Article

Comparison of Methodologies for Acid Buffering Capacity Determination—Empirical Verification of Models

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Abstract: Raw materials used in particleboard production may have different chemical properties as they have different origins, nature, and storage histories. One of the most important factors is the acidity of the wood which affects the process of bond line formation. Thus, determination of the acid buffering capacity (ABC) of a raw material helps to adjust the optimal amount of hardener in the adhesive. In the present study, three methods for pH-metric ABC determination in the presence of lignocellulosic material were compared. Models that correlate the hardener amount with the internal bonding of particleboards were built from the ABC results. The approach was tested on three materials of different acidity—pine, oak, and ammonia-treated oak. The developed models allowed the prediction of the optimal amount of hardener for the maximized internal bond of the boards. The experimental verification of the models showed a high convergence of the calculated and empirical results.

Keywords: wood acidity; buffering capacity; particleboard; internal bond; root-mean-square error (RMSE) model

1. Introduction

Particleboards produced from raw wood material are highly affected by the properties of the wood. It has been reported in the literature that changes in the raw material caused by the storage time, age of tree, location in stem, and origin may have a strong impact on its chemical properties, and, subsequently, on the mechanical and physical properties of wood-based materials [1–4]. These phenomena impose adjusting conditions on the process, especially in terms of the adhesive used and the amount of hardener.

The chemical properties of wood and wood extractives, such as pH value and buffering capacity, are considered prime factors in bonding [5]. The gel time of a urea–formaldehyde (UF) resin strongly depends on the acidity of the wood substrate which is associated with the content of the wood extractives [6,7]. The buffering capacity of a material is the sum of the buffering capacities of each individual acidic and basic component and the effect of the interactions among them [8].

Buffering capacity (β) is defined as

$$\beta = \frac{n_{acid}}{\Delta pH},$$

(1)

where n_{acid} is the number of acid moles that caused a change in the pH of a solution, expressed as ΔpH.

The buffering capacity value can be applied to woody material used in, for example, the particleboard industry. This can be the simplest and most accurate approach to describe the influence of a raw material on the adhesive gelation process without the need for deep insight into the chemical

properties or the origin of the feedstock. As a result, it is possible to find the most accurate amount of hardener so that the effects of the basic or acidic components of the wood are balanced. A commonly used methodology is based on the extraction of chips in boiling water and titration with acid solution or titration of the acetic acid liberated from the wood [9,10]. Most common protocols found in the literature are based on the titration of wood aqueous extracts to the end point at pH 3 [11,12] or pH 4 [13]. These values are the pH at the gel point for UF resins. However, it has been recently proved that such a protocol for the determination of the acid buffering capacity of wood material is not reliable [14]—not all compounds present in wood are soluble in hot water [15], although they still have an influence on the adhesive gelation process. This leads to the hypothesis that the buffering capacity determination cannot be based on the titration of wood extractives but must include the titration of a woody material suspension (chips or fibers). Several aspects investigated in a previous study revealed that the presence of lignocellulosic material in a titrated system was crucial [14]. More recently, another alternative approach to determine the ABC of woody material has been proposed [16]. A simplified method with a pre-acidification step has been shown to be more resistant to the influence of the measurement conditions and the operator.

Thus, the main aim of the present study was to compare three different methodologies for the determination of the acid buffering capacity (ABC) in the presence of woody material in the form of chips and to evaluate which one best describes the true acid buffering capacity of the wood. The obtained ABC values were correlated with the internal bond of particleboards, so that a protocol providing the most reliable results could be indicated.

In this paper, different methods of measuring acid buffering capacity were examined. Basic statistical methods, including linear regression and root-mean-square error (RMSE), were used to build and compare the models. Three materials of very different chemical characteristics were chosen for the experiments—oak, pine, and ammonia-treated oak.

2. Materials and Methods

2.1. Acid Buffering Capacity (ABC)—Methodology

Industrial pine (*Pinus silvestris* L.) chips were sorted on 0.15, 1.00, 3.00, and 6.00 mm mesh sieves and stored in a leakproof container at room temperature until the pH and buffering capacity determination. The overall procedure can be described as (1) chips cutting, (2) drying, (3) sorting, (4) suspending in water, and (5) titration. The latency time between the addition of water and the titration was 60 min. The titrant portions were added in one-minute intervals.

According to a previous study, four factors were defined as crucial—the presence of wood in the system, the chip suspension prepared at room temperature, 0.025 N (0.05 M) H_2SO_4 as a titrant, and the water-to-raw-material ratio of 200/20 (g/g) [16]. In order to determine the titration end point (pH 3 or 4), complete titrations were carried out to pH 3 (1–3 mm chips size; 60, 300, 1200, 2400, and 3600 s mixing time). For each series, three models were calculated—β for the complete set of data, $\beta_{>4}$ for the data from the titration starting point to the boundary of pH 4, and β_{4-3} for the data between pH 4 and pH 3. The resulting values were used to calculate the RMSE and the coefficient of variation for two models, $\beta\sim(\beta_{>4})$ and $\beta\sim(\beta_{>4}, \beta_{4-3})$.

The pH meter (Mettler Toledo SevenEasy), equipped with a glass pH ERH-12 electrode (Hydromet, Poland), was calibrated with a standardized buffer solution to pH 4.01 (Mettler-Toledo AG). Titrations to pH 3 or 4 were completed by the addition of 1.0 mL aliquots 0.025 N (0.05 M) H_2SO_4 in one-minute intervals. The mixing of the suspension was kept continuous (160 rpm) from the addition of 200 g of distilled water to 20 g of chips until the end of titration (orbital shaker SK-O330-PRO, Scilogex, LCC. Berlin, CT, USA). The time required to stabilize the pH of the suspension was determined by the observation of the pH drift for 60 min (continuous stirring without titration).

2.2. ABC Determination

Three methods for ABC determination were examined. For the first method (M1), 20 g dry chips were added to 200 g distilled water, stirred for 45 min, then titrated with 0.025 N H_2SO_4 until the end point at pH 4 [14]. The suspension was continuously mixed (160 rpm). For the second method (M2), 20 g dry chips were added to 250 g water pre-acidified to pH 2.6 with HCl (200 g water plus 50 g 0.05 M HCl), stirred for 45 min, and then the pH of the suspension was measured [16]. For the third method (M3), 20 g dry wood chips were suspended in 200 g distilled water and mixed (160 rpm) for 45 min. The pH drift was monitored constantly. The final pH was used for the ABC calculations. All determinations were performed at room temperature.

2.3. Particleboard Preparation

In this study, chips of pine (*Pinus silvestris* L., pH 5.0), oak (*Quercus robur* L., acidic, pH 4.10), and ammonia-treated oak (*Quercus robur* L., alkaline, pH 8.10) [17] were used as raw materials for particleboard manufacturing. Each material was cut into chips on a laboratory hammer mill with a sieve size of 5 mm (round holes). The chips were dried to 3–5% moisture content and manually sorted on 4 mm and 1 mm mesh sieves. Fractions stopped on the 1 mm sieve were used to prepare 16 mm thick, one-layer particleboards to the target density of 700 kg/m^3. The adhesive system was formulated as follows: commercial urea–formaldehyde resin (solids 65%, viscosity 230 mPas at 20 °C) and 20% ammonium chloride solution were used as a binder and hardener, respectively. The hardener was used in amounts 0, 1.1, 2.2, and 3.3 parts by weight per 50 parts of the UF resin (pbw) for pine; 0, 1.1, and 2.2 pbw for oak; and 2.2, 3.0, 4.8, and 34.3 pbw for ammonia-treated oak. The adhesive spread on the chips was 10% based on the solids. Panels of dimensions 300 mm × 300 mm × 16 mm were pressed at 180 °C under 1.0 MPa for 288 s (press factor: 18 s/mm). After conditioning for 7 days at normal conditions, the panels were cut into 50 mm × 50 mm samples and subjected to internal bond testing.

2.4. Internal Bond (IB) Tests

The measurement of the IB involves applying a tensile force perpendicular to the plane of the board. In practice, blocks bonded to the surface of the board enable a specimen to be mounted in the machine (Figure 1). Material fracture takes place in the core of the sample, most often in a plane parallel to the surface. The IB was tested on an Instron 3369 universal testing machine (Instron Ltd., Norwood, MA, USA).
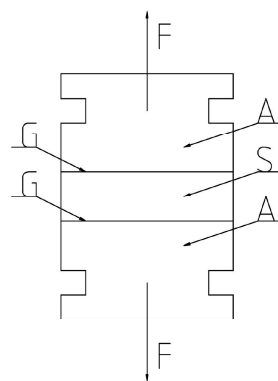
Figure 1. Tool for measuring perpendicular tensile strength in accordance with EN 319 (A—bonded block, S—particleboard specimen, G—glueline, and F—force).

2.5. Amount of Hardener

On the basis of the amount of hardener in the adhesive and the obtained IB values for pine and oak particleboards, the second-degree linear correlation between these factors was determined. The approach allowed the optimal amount of hardener to be found, indicated by the highest IB. For each

of the ABC determination methods (M1–M3), a linear correlation between the hardener amount and the ABC was established. The efficacy of each method based on these relationships was empirically verified on the particleboards made of the alkaline material—ammonia-treated oak—where the optimal amount of hardener was calculated from the models.

2.6. Statistical Analysis

For the theoretical analysis of the models with different titration limits (pH 3 or 4), the RMSE index was used. The root-mean-square error (RMSE) is a measure of the differences between the values predicted by a model and the values observed. It is defined by Equation (2):

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{n}}, \tag{2}$$

where n is the number of observations, $\hat{y}_i$ is the observation value calculated from the model, and y_i is the measured value.

3. Results and Discussion

3.1. ABC Methodology

The titration curves for different mixing times have very similar shapes, excluding the first few measurement points corresponding to 1–10 milliliters of titrant added. After reaching the boundary of pH 4, the curves are almost linear (Figure 2). A small displacement was caused by the different pH at the titration starting point. The data in Figure 2 also show the effect of the different latency time (suspension mixing prior to titration) that renders slight shifts in the curve position and, subsequently, may provide slightly different results—the final volume of the titrant added ranged between 70 mL and 82 mL.
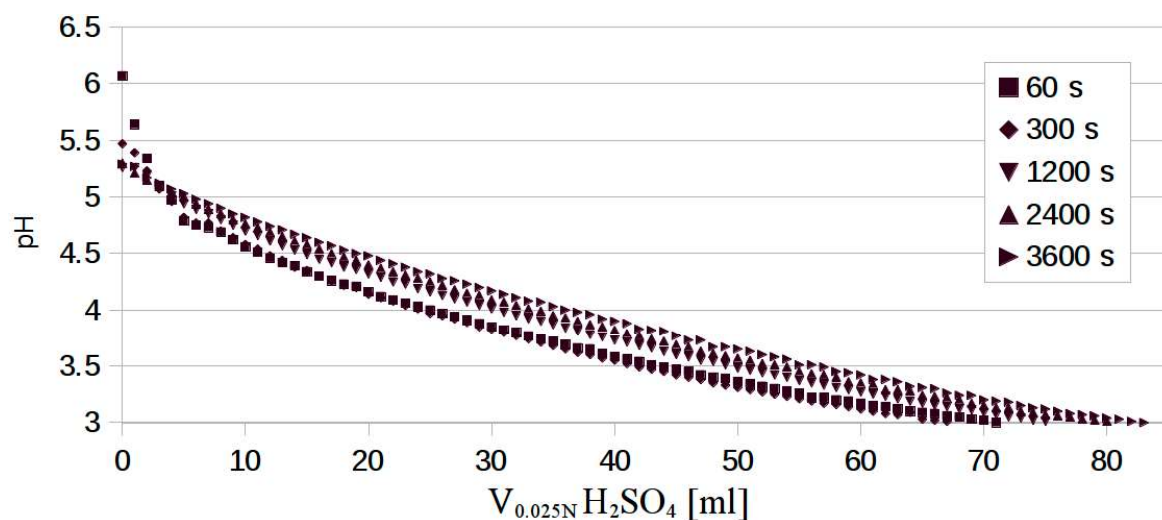
Figure 2. Pine chip suspension titration curves. Different initial latency times render a different system response. The curves can be assumed as linear under the boundary of pH 4.

The ABC values can be predicted by two models, $\beta \sim (\beta_{>4})$ and $\beta \sim (\beta_{>4}, \beta_{4-3})$, with a coefficient of determination as high as $R^2 = 0.99$. The RMSE values of 1.27 and 1.32 show differences between the predicted and observed values. The higher the RMSE value, the less accurate the model is. Thus, the $\beta \sim (\beta_{>4}, \beta_{4-3})$ model seems to be slightly inferior, though both can be considered correct [18]. These models confirm that the buffering capacity of chip suspension under the boundary of pH 4 becomes irrelevant for the study. Moreover, the "simplified" $\beta \sim (\beta_{>4})$ model exhibited a slightly smaller

coefficient of variation equal to 1.60 (Table 1). Hence, titration to pH 4 instead of pH 3 seems sufficient for a proper determination of the ABC of a woody material.

Table 1. Root-mean-square error (RMSE) and coefficient of variation (less = better) of linear regression models based on the same data.

Model	$\beta\sim(\beta_{>4})$	$\beta\sim(\beta_{>4}, \beta_{4-3})$
RMSE	1.27	1.32
Coefficient of variation (%)	1.60	1.67

As shown in Figure 3 and Table 2, particle size had a strong effect on the titration curves. Fractions of 0.15–1.0 mm provided an almost linear response, while the curves for 1.0–3.0 mm and 3.0–6.0 mm fractions became linear after some amount of time as the system required more time for equilibration. This indicates that the effective surface area of particles has a strong influence on the ABC measurement, as the equilibration rate is the highest for the smallest chips, as well as on the resultant ABC value. A high surface area in fine chips can be associated with an increased ABC. Thus, the data in Figure 3 indicate that it is not plausible to compare the ABCs found for different particle sizes. Surprisingly, the observation is contrary to reports by Pedieu et al. who found that particle size did not impact the buffering capacity [11]; however, it is coherent with the findings of Elias and Irle who recognized that particle size had an effect on wood acidity [1]. However, it is noteworthy that the authors used a classic method based on the analysis of aqueous extracts as described by Johns and Niazi [9].
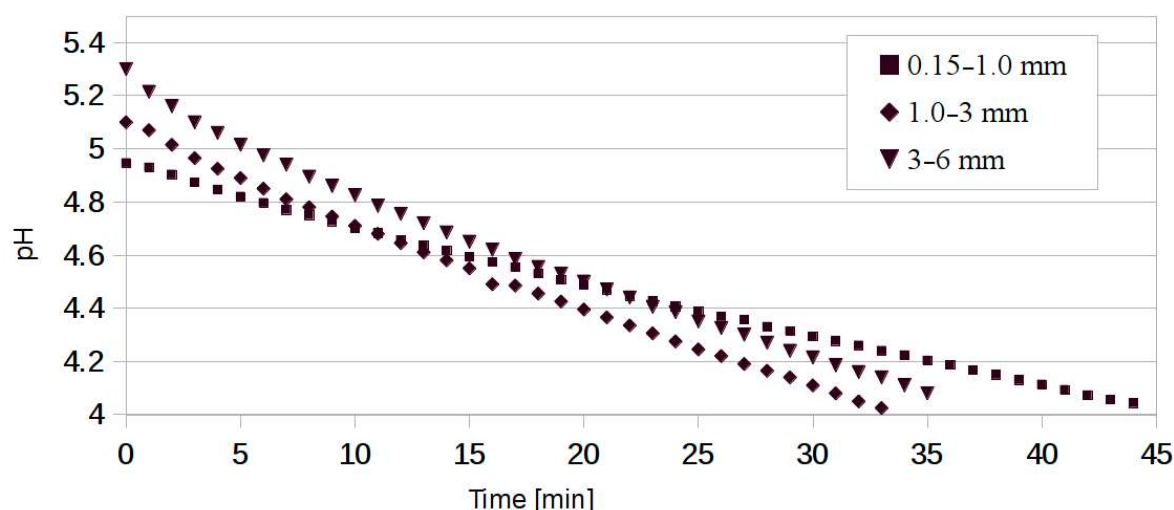
Figure 3. The effect of chip size on the pH in suspension (pine chips, 60 min latency time, end point pH 4).

Table 2. Acid buffering capacity (ABC) per gram of woody material.

Chip size (mm)	0.15–1.0	1.0–3.0	3.0–6.0
Initial pH	4.95	5.10	5.30
ABC per g wood	0.130	0.082	0.076

The data in Table 2 clearly indicate that the observed acid buffering capacity decreases as the particle size increases. The initial pH of the suspension—after 60 min—reveals that a slower penetration of water into the particles' structure causes a slower diffusion of the extractives into water, hindering acidification. The pH curves for the chip suspensions shown in Figure 4 are quite similar in shape. After some amount of time all three become almost stable and linear. The changes in pH are dynamic for the first 10 min and come from the equilibration in the system. This suggests that starting the titration of the suspension—when mixing for at least 30 min is avoided—leads to serious errors caused by a significant change in the initial pH which, subsequently, provides an incorrect ΔpH.
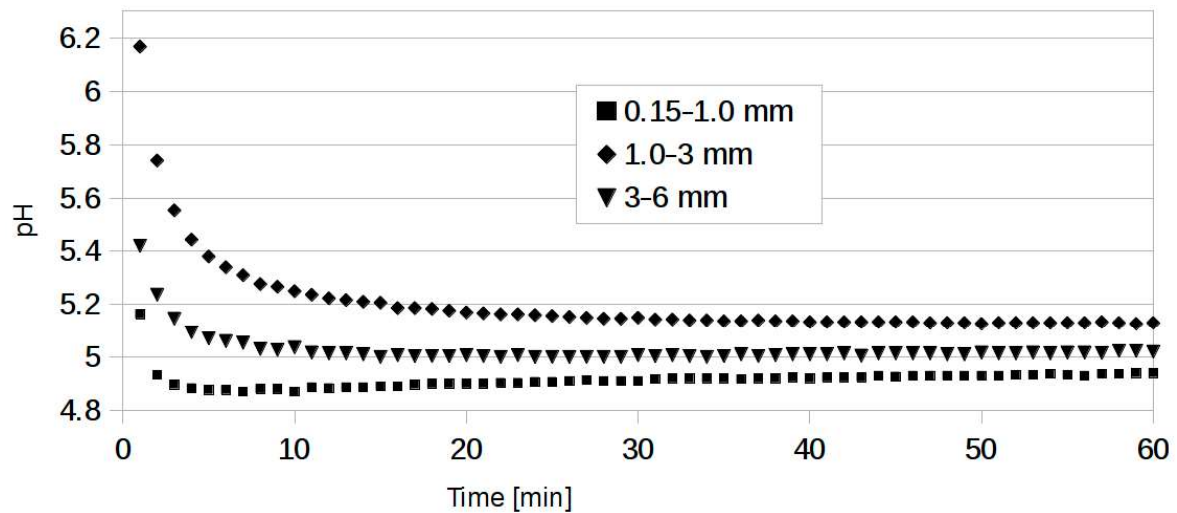
Figure 4. pH drift of pine chips in water suspension for different chip size.

According to previous investigations [14,16] and results shown in this work, it can be concluded that measuring the ABC for woody materials is a process susceptible to a number of factors (e.g., wood presence, chip size, and latency time) that affect the response of the system. None of the factors can be neglected as they have a significant influence on the measured value. Therefore, it is impossible to compare the ABC results from different methods as, for instance, different particle sizes give different ABC values even if the same determination method was used. Moreover, the presented models indicate that there is no need to titrate the chip suspension to below pH 4 as the difference in the final result is statistically insignificant. What must be considered, too, is the suspension mixing time as it is critical for the initial pH; therefore, the latency time to titration has been defined as at least 30 min.

3.2. Developed Protocol for ABC Determination

Regarding all the above, a protocol for ABC determination based on an original methodology including the presence of woody material (chips) in the titrated system has been defined. The developed protocol comprises four steps: (1) preparation of material, (2) chip suspension mixing until stabilized pH, (3) pH-metric titration of chip suspension, and (4) calculations. The presence of chips in the system and the avoidance of boiling are what makes the difference between the new method and the classic one involving aqueous extracts [9].

Thus, the procedure can be delineated as follows: 20 g chips of known moisture content and defined size range as used in a given particleboard production process are added to 200 g distilled water. (The amount of these can be changed as long as the weight ratio of 1:10 is kept.) The suspension needs to be mixed (160 rpm) at room temperature for 30 min or until a stabilized pH is reached. Do not filter the chips prior to titration. Then titrate the suspension with 0.025 N HCl or H_2SO_4 (1.0 mL titrant per minute) to pH 4. Use Equation (3) for the calculation of the acid buffering capacity per gram:

$$\beta_{pg} = \frac{\beta}{m} = \frac{\Delta n}{\Delta pH \times m} = \frac{\Delta V \times n}{\Delta pH \times m}, \tag{3}$$

where β_{pg} is the acid buffering capacity per gram, β is the acid buffering capacity, m is the dry chip mass (g), Δn is the amount of added acid, ΔpH is the resulting change in pH, ΔV is the titrant amount in 1.0 liter, and n is the mmol titrant per liter.

After the substitution of the fixed values, $m = 20$ g, $n = 50$ mmol/L, Equation (4) can be calculated:

$$\beta_{pg} = \frac{\Delta V \times n}{\Delta pH \times m} = \frac{\Delta V}{\Delta pH \times 2.5}, \tag{4}$$

3.3. ABC Effect

The tensile strength perpendicular to the surface of a board is considered a measure of the internal bond (IB) of the particleboard that is strongly correlated with the strength of the adhesive bond between the chips in a panel [18–22]. Therefore, the IB was involved in building a correlation with the ABC of the chips used as the raw material in the particleboard preparation. Boards made of pine and oak chips, with different amounts of hardener, were prepared. In the case of the pine panels (Table 3), the thickness of the P0 sample was apparently higher, while the structure on the cross-section was rough and loose. In contrast to P0, the structure in the cross-sections of P1 and P2 was more homogeneous and compact. In P3, where the hardener amount was beyond the optimum, a loose structure in the cross-section also occurred. This phenomenon results from the rapid curing of the adhesive with an excess of acidic hardener and subsequent deterioration of the bond line by acid upon storage [1,5]. In the case of the oak panels (Table 4), it was difficult to observe any significant differences in the structure or thickness of the three boards, regardless of the hardener amount. However, the IB results shown in Figure 5 clearly indicate that the maximum internal bonding is achieved with a hardener addition as small as 0.75 pbw. This is in accordance with the observations reported by Roffael and co-workers who found that highly acidic oak chips can be bonded with UF resins without any hardener at all [23].
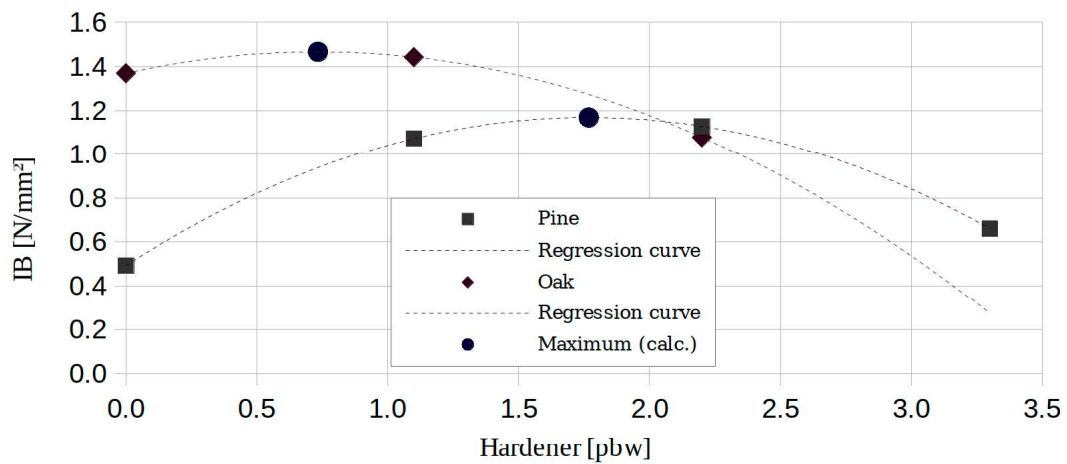
Figure 5. The correlation between the internal bond (IB) and the amount of added hardener in pine and oak particleboards.

Table 3. Sample appearance of the boards made of pine.

Sample	P0	P1	P2	P3
Hardener	0	1.1	2.2	3.3
Species		*Pinus silvestris* L.		
Surface				
Cross-section				

Table 4. Sample appearance of the boards made of oak.

Sample	Q0	Q1	Q2
Hardener	0	1.1	2.2
Species		*Quercus robur* L.	
Surface			
Cross-section			

As indicated in Figure 5, different amounts of hardener result in different IBs for particleboards. For both pine and oak particleboards, a second-degree linear correlation ($R^2 > 0.99$) between the IB and the hardener amount were found. Thus, the hardener amount for the highest IB could be predicted. The correlation of $IB = f$(hardener amount) calculated for the pine and oak particleboards can be used to predict the optimal amount of hardener for a material with a totally different chemical nature. Hence, the optimal hardener amount was calculated for the ammonia-treated oak (Table 5), taking into account the three different ABC measuring methods (M1–M3).

Table 5. ABC values for different materials, calculated amount of hardener for highest value of IB for different raw materials.

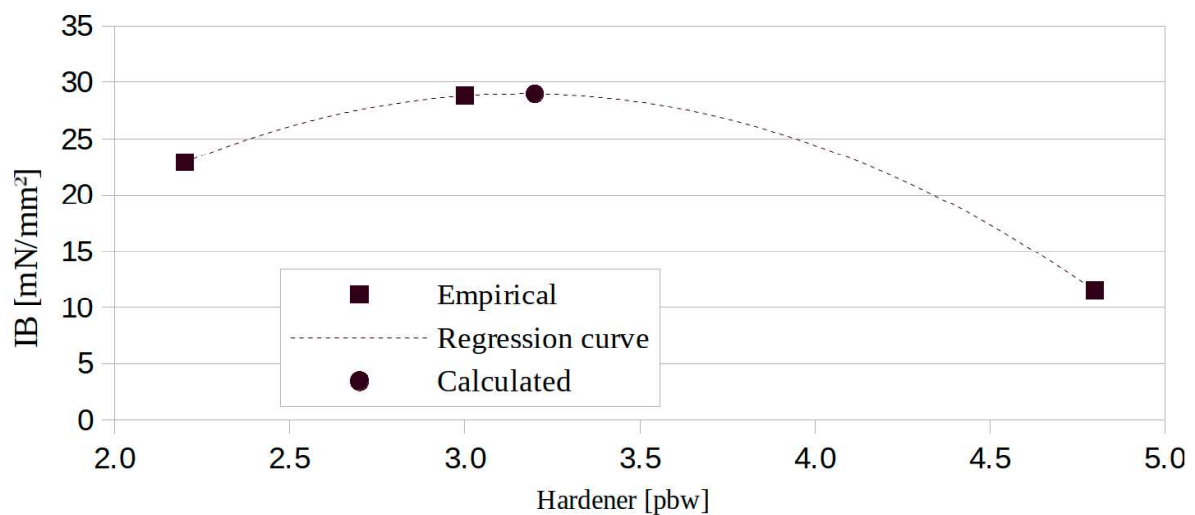| Method	Pine		Oak		Ammonia-Treated Oak	
	ABC	Hardener [1] [pbw]	ABC	Hardener [1] [pbw]	ABC	Hardener [2] [pbw]
M1	0.68		0.48		7.23	34.31
M2	0.89	0.73	0.23	1.77	2.82	4.81
M3	5.00		4.19		5.97	3.02

[1] calculated optimal amount—see Figure 5, [2] predicted, pbw—parts by weight.

Predicted amounts of hardener were used to produce panels from ammonia-treated oak chips (Table 5). In the case of ammonia-treated oak, the A4 variant, where the amount of hardener was far beyond the typical values, disintegrated during removal from the press (Table 6). It is worth noting that the thickness of specimens A1 and A2, as well as the quality of the chip bonding in the core, were clearly better than those in A3. The obtained results were used to calculate the optimal amount of hardener using a linear correlation of the second degree (Figure 6). It can be seen in Table 5 that the most accurate prediction was obtained from Method M3, i.e., 3.0 g hardener per 50 g resin against 3.2 g hardener per 50 g resin calculated from the model based on the empirical IBs. The results show that Methods M1 and M2 provided erroneous data, which proved them to be inapplicable in the described approach.

Table 6. Sample appearance of boards made from ammonia-treated oak.

Sample	A1	A2	A3	A4
Hardener (pbw)	2.2	3.0	4.8	34.3
Species	Ammonia-treated *Quercus robur* L.			
Surface				
Cross-section				

Figure 6. Empirical and predicted IB of particleboards made of ammonia-treated oak.

Regardless of the extremely low IBs observed for the ammonia-treated oak boards (0.012–0.028 N/mm^2) that make such material inapplicable for particleboards at all, the results obtained in this study proved that the developed procedure for ABC determination based on pH drift in chip suspension (M3) is reliable and applicable for woody material. It was shown that the methods based on either titration of the chip suspension (M1) or pre-acidification of the chip suspension (M2) provided less useful outcomes and, thus, were considered ineffective. It was possible to develop an efficient model based on the ABC of chips that allows the prediction of the amount of hardener for the maximized IB of a particleboard.

Keeping in mind that the conditions of raw material storage render changes in the raw material's chemical properties (e.g., acidity and extractive content) [1,24–26], a proper ABC determination may help in order to adjust the amount of hardener in the adhesive system to the acidity of the raw material (chips, fibers), so that an excessive acidification of the bond line is avoided and the mechanical properties of the boards are not lowered upon service.

4. Conclusions

Methodologies of acid buffering capacity determination found in the literature do not take into account the presence of wood and, thus, provide variable results that seem to be burdened with error. In this work, it was shown that a newly developed effective method of ABC determination for wood can be a basis for building mathematical models that correlate the hardener amount with the internal bonding of a board, so that the optimal amount of hardener can be predicted for the maximized mechanical properties of the board. Empirical verification of the models revealed that the method involving the monitoring of the pH drift in the chip suspension until equilibration exhibited a high convergence of the calculated and empirical results. Future investigations will be aimed at the verification of the methodology on the fibers used in fiberboard manufacturing as well as the transfer of the approach to industrial conditions.

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