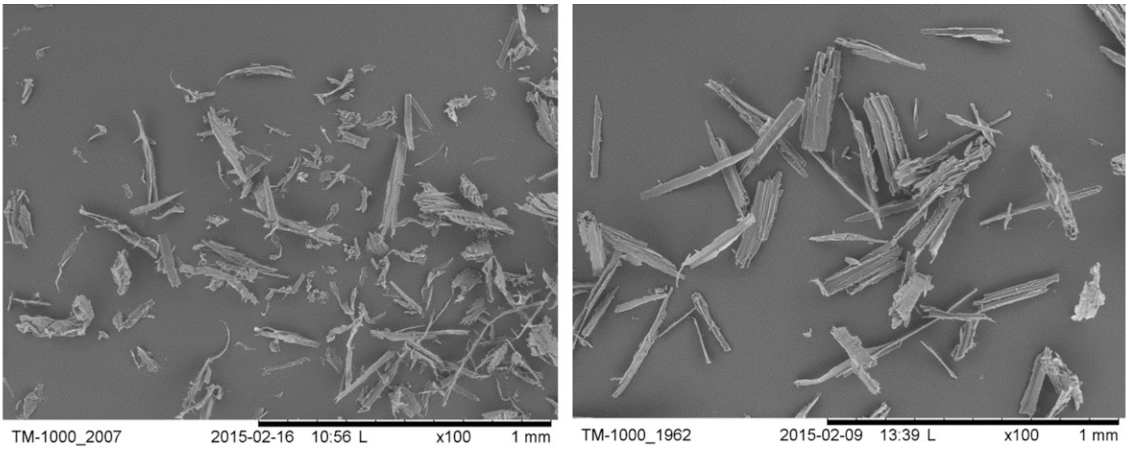
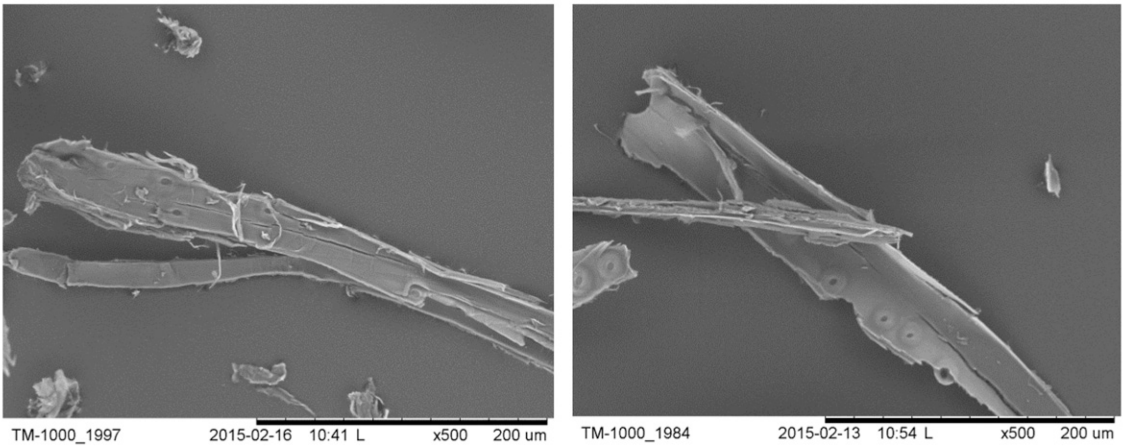


Figure 2. Length frequency distribution of the unmodified and thermally modified wood components, measured with the kajaaniFiberLab™ apparatus.

Figure 3 shows some representative SEM micrographs at two different magnifications of the micromorphology and size/shape variability of the unmodified and the thermally modified wood components. The micrographs confirmed the results from the kajaaniFiberLab™ analyses, which showed a higher fraction of shorter wood components for the unmodified than thermally modified wood sample. The SEM micrographs at the higher magnification also indicate that there was a difference in micromorphology between the unmodified and the thermally modified wood components. The thermally modified components were more splintered and needle-like compared with the unmodified components. Such differences in micromorphology between the unmodified and thermally modified wood components are suggested to be related to the chemical changes of the modified wood substance which seem to



Unmodified **Thermally modified**



Unmodified **Thermally modified**

Figure 3. SEM micrographs of the unmodified and thermally modified wood components in a lower (the upper images) and a higher (the lower images) magnification.

result in alternated fracture surfaces created in the grinding processes.

MC

Obtained MC of the unmodified and thermally modified samples after conditioning in the IGC apparatus are presented in Table 3. The MC values are in this case an average of the MC obtained during three dry–moist cycles using IGC for both the unmodified and the thermally modified wood samples. The MC of the same type of wood components obtained from DVS measurements are also presented in Table 3. The data from the two different analyses are in rather good agreement, which indicates successful conditioning during the IGC measurements. Furthermore, the MC of the thermally modified samples at RH 25% was 3.9 ± 0.4%.

Table 3. The average MC of the unmodified and thermally modified wood component samples after conditioning at 30°C, 75% RH, using IGC (average of three cycles) and DVS at 30°C (data from the sorption curve).

Sample	MC in IGC (%)	MC in DVS (%)
Unmodified	12.2 ± 0.6	13.4
Thermally modified	6.9 ± 0.2	6.1

BET-specific Surface Area

Figure 4 shows the obtained BET-specific surface areas for the different samples ranging between 1.25 and 1.97 m^2/g, where the thermally modified wood components had a lower surface area than the unmodified wood components. Similar results, in terms of unmodified wood, have been reported by Karinkanta et al (2012), using adsorption with nitrogen for surface area analyses of dried Norway spruce sawdust (23-250 μm). Their results showed surface areas ranging from 1.5 to 3.7 m^2/g. Another study by Wiman et al (2012), also using nitrogen adsorption, showed a surface area value of 0.4 m^2/g for unmodified Norway spruce chips (size: 2-10 mm). It should be noted that when using both nitrogen and octane as sorptives, the molecules have limited access to the smallest pores, in the wood substance. A study on the surface properties of thermally modified Norway spruce sawdust (sieved through a 0.2 mm net) was done by Lagana et al (2006). The specific surface area at three different temperatures was analyzed using nitrogen adsorption and indicated an increase in the surface area with increasing temperature, ranging between 1.30 and 2.11 m^2/g.

The BET values furthermore strengthen the results obtained from the kajaaniFiberLab™ and SEM, discussed earlier. The influence of increased RH generally showed a small decrease of the BET-specific surface area at the moist state, both for the unmodified and thermally modified wood components. The same trend could be observed both at RH 75% and 25%, with occasional exceptions. An explanation for this could be attributable to the more polar nature of the water molecules which are likely to interact more strongly with the wood surface than the nonpolar alkane molecules. The hygroscopicity is further reduced in the thermally modified wood components, mainly because of the reduction of the available hydroxyl groups that could bind to the water molecules (Hill et al 2012). This could have an impact in the attraction and binding of the water to the surface of the wood components. The water molecules would therefore have a possibility to interact with more polar sorption sites in the adsorption process for the unmodified wood compared with the thermally modified wood.

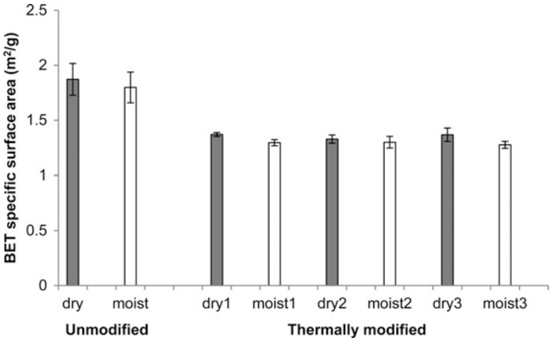


Figure 4. The average BET-specific surface area determined using IGC at 30°C of the unmodified wood components at dry (0% RH) and moist (75% RH) conditions, and the thermally modified wood components exposed to three cycles of dry (0% RH) and moist (75% RH) conditions.

Dispersive Component of the Surface Energy

Figure 5 shows the obtained dispersive component of the surface energies vs different surface coverages for the studied wood samples. The repeatability was satisfactory between the two replicate columns, both for unmodified and thermally modified wood. The grinding will lead to new surfaces created and further lead to an initiated aging of the new surfaces. However, in the thermal

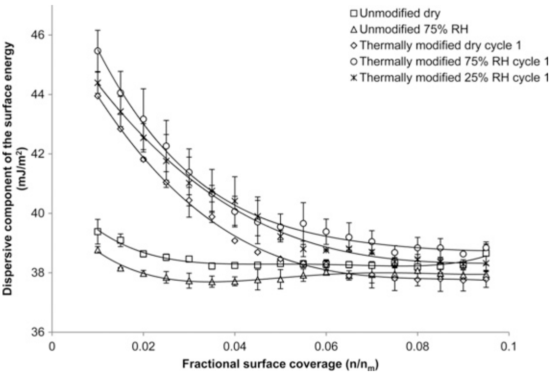


Figure 5. The dispersive component of the surface energy vs different target fractional surface coverage obtained using IGC at 30°C for the unmodified wood components at dry (0% RH) and moist (75% RH) conditions, and for the thermally modified wood component at dry (0% RH) and moist (75% RH and 25% RH) conditions cycle 1. The average of both samples is shown and the error bars represent the standard deviation of the two replicate columns.

modification process, the whole piece of the solid wood will be modified in terms of chemical changes together with compounds evaporating and migrating. The unmodified and thermally modified wood components were ground and sieved using the same method and thereafter aged to a point were changes because of surface aging could be disregarded. As can be seen, the thermally modified wood has a distinctly higher variability, or heterogeneity, of the surface energy compared with the unmodified sample. For the thermally modified wood in the dry condition, a surface energy distribution ranging between 44 and 38 mJ/m^2 for fractional surface coverages between 1% and ca 10% (equal to 0.01-0.1 n/n$_m$) was obtained. The corresponding values for the unmodified sample were between 39-38 mJ/m^2. Only one cycle for measuring the dispersive component of the surface energy was performed for the unmodified wood samples, used for comparison reasons. It should also be noted that the thermally modified wood components show distinctly higher dispersive component of the surface energy at lower fractional surface coverage than the unmodified wood components.

For the thermally modified wood, a slight increase in the dispersive component of the surface energy could be seen when exposed to higher RH conditions (75% RH), ranging between 46 and 39 mJ/m^2. The exposure to 25% RH gave results which were somewhere in between the results from the dry and the 75% RH conditions. No clear difference could be observed comparing the different dispersive component of the surface energies at the moist condition between the cycles 1 and 3. This indicates that there is none or very little change of the surface properties which would cause variations in the dispersive component of the surface energy because of humidity cycling up to 75% RH. There was also a smaller difference between the results obtained from the dry and moist states for the unmodified wood, which furthermore showed a somewhat lower dispersive component of the surface energy during 75% RH conditions. This trend was also observed for unmodified Norway spruce by Laiveniece and Morozovs (2014) using contact angle measurements, where it was noted that the dispersive part of the surface energy decreased with increased MC.

Little research has been carried out analyzing the heterogeneity profile of wood using IGC at different target fractional surface coverage. Table 4 shows a summary of IGC data presented in the literature where the dispersive component of the surface energy of some wood species has been determined. Previous studies are mostly based on a low solute concentration at infinite dilution giving only a single value of the dispersive component of the surface energy, compared with the measurements performed in this study, resulting in a distribution of the surface energy. Earlier work on analyzing the surface energy of spruce fibers showed values of 42 mJ/m^2 (Wålinder and Gardner 2000) and 41 mJ/m^2 (Cordeiro et al 2012) for the dispersive component. It should be remembered that variation in surface area and surface energy depends on several factors, such as the chemical composition, the growth environment, weather conditions, age of the tree, what part of

Table 4. A summary of dispersive component of the surface energy results of different wood components obtained from IGC measurements.

Type	Dispersive component of the surface energy (mJ/m^2)	Temperature (°C)	Size	Reference
Spruce	41	27	60 mesh	Cordeiro et al (2012)
Spruce (*Picea abies* Karst)	42	20	60 mesh	Wålinder and Gardner (2000)
Loblolly pine (*Pinus taeda* L.)	41	27	60/80 mesh	Tshabalala et al (1999)
White pine wood meal	34	50	20-60 mesh	Liu and Rials (1998)
Eastern white pine (*Pinus strobus*)	37	40	60/80 mesh	Tshabalala (1997)
Southern hardwood (mix)	37	35-55	40 mesh	Oporto et al (2011)
Wood flour (spruce and pine)	35	50	45 mesh	Kazayawoko et al (1997)
White birch (*Betula papyrifera*)	43	50	40-80 mesh	Kamdem et al (1993)

the tree that is used for analysis among others. Specimens from one tree cannot in all aspects be comparable with specimens from another tree. Even within the same tree different parts will show variations in properties and anatomy. In agreement with this study, others have shown results of higher dispersive component of the surface energies of thermally modified solid wood (modified to temperatures above 160°C) compared with that of unmodified wood. This has been reported in various studies using contact angle measurements; the Wilhelmy plate method (Gérardin et al 2007; Kutnar et al 2013) and the sessile drop method (Jennings et al 2006; Sansonetti et al 2013).

CONCLUSIONS

IGC at different surface coverage was used to characterize the surface energetics of unmodified and thermally modified wood. The results indicate that the dispersive component of the surface energy of the thermally modified wood have a more heterogeneous nature compared with that of the unmodified wood. The influence of exposure to higher RH conditions during the measurements resulted in small changes in the dispersive component of the surface energy.

The unmodified wood sample consisted of a higher fraction of wood components with distinctly shorter lengths (more fines) compared with the thermally modified samples. This was also visible in SEM micrographs. This observation was furthermore strengthened by the higher BET-specific surface area of the unmodified wood.

ACKNOWLEDGMENTS

Financial support from Stiftelsen Nils och Dorthi Troëdssons forskningsfond (Projektnr 793/12 Hydro-termo-mekanisk modifiering av trä), the Swedish Research Council Formas (project EnWoBio 2014-172), and EcoBuild Institute Excellence Centre are greatly acknowledged. The authors wish to thank Albert Hernandez Estrada and Lauri Rautkari (Aalto University, Finland) for scientific input and technical support.

REFERENCES

Anon (2003) ThermoWood Handbook. International ThermoWood Association. Helsinki, Finland. www.thermowood.fi (23 March 2015).

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60(2):309-319.

Bryne LE, Wålinder MEP (2010) Ageing of modified wood. Part I: Wetting properties of acetylated, furfuylated, and thermally modified wood. Holzforschung 64(3):295-304.

Cordeiro N, Ornelas M, Ashori A, Sheshmani S, Norouzi H (2012) Investigation on the surface properties of chemically modified natural fibers using inverse gas chromatography. Carbohyd Polym 87:2367-2375.

Csiszár E, Fekete E (2011) Microstructure and surface properties of fibrous and ground cellulosic substrates. Langmuir 27:8444-8450.

Davies MJ, Kerry TD, Seton L, Murphy MF, Gibbons P, Khoo J, Naderi M (2013) The crystal engineering of salbutamol sulphate via simulated pulmonary surfactant monolayers. Int J Pharm 446:34-45.

Dorris GM, Gray DG (1980) Adsorption of n-alkanes at zero surface coverage on cellulose paper and wood fibers. J Colloid Interface Sci 77(2):353-362.

Gamble JF, Leane M, Olusanmi D, Tobyn M, Šupuk E, Khoo J, Naderi M (2012) Surface energy analysis as a tool to probe the surface energy characteristics of micronized materials: A comparison with inverse gas chromatography. Int J Pharm 422(1-2):238-244.

Gérardin P, Petrič M, Petrissans M, Lambert J, Ehrhrardt JJ (2007) Evolution of wood surface free energy after heat treatment. Polym Degrad Stabil 92:653-657.

Hill CAS (2006) Wood modification: Chemical, thermal and other processes. Wiley, Chichester. 260 pp.

Hill CAS, Ramsay J, Keating B, Laine K, Rautkari L, Hughes M, Constant B (2012) The water vapour sorption properties of thermally modified and densified wood. J Mater Sci 47(7):3191-3197.

Jennings JD, Zink-Sharp A, Frazier CE, Kamke FA (2006) Properties of compression-densified wood, Part II: Surface energy. J Adhesion Sci Technol 20(4):335-344.

Kamdem DP, Bose SK, Luner P (1993) Inverse gas chromatography characterization of birch wood meal. Langmuir 9:3039-3044.

Karinkanta P, Illikainen M, Niinimäki J (2012) Pulverisation of dried and screened Norway spruce (*Picea abies*) sawdust in an air classifier mill. Biomass Bioenerg 44:96-106.

Kazayawoko M, Balatinecz JJ, Romansky M (1997) Thermodynamics of adsorption of *n*-alkanes on maleated wood fibers by inverse gas chromatography. J Colloid Interface Sci 190:408-415.

Kutnar A, Kričej B, Pavlič M, Petrič M (2013) Influence of treatment temperature on wettability of Norway spruce thermally modified in vacuum. J Adhesion Sci Technol 27(9):963-972.

Källbom S, Rautkari L, Johansson L-S, Wålinder MEP, Segerholm BK, Jones D, Laine K (2015) Surface chemical analysis and water vapour sorption of thermally modified wood exposed to increased relative humidity. In: Proceedings of the Eight European Conference on Wood Modification (ECWM8). M Hughes, L Rautkari, T Uimonen, and H Militz, eds. October 26-27, Helsinki, Finland (in press).

Lagana R, Dizhbite T, Telysheva G (2006) An influence of thermal treatment on surface properties of wood. Pages 289-291 *in* S Kurtjatko, J Kúdela, and R Lagana, eds. Proc Wood Structure and Properties '06, September 3-6, 2006, Sielnica, Slovakia. Technical University, Zvolen, Slovakia.

Laiveniece L, Morozovs A (2014) Penetration depth of adhesive depending on wood anatomical structure. Eng Rural Dev 13:204-209.

Lide DR. eds. (1995) CRC handbook of chemistry and physics, 76th edition. Pages 6-138, CRC Press, Boca Raton, FL.

Liu FP, Rials TG (1998) Relationship of wood surface energy to surface composition. Langmuir 14:536-541.

Lloyd DR, Ward TC, Schreiber HP. eds (1989) Inverse gas chromatography: Characterization of polymers and other materials. ACS Symposium Series 391, American Chemical Society, Washington, DC.

Matuana LM, Balatinecz JJ, Park CB, Woodhams RT (1999) Surface characteristics of chemically modified newsprint fibers determined by inverse gas chromatography. Wood Fiber Sci 31(2):116-127.

Naderi M, Khoo J, Acharya M, Burnett D (nd) Isotherm measurements for BET surface area calculations using inverse gas chromatography. iGC SEA Application Note 225. Surface Measurement Systems Ltd., London, UK.

Oporto GS, Gardner DJ, Kiziltas A, Neivandt DJ (2011) Understanding the affinity between components of wood–plastic composites from a surface energy perspective. J Adhesion Sci Technol 25(15):1785-1801.

Peterlin S, Planinšek O, Moutinho I, Ferreira P, Dolenc D (2010) Inverse gas chromatography analysis of spruce fibers with different lignin content. Cellulose 17(6):1095-1102.

Sansonetti E, Andersons B, Biziks V, Grinins J, Chirkova J (2013) Investigation of surface properties of hydrothermally modified soft deciduous wood. International Wood Prod J 4(2):122-127.

Schultz J, Lavielle L, Martin C (1987) The role of the interface in carbon fibre-epoxy composites. J Adhesion 23(1):45-60.

Segerholm BK, Vellekoop S, Wålinder MEP (2012) Process-related mechanical degradation of the wood component in a high-wood-content wood-plastic composites. Wood Fiber Sci 44(2):145-154.

Shi B, Wang Y, Jia L (2011) Comparison of Dorris-Gray and Schultz methods for the calculation of surface dispersive free energy by inverse gas chromatography. J Chromatogr A 1218:860-862.

Siddiqui N, Mills RH, Gardner DJ, Bousfield D (2011) Production and characterization of cellulose nanofibers from wood pulp. J Adhesion Sci Technol 25(6-7):709-721.

Tshabalala MA (1997) Determination of the acid-base characteristics of lignocellulosic surfaces by inverse gas chromatography. J Appl Polym Sci 65(5):1013-1020.

Tshabalala MA, Denes AR, Williams RS (1999) Correlation of water vapor adsorption behavior of wood with surface thermodynamic properties. J Appl Polym Sci 73(3):399-407.

Tze WTY, Wålinder MEP, Gardner DJ (2006) Inverse gas chromatography for studying interaction of materials used for cellulose fiber/polymer composites. J Adhesion Sci Technol 20(8):743-759.

Wiman M, Dienes D, Hansen MAT, van der Meulen T, Zacchi G, Lidén G (2012) Cellulose accessibility determines the rate of enzymatic hydrolysis of steam-pretreated spruce. Biores Technol 126:208-215.

Wålinder MEP, Gardner DJ (2000) Surface energetics of extracted and non-extracted spruce wood particles studied by inverse gas chromatography (IGC). Wood Fiber Sci 32(4):478-488.

Wålinder MEP, Gardner DJ (2002) Acid-base characterization of wood and selected thermoplastics. J Adhesion Sci Technol 16(12):1625-1649.

Ylä-Mäihäniemi PP, Heng JYY, Thielmann F, Williams DR (2008) Inverse gas chromatographic method for measuring the dispersive surface energy distribution for particulates. Langmuir 24:9551-9557.