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Article

Chitosan-Based Adhesive: Optimization of Tensile Shear Strength in Dry and Wet Conditions

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Abstract: Commercial adhesives present a high bond strength and water resistance, but they are considered non-healthier products. Chitosan can be considered as an interesting biosourced and biodegradable alternative, despite its low water resistance. Here, its wood bonding implementation and its tensile shear strength in dry and wet conditions were investigated depending on its structural characteristics. Firstly, the spread rate, open assembly time, drying pressure, drying temperature, and drying time have been determined for two chitosans of European pine double lap specimens. An adhesive solution spread rate of 1000 g·m⁻², an open assembly time of 10 min, and a pressure temperature of 55 °C for 105 min led to a bond strength of 2.82 MPa. Secondly, a comparison between a high molecular weight/low deacetylation degree chitosan and a lower molecular weight/higher deacetylation degree chitosan was conducted. Tests were conducted with beech simple lap specimens in accordance with the implementation conditions and the conditioning treatments in wet and dry environments required for thermoplastic wood adhesive standards used in non-structural applications (EN 204 and EN 205). The results clearly revealed the dependence of adhesive properties and water resistance on the structural features of chitosans (molecular weight and deacetylation degree), explaining the heterogeneity of results published notably in this field.

Keywords: adhesive; chitosan; mechanical properties; water resistance

1. Introduction

Commercial adhesives for wood-based panels are commonly formaldehyde-based adhesives regrouped in various sub-families, namely: phenyl formaldehyde (PF), melamine formaldehyde (MF), urea formaldehyde (UF), and resorcinol formaldehyde (RF) [1]. Even if they present a high bond strength and water resistance, their volatile organic compounds make them less and less attractive. The market demands more natural or renewable and healthier adhesives. Biopolymer-based adhesives are often expensive and exhibit a poor water resistance [1]. One solution to this is mixing formaldehyde-based adhesives with lignin as a substitution, such as a phenol formaldehyde, until a 50 wt.% for kraft lignin and 50 wt.% for eucalyptus bark lignin are reached [2–4]. Waterborne adhesive such as poly(vinylacetate) present a good mechanical performance in dry conditions, but do not

provide resistance in a humid atmosphere. Peruzzo et al. have shown that it is possible to increase mechanical properties in humid conditions with the incorporation of nanoclay, but without the obtained the requirements of the European standard EN 204 for non-structural wood adhesive [5,6]. Norström et al. obtained the same behavior with locust bean gum dispersion [7]. Protein-, tannin-, and polysaccharides-based adhesives can be used as wood adhesives [8].

Considering polysaccharides, chitosan has been the subject of several studies. Chitosan is a heteropolymer, composed of 2-acetamido-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-D-glucopyranose, obtained after the alkaline deacetylation of chitin from crustaceans, insects, and fungi [9]. Even if acidic solutions of chitosan, alone or mixed with other polysaccharidic components such as Konjac glucomannan or xanthan, can be used as adhesives, they present poor bonding properties in a wet environment [10–14]. Chitosans constitute an interesting group of adhesive polysaccharides, as their numerous hydroxyl and amine groups can interact with a lot of chemical functions. It is well-known that because amine ($-NH_2$) with a pKa of 6.5 functions at an acidic pH (<5), the global positive charge of the chitosan ($R-NH_3^+$) could interact more strongly with the surface via electrostatic interactions, which would increase the stability of the polycationic chitosan structure at the interfacial membrane [9]. Consequently, the adhesive properties of chitosan could be correlated to the following: (1) the acetylation degree, the higher the acetylation, the lower the distribution of $R-NH_3^+$ (net positive charge) and, consequently, the adhesive properties will be reduced, and (2) the molecular weight, the higher the molecular weight, the higher the distribution of positive charge in the of chitosan and, consequently, the adhesive properties will increase. Chen and Hwa have also shown that the tensile strength and tensile elongation of films made with high molecular weight chitosans are higher than those obtained with low molecular weight ones [15]. However, the same authors have also shown that chitosan films with a high deacetylation degree achieve better water barrier properties and tensile strengths than those obtained with a low deacetylation degree chitosan [15]. To increase the water resistance of chitosan formulations, Mati-Baouche et al. suggested substituting the amine functions of chitosan through alkyl groups [16]. These alkyl-chitosans (with substitution degrees of 10 and 15%) had sufficient adhesive properties on wood and exhibited better water resistance compared with native ones. Nonetheless, the substitution of amine functions led to weak strength resistance. Indeed, Noto et al. have shown that the amino groups positively influence the chitosan adhesive strength [17]. The low performance of chitosan-based adhesives in wet environments can be mitigated by combining them with other biopolymers-based adhesives and chemical modifications in order to increase their water resistance; however, this would significantly increase their costs [13]. If bio-based adhesives have a good strength resistance only under dry conditions, few will be able to withstand low water presence and almost none will be suitable in the case of contact with cold or hot waters.

Umemura et al. have shown that the optimal pressure and temperature conditions for a high bonding efficiency with chitosan solutions were 0.98 MPa and 120 °C, respectively, and observed a maximum of chitosan bond adhesive of around $16 \text{ g}\cdot\text{m}^{-2}$ in a solid state [18]. The aim of this study was to obtain a chitosan-based adhesive resistant to wet conditions and also to validate the impacts of molecular weights and deacetylation degrees on the adhesive performances of chitosan. Thus, implementation conditions have been explored for a high molecular weight/low deacetylation degree chitosan. Next, two different chitosans (different molecular weights and deacetylation degrees) were carried out according to the best implementation conditions and were tested according to European standard EN 204 [6] in order to evaluate the water resistance adhesion.

2. Materials and Methods

2.1. Adhesives Preparation

Two chitosans (CSs) from the chitin of shrimp shells, CSA (Sigma C 3646) and CSB (France-Chitin, n°342), characterized for their physico-chemical parameters, were used

(Table 1). CSA and CSB were solubilized at room temperature for 2 h while stirring in 1% acetic acid (*v/v*) (Sigma Aldrich, St Louis, Missouri, USA 98.9%, N°33209). The concentration was 4% (*w/v*) for CSA and 6% (*w/v*) for CSB. Glycerol (Acros organics 99%) was added with a concentration of 1% (*v/v*). The pHs were between 4.8 and 5.15.

Table 1. Weight average molecular weights (Mw), number average molecular weights (Mn), polydispersity index (Đ), and deacetylation degree (DD) of CSA and CSB chitosans (CSs).

	Mw (g·mol ⁻¹)	Mn (g·mol ⁻¹)	Đ	DD (%)	References
CSA	3.038×10^5	2.251×10^5	1.35	≥75	[19]
CSB	9.842×10^4	8.671×10^4	1.135	90	[20]

2.2. Double Lap Specimens' Preparation

To optimize the conditions of the CS adhesive implementation, double lap specimens were carried out according to the protocol used by Patel et al. [19] and Mati-Baouche et al. [16]. Each specimen was composed of four plates of European pine (*Pinus pinaster*), as represented in Figure 1. The plates dimensions were 150 × 18 × 5 mm (length × width × thickness) and the bonding area was 50 × 18 mm. The CSA-based adhesive was spread with a spatula on the two faces. The specimens were dried in an oven (55 °C) under a pressure of 0.01 MPa.

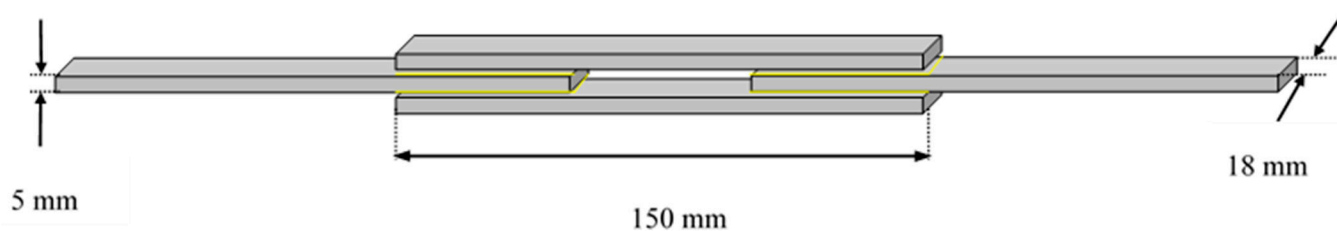


Figure 1. View of double lap specimens. Adhesive thickness of 0.1 mm.

Six implementation parameters were considered, namely: spread rate, open assembly time, drying pressure, drying temperature, and drying time. Drying was done at 0.01 MPa in an oven. Drying time is highly dependent on temperature. It was chosen in order to couple drying time and temperature in one parameter. With the pressure being low, the pressed period was not taken into account. We used five levels per parameter (Table 2).

Table 2. Adhesive processing conditions for the double lap specimens.

	Level 1	Level 2	Level 3	Level 4	Level 5
Wet Spread rate (solid spread rate) (g·m ⁻²)	200 (9.99)	326 (16.29)	500 (24.98)	710 (35.48)	1000 (49.97)
Open assembly time (min)	0	5	10	15	20
Drying temperature (°C)	18	39	55	76	92
Drying time (min)	30	60	105	150	180

2.3. Tensile Shear Specimens' Preparation

The realization of the tensile shear specimens was based on the European Standard EN 205 conditions [21]. Two panels of beech (*Fagrus sylvatica* L.) with a 7 mm thickness were cut across the direction of the grains to a length of 300 mm and a width of 140 mm. The condition of the angle between the growth rings and the surface was respected, i.e., between 30° and 90°. The two types of chitosan were tested. The adhesive was spread with

a spatula. The adhesive processing conditions are summarized in Table 3. After 7 days in a standard atmosphere, the assemblies were cut to obtain tensile shear specimens, as described in Figure 2.

Table 3. Adhesive processing conditions for the tensile shear specimens.

Adhesive spread rate	$500 \text{ g}\cdot\text{m}^{-2}$
Open assembly time	120 s
Closed assembly time	180 s
Pressing temperature	$55 \text{ }^{\circ}\text{C}$
Pressing pressure	$0.7 \text{ N}\cdot\text{mm}^{-2}$
Pressing time	2 h

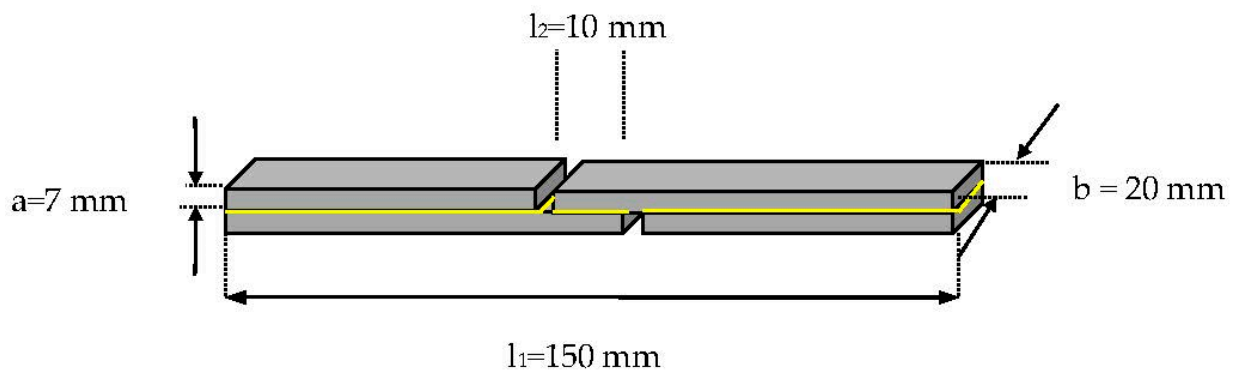


Figure 2. View of tensile shear specimens. Adhesive thickness of 0.1 mm.

2.4. Conditioning Treatments

Wood adhesives for non-structural applications are classified into durability classes D1 to D4, according to European standard EN 204 [6]. Classes are based on the dry and wet strengths, which are measured under specified conditions after various conditioning treatments. All of the classes correspond to an interior climatic condition. D1 is associated with a condition where the moisture content of the wood does not exceed 15%. D2 corresponds to occasional short-term exposure to running or condensed water and/or to occasional high humidity, provided the moisture content of the wood does not exceed 18%. The case of frequent short-term exposure to running or condensed water and/or to heavy exposure to a high humidity is associated with D3. Woods subjected to frequent long-term exposure to running or condensed water correspond to D4. D3 and D4 are associated with exterior climatic conditions, provided that the wood is not exposed to weather (D3) or is exposed to weather, but with surface coating protection (D4). An adhesive belongs to one of the classes if it reaches the minimum values of strength in the conditioning and measurement conditions summarized Table 4.

Table 4. Minimum values of adhesive strength according to European Standard EN204. Standard atmosphere: 20 ± 2 °C and $65 \pm 5\%$ relative humidity; – no test required.

Sequence Number		Adhesive Strength in MPa Durability Classes			
Sequence Number	Durations and Conditions	D1	D2	D3	D4
1	7 days in standard atmosphere	≥ 10	≥ 10	≥ 10	≥ 10
2	7 days in standard atmosphere	–	≥ 8	–	–
	3 h in water at (20 ± 5) °C				
3	7 days in standard atmosphere	–	–	≥ 2	≥ 4
	4 days in water at (20 ± 5) °C				
4	7 days in standard atmosphere	–	–	≥ 8	–
	4 days in water at (20 ± 5) °C				
5	7 days in standard atmosphere	–	–	–	≥ 4
	6 h in boiling water				
	3 h in water at (20 ± 5) °C				

2.5. Mechanical Characterizations

The mechanical characterization of the double lap specimens was performed using a Zwick Troell testing machine (Zwick GmbH and Co, Ulm, Germany). The crosshead speed was $3 \text{ mm} \cdot \text{min}^{-1}$ and the force versus displacement was recorded according to Mati-Baouche et al. [16] and Patel et al. [19]. The bond strength was deduced using the following Equation (1):

$$\sigma = F/2A, \quad (1)$$

where F is the applied maximum force (N) and A is the lap area (mm^2).

The mechanical characterization of the tensile shear specimen was performed using the same testing machine. The crosshead speed was $50 \text{ mm} \cdot \text{min}^{-1}$ and the force versus displacement was recorded according to the European Standards EN204 [6]. The shear strength was calculated using Equation (2):

$$\sigma = F/l_2b, \quad (2)$$

where F is the applied maximum force (N), l_2 is the length of the bonded test surface (mm), and b is the width of the bonded test surface (mm).

2.6. Rheological Measurements

Apparent viscosity measurements were carried out using parallel plate geometry with a stress-controlled rheometer AR-G2 (TA Instruments, France), equipped with a Peltier temperature control system. Temperatures were set at 18 °C and 55 °C, and viscosity was monitored in the range of shear rate (10^{-2} – 10^3 s^{-1}). Viscosity data were collected and analyzed using the Rheology Advance software package and the Williamson model (3) [22].

$$\eta = \frac{\eta_0}{1 + (k\dot{\gamma})^n} \quad (3)$$

where η is the apparent viscosity (Pa·s), η_0 is the zero-shear viscosity (Pa·s), k is the time constant (s), $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the rate constant (dimensionless).

3. Results

3.1. Double Lap Specimen Characterization

For all of the specimens made with a CSA adhesive, the thickness of adhesive strips was lower than 0.1 mm. The bond strengths obtained for all of the adhesive processing conditions are summarized in Table 5. The optimum implementation conditions were

for a spread rate of $1000 \text{ g}\cdot\text{m}^{-2}$ (wet adhesive, equivalent to $49.97 \text{ g}\cdot\text{m}^{-2}$ of a solid-state adhesive), an open assembly time of 10 min, and a pressure temperature of $55 \text{ }^\circ\text{C}$ during 105 min (Table 5).

Table 5. Bond strength results for the CSA-based adhesive double lap specimens. The brackets indicate the open assembly time (min)/pressure time (min).

Wet Spread Rate (Dry Spread Rate)	Temperature				
	18 °C	39 °C	55 °C	76 °C	92 °C
200 $\text{g}\cdot\text{m}^{-2}$ (9.99 $\text{g}\cdot\text{m}^{-2}$)			0.61 MPa (10/105)		
326 $\text{g}\cdot\text{m}^{-2}$ (16.29 $\text{g}\cdot\text{m}^{-2}$)		0.98 MPa (5/150) 1.03 MPa (15/150)		1.82 MPa (5/60) 1.14 MPa (15/60)	
500 $\text{g}\cdot\text{m}^{-2}$ (24.98 $\text{g}\cdot\text{m}^{-2}$)	1.83 MPa (10/180)		2.17 MPa (0/105) 1.91 MPa (10/105) 1.11 MPa (20/105)		1.70 MPa (10/30)
710 $\text{g}\cdot\text{m}^{-2}$ (35.48 $\text{g}\cdot\text{m}^{-2}$)		2.38 MPa (5/150) 1.62 MPa (15/150)		2.32 MPa (5/60) 2.08 MPa (15/60)	
1000 $\text{g}\cdot\text{m}^{-2}$ (49.97 $\text{g}\cdot\text{m}^{-2}$)			2.84 MPa (10/105)		

To confirm the maximum spread rate, tests were realized in the following conditions: 10 min of open assembly time and $55 \text{ }^\circ\text{C}$ of pressure temperature for 105 min (Figure 3). A spread rate that is too low leads to poor adhesion, but also a spread rate that is too high leads to poor bonding.

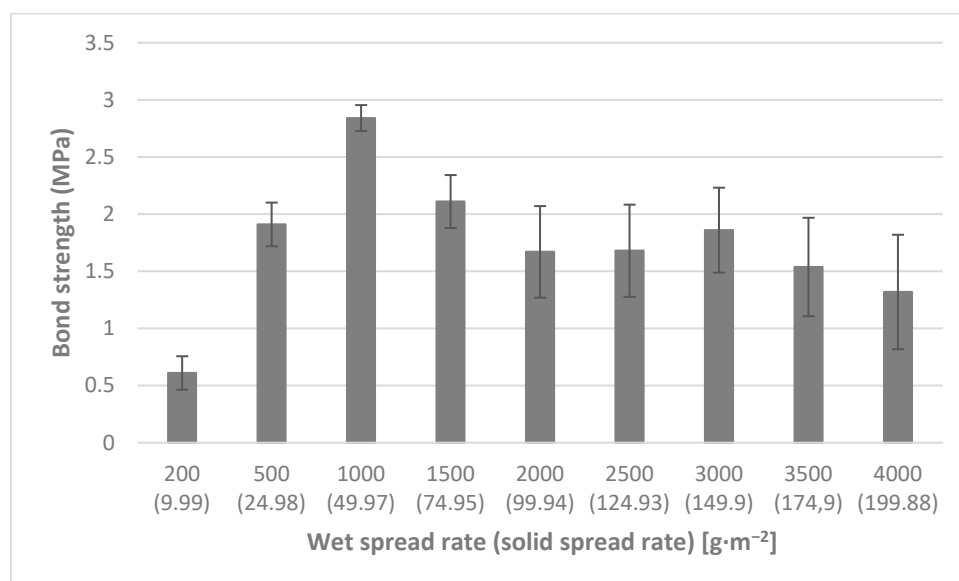


Figure 3. Influence of the spread rate on bond strength (10 min of drying time, $55 \text{ }^\circ\text{C}$ of drying temperature for 105 min) for the CSA adhesive.

A concentration of 4% (*w/v*) for the CSA-based adhesive was chosen according to results of the Mati-Baouche et al. study [14]. In order to develop the low-cost chitosan-based adhesive, CSB chitosan, a low-grade industrial chitosan was chosen. Its optimum concentration was evaluated with the optimum adhesive conditions as described in Section 3.1, using double lap specimens (Table 6). As would be expected, the best value was obtained for higher concentrations compared with CSA. However, because a concentration of 8% (*w/v*) would make the adhesive difficult to implement, a CSB concentration of 6% (*w/v*) was considered to be a good compromise between the mechanical properties, implementation, and cost. Indeed, the 6%CSB (*w/v*) bond strength is close to the 4% CSA (*w/v*) one. A cost estimate was made based on the raw material purchase prices. The CSB adhesive cost was close to 1 €/m² (1 €/kg), while the CSA adhesive was up to 32 €/m² (32 €/kg). A typical wood adhesive binder such as poly(vinylacetate) is estimated to cost 2 €/kg [23].

Table 6. Bond strength results for CSB-based adhesive double lap specimens as a function of the chitosan concentration (wet spread rate: 1000 g·m⁻², 10 min of open assembly time, and temperature of 55 °C for 105 min).

Formulation	Bond Strength (MPa)
CSB 4% (<i>w/v</i>) + acetic acid 1% + glycerol 1%	1.92
CSB 6% (<i>w/v</i>) + acetic acid 1% + glycerol 1%	2.82
CSB 8% (<i>w/v</i>) + acetic acid 1% + glycerol 1%	3.57

3.2. Determination of Chitosan-Based Adhesive Classification for Non-Structural Applications

Tests were performed according to conditioning treatments of European Standard EN 204 [6] using tensile shear specimens with CSA- and CSB-based adhesives and with the optimum adhesive conditions identified in Section 3.1, i.e., a spread rate of 1000 g·m⁻², 10 min of open assembly time, and 55 °C of pressure temperature for 105 min (Table 7). Sequence 3 corresponds to a test in wet conditions, while sequence 4 corresponds to a test after 7 days of drying. During their passage in water, the chitosans swelled, which led to a drastic decrease in their mechanical properties. After drying, the chitosan adhesives recovered almost all of their mechanical properties. Under dry conditions (sequence numbers 1, 2, and 4), the CSA-based adhesive presents better mechanical performances than the CSB-based one.

Table 7. Shear strength of CSA- and CSB-based adhesive after European Standard EN 204 duration and conditions treatments.

Sequence Number	Duration and Conditions	Shear Strength (MPa)	
		CSA-Based Adhesive	CSB-Based Adhesive
1	7 days in standard atmosphere	14.48 ± 1.52	13.41 ± 0.83
2	7 days in standard atmosphere 3 h in water at (20 ± 5) °C 7 days in standard atmosphere	14.75 ± 1.53	13.72 ± 0.61
3	7 days in standard atmosphere 4 days in water at (20 ± 5) °C	1.11 ± 0.27	2.15 ± 0.62
4	7 days in standard atmosphere 4 days in water at (20 ± 5) °C 7 days in standard atmosphere	11.97 ± 4.61	10.74 ± 3.18

3.3. Rheology Properties

The rheological behavior of the chitosan solutions provides important information in the field of adhesives. The viscosity of chitosan solutions is linked to their deacetylation degrees and pHs, two parameters influencing the charge density [24]. Figure 4 represents

the variation of the viscosity as a function of the shear rates and temperatures for CSA and CSB solutions. All of the solutions presented a shear thinning behavior and the curves exhibited a Newtonian plateau at low shear rates ($\dot{\gamma} < 0.1 \text{ s}^{-1}$). The η_0 obtained by the Williamson model for CSA solutions at 18 and 25 °C were 2159 (K value: 13.74 and n value: n.d.) and 3632 (K value: 129.6 and n value: 0.93), respectively, whereas those of CSB were $5.26 \times 10^5 \text{ Pa}\cdot\text{s}$ (K value: 3309 s and n value: 0.88) and 1817 Pa·s (K value: 35.47 s and n value: 0.87), respectively, for the same temperatures. At a high shear, the viscosity decreased as the shear rate increased following a power law. The shear tends to separate the polymer chains and therefore the viscosity decreases [25,26].

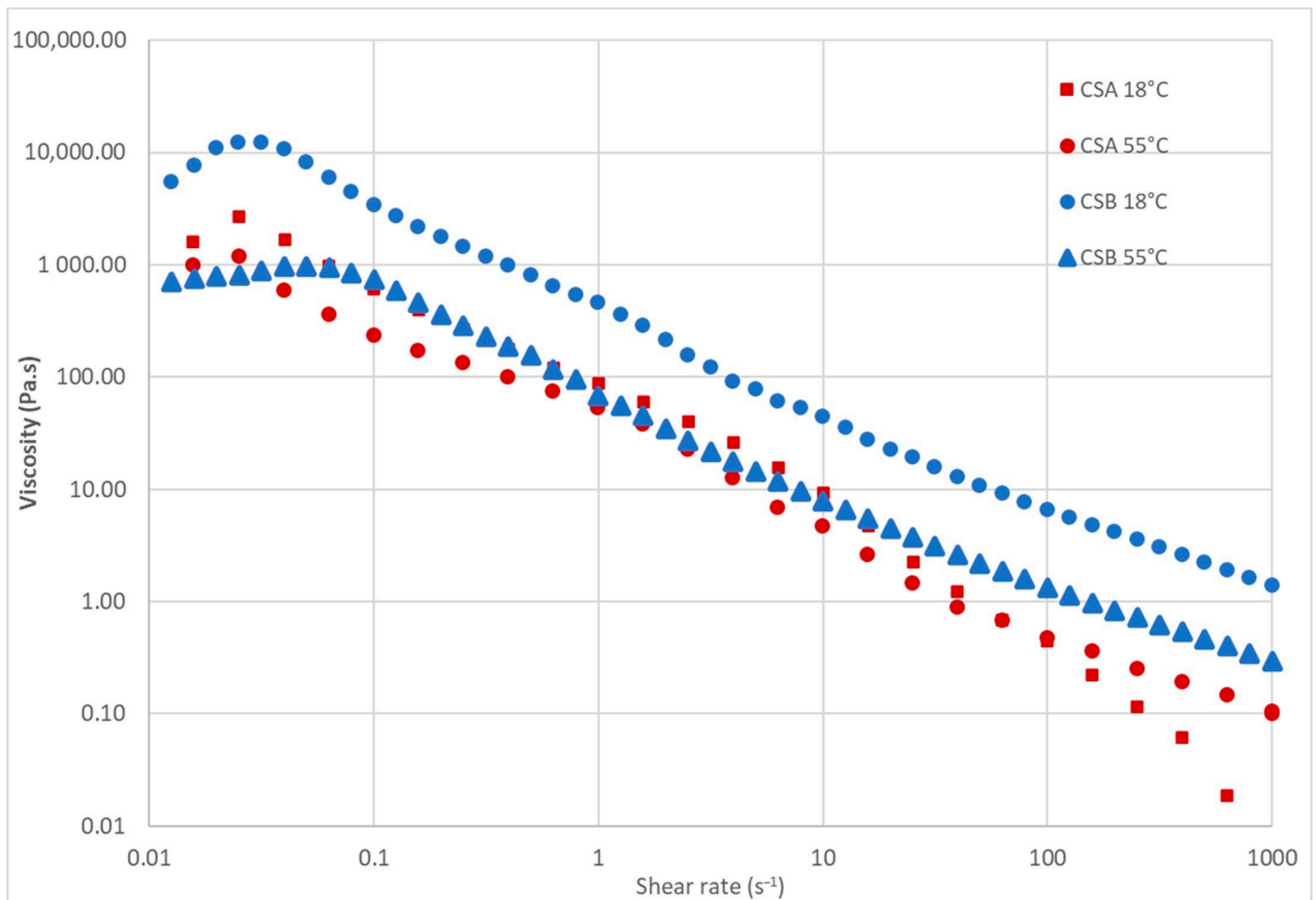


Figure 4. Influence of the shear rate on the rheological curves of the CSA and CSB solutions at 18 °C and 55 °C.

4. Discussion

In this study, the effect of the drying time and drying temperature on the mechanical properties of chitosan-based adhesives were linked. The increase in drying temperature associated with a decrease in drying time led to a decrease in the mechanical properties. For a drying pressure of 0.7 MPa, a drying temperature/time pair of 55 °C/105 min was the best compromise. This phenomenon can be explained considering the open assembly time. Indeed, it was necessary to wait the absorption of adhesive by the porosity of wood to obtain the optimal interaction between the adherent and the adhesive. Logically, there was a compromise between the temperature and time required to dry the adhesive without stop its diffusion in wood. Moreover, if the open assembly time was too long, the adhesive dried, thus reducing its adhesive capacity. The spread rate also has an influence on the bond adhesive. Marra estimated that the interface can be seen as a succession of several layers: pure adhesive phase/adhesive boundary layer/interface between the

boundary layer and the substrate/wood cells modified by the boundary process [27]. The interface between the boundary layer and wood substrate constitutes the adhesion mechanism (mechanical interlocking, covalent bonding, or secondary chemical bonds). A boundary layer is formed by the gradient of the adhesive composition, especially with a plasticizer [28]. No information about the thickness of the boundary layer was obtained, but it can be assumed that for a high spread rate, the bulk adhesive is predominant, while for a lower value of spread rate, the boundary layer is the main factor increasing the bonding strength. Here, a spread rate of $49.97 \text{ g}\cdot\text{m}^{-2}$ for the solid-state adhesive led to the optimal bond strength for CSA. This result was not really comparable with some other results reported in the literature, such as that of Umemura et al. (2005), as they used a chitosan with a lower molecular weight and at a lower concentration, thus resulting in a lower spread rate ($16 \text{ g}\cdot\text{m}^{-2}$) [18]. An increase in the spread rate is not really noteworthy as the chitosan concentration is the most significant factor influencing the spread rate, as higher concentrations lead to a viscous adhesive, which is difficult to spread, whereas it is the inverse for lower concentrated solutions. Despite an increase of the viscosity for the CSB solutions, the chitosan-based adhesives (CSA and CSB) presented a viscoelastic behavior at the concentrations used, and as the adhesive implementation was done with a spatula, it was possible to obtain adhesive layers with a similar thickness.

The differences of adhesives' properties and performances can be explained by the difference in the molecular weights between CSA and CSB. Under dry conditions, all of the failures occurred in the wood. The CSA- and CSB-based adhesives presented a shear strength superior to the minimal values according EN204 for conditioning sequences 1, 2, and 4, of 10 MPa and 8 MPa, respectively. CSA- and CSB-based adhesive can be considered to belong to D1 and D2 durability class adhesives (interior climatic condition with occasional short-term exposure to running or condensed water). To belong to D3, the shear strength of an adhesive must be greater than 8 MPa for conditioning treatment 4 and greater than 2 MPa for conditioning treatment 3 (Table 6). The CSA-based adhesive did not achieve these two conditions, unlike CSB. The higher deacetylation degree and higher chitosan concentration could explain the better results of the CSB-based adhesive, but the molecular weight influenced the adhesion at the same time. Indeed, the high deacetylated degree chitosan had better water barrier properties than the low deacetylated one, even if its molecular weight was lower. This phenomenon of moisture absorption limitation of highly deacetylated chitosans can be explained by their swelling index, depending on their deacetylation degree. Indeed, it is well known in literature that even if the increase in the molecular weight of chitosans is concomitant to an increase in its tensile strength and moisture absorption, the increase of their deacetylation degree increases or decreases their tensile strength, depending on their molecular weight, but in all cases it decreases their moisture absorption capacities [29,30]. There were more crystalline regions in the highly deacetylated chitosans compared with the chitosans with low deacetylated degrees exhibiting a higher amorphous character, which interacted easier with water. So, for relatively similar molecular weights, highly deacetylated chitosans should be preferred for chitosan-based adhesive formulations when considering their water resistance and tensile strengths.

5. Conclusions

Optimal implantation conditions have been obtained with a high molecular weight/low deacetylation degree chitosan (CSA) with a spread rate of $1000 \text{ g}\cdot\text{m}^{-2}$, an open assembly time of 10 min, and a pressure temperature of $55 \text{ }^\circ\text{C}$ for 105 min. The CSA performance in dry conditions was compared with a low molecular weight/high deacetylation degree chitosan (CSB) according to European Standard EN 204. They can be classified as D2 and D3 adhesives, respectively. These results revealed the complexity of adhesion understanding with biopolymers. Indeed, natural polysaccharides are complex mixtures of macromolecules with an average molecular weight but a variable range of molecular weights, depending on the polydispersity index. In these mixtures, even if all macro-

molecules have the same backbone, they can have some specific structural features, leading to the heterogeneity of structure–functions relationships. For chitosan, the sole deacetylation degree and the localization of deacetylated units in the backbone may be very heterogeneous, leading to an average deacetylation degree not really representative of each molecule structure. Thus, in these complex mixtures, only a part of the macromolecules can sometimes develop specific physico-chemical properties. It is then a little naïve to limit the adhesive properties of chitosans to their molecular weights or deacetylation degrees, as no standards considering only one parameter are available. So, the development of industrial solutions for applications of chitosan as adhesives will be strongly dependent to the ability of suppliers to provide constant quality raw materials.

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