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Shear Refinement of Formaldehyde-Free Corn Starch and Mimosa Tannin (*Acacia mearnsii*) Wood Adhesives

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Abstract

The aim of this work was to reduce the viscosity of formaldehyde-free corn starch–mimosa tannin wood adhesives, without adversely affecting the mechanical properties of the product. The reduction of viscosity was achieved using shear refinement. The study focused on the physical phenomena before cross-linking of the wood adhesive. The physical (rheological characterization) and mechanical (bond strength) properties of formaldehyde-free corn starch and mimosa tannin wood adhesives were measured.

The results showed that the shear refinement (290 rpm and 5 min, optimal conditions) reduced the viscosity of the corn starch–mimosa tannin wood adhesives (from 100 000 to 458 Pa s) with the advantage of being stable over time. Mechanical tests showed that the shear refinement did not influence the mechanical properties of corn starch–mimosa tannin wood adhesives.

Keywords

Corn starch, mimosa tannin, shear refinement, viscosity, wood adhesives

1. Introduction

Currently, the adhesives used in the wood products industry are petrochemically based (phenol formaldehyde, urea formaldehyde and melamine urea formaldehyde) [1]. Many of these adhesives contain volatile organic compounds (VOCs) and many are produced by processes that involve VOCs and toxic raw materials [2]. Ris-

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ing environmental and economical concerns have sparked numerous changes in the adhesive industry in the last decades and this has prompted the development of bio-based adhesive systems [1, 3–5].

Corn starch is abundant, inexpensive and is a renewable material. A small quantity, of about 5%, is used in the production of construction material [6]. Corn starch is composed of a mixture of two highly polymeric and isotactic molecules: amylose (a linear chain molecule composed of α -D-glycopyranose units which are linked by α -D-(1–4) bonds) and amylopectin (a branched molecule composed of α -D-glycopyranose held together by 1,4-linkages except at the branch points which are 1,6-bonds). Starch has a high affinity for cellulose and many porous substrates [7]. Basically the polar character is the reason for using starch adhesive even for wood-to-wood bonding. Also good cohesion results from the interaction of the hydrogen bonds between the starch molecules [8, 9]. Tannin is another example of such a renewable material. Certain condensed tannins such as mimosa and quebracho are produced commercially from woods and barks and they have been used as a raw material for the production of wood adhesives since the 1970s [10–12].

Initial investigations in the use of mimosa tannin in starch corrugating adhesives were carried out at the Division of Forest Products, CSIRO, in 1968. Since an alternative material to resorcinol was urgently needed in 1969, the project was extended to include some studies designed to establish reasons for the poor performance of water-resistant starch adhesives [13]. Further research and developments in the field of fortified starch adhesives with mimosa tannin were carried out in South Africa [14] and the industrial production of one such system was started in South Africa in the late 1970's [15]. Based on our previous results, the overall quality performance of corn starch and mimosa tannin appeared to be acceptable as a wood adhesive [16, 17], but their high viscosity posed a serious problem for use in industry. The current industrial adhesives have a viscosity between 0.1 and 2 Pa s and our natural adhesives have a viscosity between 1000 and 100000 Pa s. Thus in order to use these natural adhesives in industry, it is necessary to decrease this viscosity.

The high viscosity of polysaccharides is a result of hydrogen bonding and the entanglement of macromolecules of very high molecular weight, such as the amylopectin. In this frame work, one way to decrease the viscosity of our natural adhesives is to decrease the number of entanglements per chain and one way to do this is to add molecules smaller than the distance between two entanglement points. In the plastics industry, these smaller molecules are called plasticizers. Their role is to swell the polymer network. In this way, the distance between entanglements increases and the number of entanglements per chain and the viscosity decreases. Another possible solution to reduce the viscosity of entangled polymers is to use an old technique called 'shear refinement'. To understand shear thinning induced by the shear refinement, one should refer to the work of Doi and Edwards [18]. These authors have shown that the orientation of the molecules under flow decreases the number of entanglements and this has been tested in the work presented in this paper.

The objective of this investigation was to evaluate the influence of the shear refinement on the viscous and mechanical properties of formaldehyde-free corn starch and mimosa tannin wood adhesives and the first results seem promising.

2. Background

2.1. Polymer Entanglements

Macromolecules in a molten or in a solution state are entangled in much the same way as the strands of spaghetti are entangled in a dish of spaghetti. With this picture in mind, it is easy to imagine that when the molecular chain dimension increases, the number of entanglements per chain also increases, resulting in poor diffusion in macromolecular material.

In a linear viscoelasticity regime for small deformations, within the mean-field theory, the distance between two successive entanglements is characterized by a constant molecular weight between entanglements M_e [19]. This mass depends on the chemical species considered. De Gennes [20] showed that the number of entanglements per chain describes the variation of viscosity with molecular weight M_w of the polymer.

In a non-linear viscoelasticity regime for large deformations, Doi and Edwards [18] showed that the distance between the points of entanglement increases, inducing a decrease in the viscosity of the bulk material, thus explaining the shear thinning character of polymer melts.

2.2. Shear Refinement

The shear refinement of polymer melts and its direct application to the improvement of fluidity is not new and has been reported in numerous works over the past 20 years [21, 22]. For a long time, in the polymerization units of the low-density polyethylene (LDPE), enormous extruders have been used, downstream from the last reactors zone, to produce a particular grade of polymer; i.e., to give a viscosity without adversely affecting mechanical properties of the product. This process is not fully understood and to date no convincing explanation has been given other than to suggest the possibility of disentanglement of macromolecular chains [21].

Shear refinement has recently been the subject of extensive experimental and theoretical investigation by Bourrigaud [23]. This author studied the shear-refinement of several well characterized low density branched polyethylene grades and obtained proof of the influence of the strain amplitude of shear deformation on the degree of viscosity reduction during subsequent processing. Bourrigaud [23] suggested that molecular topology is critical, and his results support the view that very long-chain branched molecules are highly affected by shear refinement, whereas linear polyethylene seemed to undergo much smaller changes under the experimental shear refinement conditions used. Bourrigaud and co-workers [23] proposed that the degree of branching or ramification qualifies or disqualifies, for the most part,

the degree of viscosity reduction observed by shear refinement. In other words, controlled alteration by branching of the molecular weight distribution, will lead to the optimization of shear-refinement and of its benefits. Furthermore, it was shown that refinement by elongation is more effective than refinement by shear for the same flow strength.

As corn starch–mimosa tannins adhesive is composed largely of branched macromolecules (amylopectin and mimosa tannins), we decided to use the shear refinement technique to mechanically reduce the viscosity of our natural adhesives.

3. Experimental Methods

Unmodified commercial grade corn starch (extra pure, 99%) was obtained from ACROS ORGANICS; the moisture content was in the range of 10–12%. Figure 1(a) shows the chemical structure of glucose. Sodium hydroxide ($M_w = 40.00$ g/mol) was purchased from VWR prolabo. Commercial flavonoid mimosa barks tannin (*Acacia mearnsii*, Mimosa OP) was obtained from SILVATEAM (Italy). Figure 1(b) shows the chemical structure of mimosa tannin. The hardener, hexamethylenete-

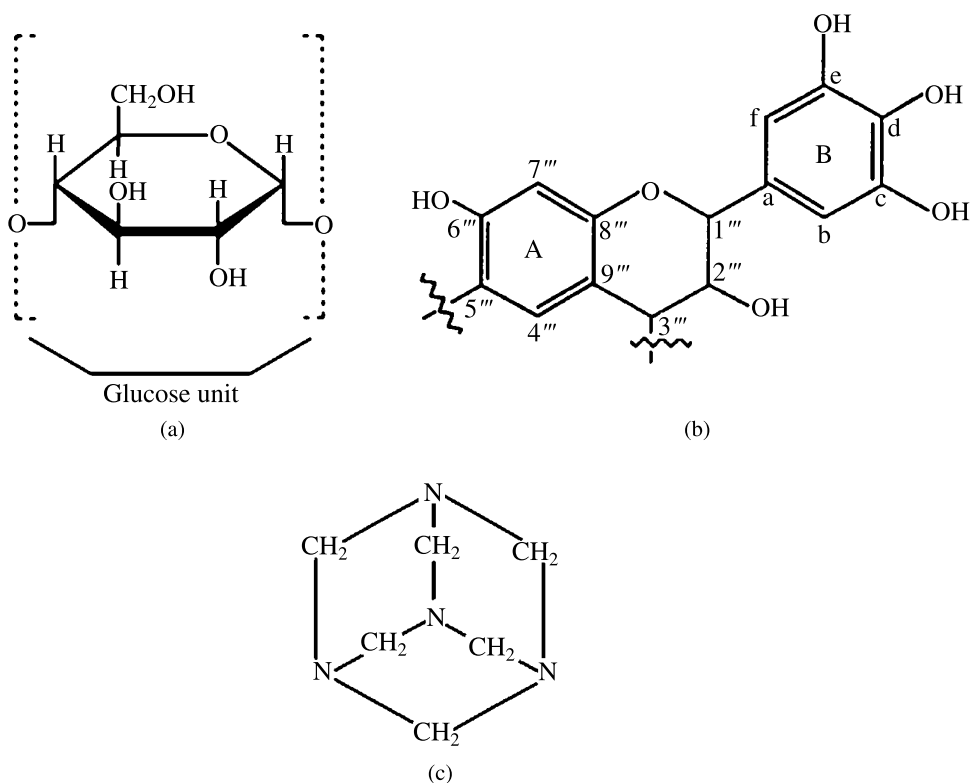


Figure 1. The chemical structure of glucose (a), mimosa tannin (*Acacia mearnsii*) flavonoids (b) and hexamine (c).

tramine 99% (hexamine) (Fig. 1(c)), was supplied by Aldrich. Maritime pine (*Pinus pinaster*) veneer was provided by the sawmill — Ets Labadie (Roquefort — France) Sd (moisture content around 8–10%).

3.1. Preparation of Corn Starch–Mimosa Tannin Adhesives [16, 17]

To prepare 500 g of adhesive, a 65% (w/v) corn starch water solution was prepared by dissolving 130 g of corn starch in 200 ml of deionised water and stirred at room temperature, to which 13 g of mimosa tannin are added. Hardener content used was 5% hexamine by weight on tannin extract solids content. The hexamine was dissolved in water to yield a 30% concentration solution in water before being added to the cornstarch–tannin solution. The solution was mixed and 100 ml of sodium hydroxide (33%) was added.

3.2. Shear Refinement

The preparation and mixing of the corn starch–mimosa tannin adhesives was performed in a laboratory aluminium beaker using a Caframo Mixer (Model BDC 1850) (Fig. 2). The shear refinement conditions were: a heterogeneous system; temperature of 25°C; rotational speeds of 250, 260, 270, 280, 290, 300 rpm; and mixing times of 3, 5, 7 and 8 min. The temperature elevation ΔT due to the shear refinement was of the order of 10°C.

3.3. Characterization of Shear Refinement

To characterize the shear refinement effect, the resins were tested with a rotary rheometer (ARES) with parallel plate geometry; the plate diameter used was 25 mm and the gap between the plates was 1.5 mm. The experiments were carried out in an environment with a controlled temperature and silicone oil was used to prevent water evaporation.

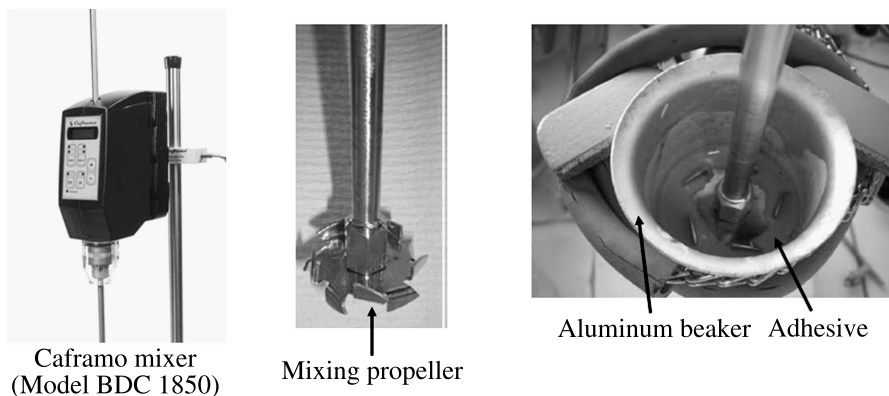


Figure 2. Experimental set-up used in the study of mechanical mixing.

3.4. Sample Preparation and Mechanical Testing

Maritime pine veneer with a thickness of 3 mm was cut into rectangular specimens of 2.5 cm × 11.5 cm (according to British Standard [24]). The adhesive was applied to one side of each piece of veneer. The application area was 2.5 cm × 2.5 cm for each veneer. The spread rate of corn starch–tannin adhesive was 120–150 g/m² on a dry weight basis [16, 17, 25–27]. Two adhesive-coated veneer boards were lapped together with the grain parallel to each other and then pressed at 0.45 MPa [16, 17, 25]. The press temperature and press time were fixed at 170°C and 4 min respectively. After bonding, the assemblies were conditioned in a Vötsch climate room (25°C and 65% relative humidity) for 24 h. For mechanical testing an Instron testometric M500-50 AT universal testing machine with an average speed of 0.5 mm/min was used to achieve breakage of joints within 60 ± 30 s. The percentage of wood failure was evaluated visually. Twenty samples were prepared for the mechanical tests.

4. Results and Discussion

In dynamic measurements, the elasticity can be described by the storage shear modulus G' , and the viscous property can be described by the loss shear modulus G'' . The determination of the linear domain is an essential step in studying the rheological behaviour of a product. This step allows one to determine the area where both viscous (G'') and elastic (G') modules are completely independent of the deformation applied to the sample.

This determination was performed by applying a strain sweep (0–5%) at 25°C and 1 rad/s. Figure 3 shows that for a deformation between 3 and 5%, the values of elastic moduli (G') and viscous moduli (G'') are practically constant and does not depend on the value of the deformation. All rheological analysis, to be presented later in this work, were done on samples which were deformed by 3%.

The dependence of G' and G'' on the time sweep (dynamic oscillatory measurements) were used to characterize the chemical or physical stability of corn starch–mimosa tannin adhesives. Figure 4 displays the elastic modulus G' and viscous modulus G'' plotted against time at 25°C, 3% strain and 1 rad/s of formaldehyde-free corn starch–mimosa tannin adhesive. Here, it can be seen that dynamic moduli (G' and G'') increase progressively with time up to 3:30 h and the corn starch–mimosa tannin adhesive seems to have been restructured or 'build up'. Beyond 3:30 h they remain quasi-constant. This indicates excellent structural stability of the adhesive. On the other hand, this figure shows a predominant elastic character of the adhesive ($G' > G''$).

If the natural adhesive is sensitive to strain, viscosity or dynamic moduli (G' and G'') should decrease with percentage of strain. In the following section we present the results of the effect of strain on the viscosity of corn starch–mimosa tannin adhesives.

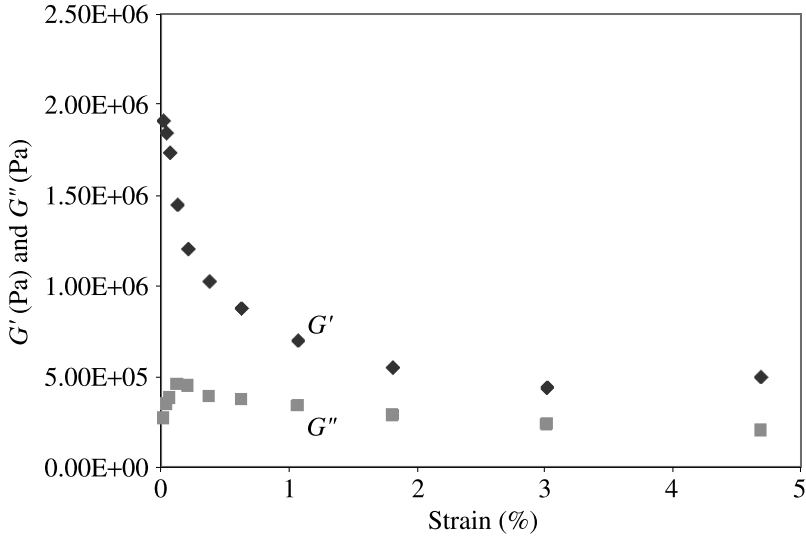


Figure 3. Strain dependence of storage (G') and loss (G'') modules of the corn starch–mimosa tannin adhesive at 25°C and 1 rad/s. Curves represent average of three measurements.

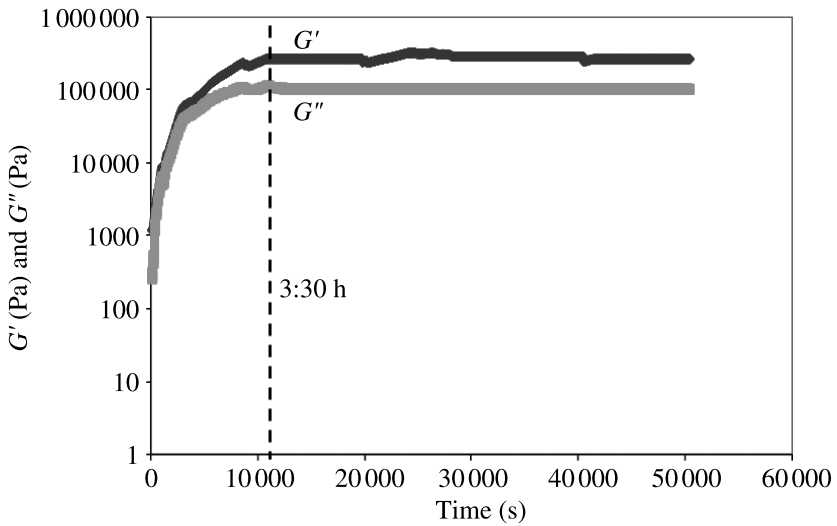


Figure 4. Time evolution of storage modulus (G') and loss modulus (G'') of corn starch–mimosa tannin adhesive at 25°C, 1 rad/s and 3%. Curves represent average of three measurements.

The variation of the elastic modulus G' and viscous modulus G'' with strain at 25°C and 1 rad/s of corn starch–mimosa tannin adhesives is shown in Table 1 and as can be seen the dynamic moduli (G' and G'') decreases with strain. This indicates that corn starch–mimosa tannin adhesive is sensitive to strain. The increase of deformation leads to the decomposition of the granular structure. This causes decomposition of polymers, which results in viscosity reduction of the wood ad-

Table 1.

Strain dependence of storage (G') and loss (G'') modules of the corn starch–mimosa tannin adhesive at 25°C and 1 rad/s. S.D.: standard deviation

Strain (%)	G' (Pa) Mean \pm S.D.	G'' (Pa) Mean \pm S.D.
5	19700 \pm 94	16874 \pm 134
10	9525 \pm 45	7556 \pm 57
15	6456 \pm 31	5051 \pm 42
20	4966 \pm 28	3888 \pm 24
30	3495 \pm 16	2729 \pm 18
100	1286 \pm 7	1032 \pm 8
200	982 \pm 10	929 \pm 11

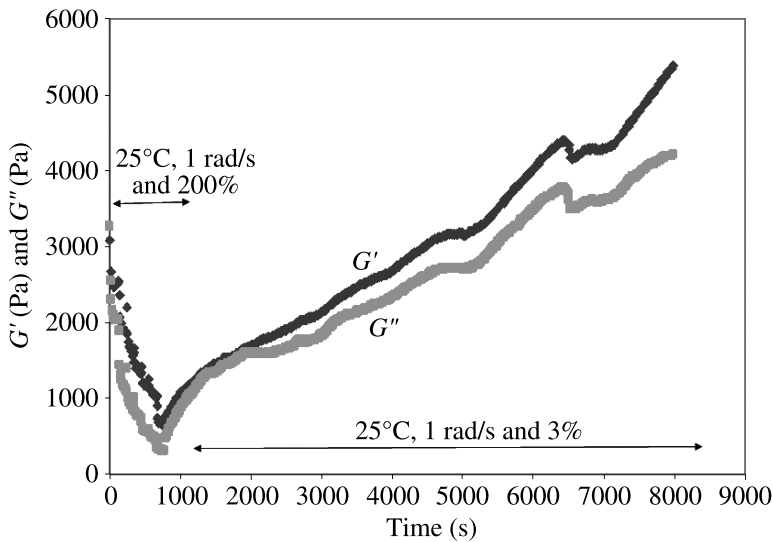


Figure 5. Time evolution of storage modulus (G') and loss modulus (G'') of corn starch–mimosa tannin adhesive after increasing strain at 25°C, 1 rad/s and 3%. Curves represent average of three measurements.

hesives. This result confirms that shear refinement can significantly decrease the viscosity of the wood adhesives.

Figure 5 shows the time dependence of G' and G'' for corn starch–mimosa tannin adhesive after increasing strain, at 25°C, 3% strain and 1 rad/s. Here, it can be seen that the dynamic modules (G' and G'') increase progressively with increasing time. This shows a re-organisation of corn starch–mimosa tannin adhesives (return to equilibrium) which appears to exhibit thixotropic behaviour. It appears that it is the amylase that is predominantly responsible for the stiffness of the gel, due to its linear structure and hence the strong association due to hydrogen bonds [28, 29].

Table 2.

The influence of rotational speed and time of mixing on the viscosity of corn starch–mimosa tannin adhesive at 25°C

Rotational speed (rpm)	Time of mixing (min)	Viscosity (Pa s) Mean \pm S.D.
250	5	591 \pm 19
260	5	563 \pm 24
270	5	525 \pm 14
280	5	487 \pm 09
290	5	458 \pm 17
300	5	456 \pm 10
290	3	333 \pm 21
	5	458 \pm 17
	7	488 \pm 11
	8	509 \pm 16

The next section is devoted to the optimization of the shear refinement conditions. The different variable parameters with the mixer are: rotational speed of the rotor (rpm) and time of mixing (min). Mixing tests were conducted to identify the influence of both parameters on the viscosity of the corn starch–mimosa tannin adhesives. The influence of rotational speed and time of mixing on the viscosity of the adhesive is shown in Table 2. It can be seen that at a given time of mixing (5 min), the viscosity of the corn starch–mimosa tannin adhesives decreased up to a speed of mixing of 290 rpm. A high rotational speed means more energy is needed for the decomposition of the polymers. This is the reason for the decrease of the viscosity with increasing rotational speed. From the above, it appears that, a rotational speed of 290 rpm (maximal rotational speed) is optimal for the preparation of corn starch–mimosa tannin adhesives. However, at an optimal rotational speed of 290 rpm, decreasing the time of mixing appears to decrease the viscosity of the adhesives. In general, increasing the rotational speed on the one hand and the reduction of the time of mixing on the other can reduce the viscosity of the corn starch–mimosa tannin adhesives. This is in accordance with results by Van den Einde *et al.* [30].

In the corn starch–mimosa tannin adhesive amylose, amylopectin and mimosa tannin were detached for the most part and consequently able to interact on a bigger scale with the wooden surface [9].

Another problem concerning the formulation of this adhesive is its stability over time. The industrial use of corn starch–mimosa tannin adhesives requires that its viscosity after pre-treatment is stable over time. It has been shown previously that the corn starch–mimosa tannin adhesive after its formulation tends to restructure itself over time. A time sweep study was conducted on the adhesive after mixing for 5 and 3 min at 290 rpm. Figure 6 shows the variation of the elastic modulus G' and viscous modulus G'' of corn starch–mimosa tannin adhesive after mixing for 5 min

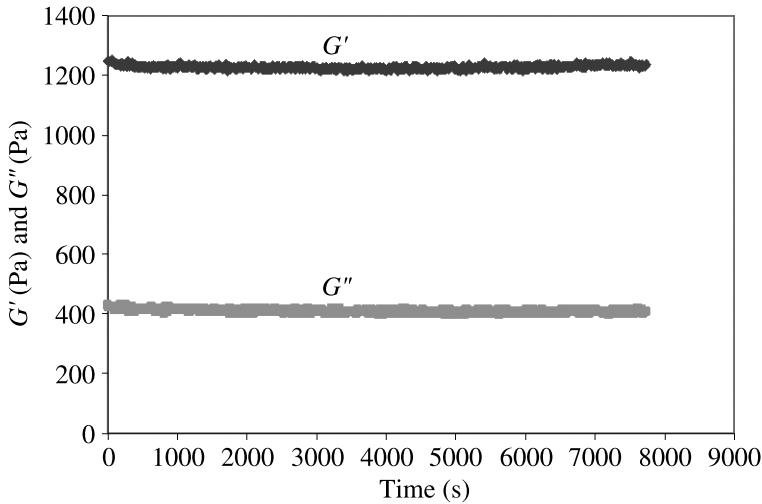


Figure 6. Time evolution of storage modulus (G') and loss modulus (G'') of corn starch–mimosa tannin adhesive after mixing for 5 min at 290 rpm, 25°C, 1 rad/s and 3%. Curves represent average of three measurements.

at 290 rpm. It can be seen that dynamic moduli (G' and G'') remain constant and parallel with increasing time. That shows excellent structural stability of the adhesive. Figure 7 displays the G' and G'' plotted against time for corn starch–mimosa tannin adhesive after mixing for 3 min at 290 rpm. The dynamic moduli (G' and G'') increase with time. This shows that the corn starch–mimosa tannin adhesive is not stable over time. A short mixing time does not allow the total destruction of natural polymers to overcome the thixotropic behaviour of the adhesives. From the above, it appears that, a mixing time of 5 min at 290 rpm is optimal for the reduction of viscosity of corn starch–mimosa tannin adhesives.

The mechanical properties (bond strength and wood failure percentage) data of the two-ply wood made using corn starch–mimosa tannin adhesive after manual and shear refinement are illustrated in Table 3. Two-ply wood bonded with corn starch–mimosa tannin adhesive after manual mixing showed comparable mechanical properties to the two-ply wood glued with corn starch–mimosa tannin adhesive after shear refinement (290 rpm and 5 min). This result shows that the shear refinement does not affect the mechanical properties of the corn starch–mimosa tannin adhesive. The test revealed that in most cases, the rupture is not in the adhesive but is interfacial and more precisely within the wood.

There are some disadvantages of the lap joint testing method, especially when there is good adhesion of the glue. When shear strength of the adhesive bond is equal or even exceeds shear strength of the wood, no significant differences between different bonding conditions can be identified. In this case the failure mode of lap joints was mainly wood failure and primarily the shear strength of the wood being evaluated [31].

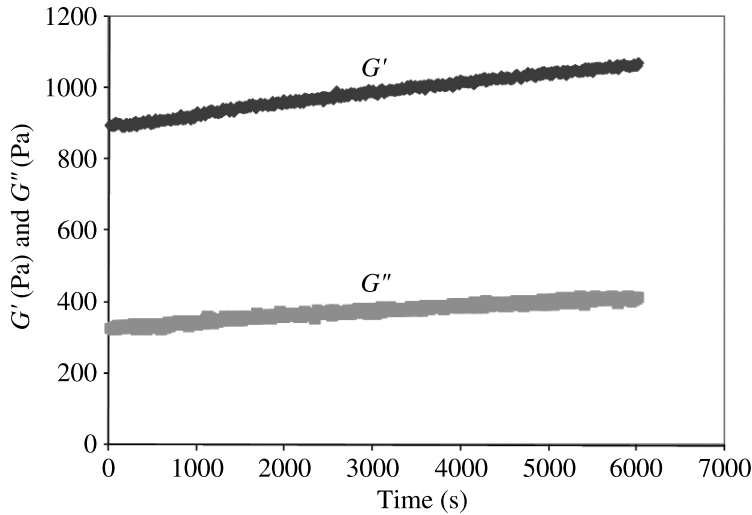


Figure 7. Time evolution of storage modulus (G') and loss modulus (G'') of corn starch–mimosa tannin adhesive after mixing for 3 min at 290 rpm, 25°C, 1 rad/s and 3%. Curves represent average of three measurements.

Table 3.

The bond strength and wood failure for the two-ply wood bonded with corn starch–mimosa tannin adhesives (pressed at 170°C, 4 min and 0.45 MPa) after a manual mixing and mechanical mixing (290 rpm and 5 min). Ten replicates of each adhesive. S.D.: standard deviation

Mixing mode	Viscosity (Pa s)	Bond strength (MPa) mean \pm S.D.	Wood failure (%)
Manual	10 000	5.12 \pm 0.58	80
Mechanical 5 min and 290 rpm	458	4.91 \pm 0.45	70

5. Conclusion

This work shows that the shear refinement is a very promising way to reduce the viscosity of corn starch–mimosa tannin wood adhesives. Increasing the rotational speed on the one hand and the reduction of the time of mixing on the other can reduce the viscosity of corn starch–mimosa tannin adhesives from 10 000 Pa s to 458 Pa s. The mechanical properties (bond strength and wood failure percentage) showed that excellent adhesive bond strength could be performed with the used corn starch and mimosa tannin glue without formaldehyde.

Research is in progress to reduce viscosity by using other methods such as ultrasound, microwave or enzymatic digestion.

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