INFLUENCE OF THE ACIDITY AND SIZE OF BEECH PARTICLES ON THE HARDENING OF THE UREA–FORMALDEHYDE ADHESIVE

Sergej Medved and Jože Resnik

University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology, Rožna dolina, Cesta VIII/34, 1000 Ljubljana, Slovenia

Abstract

Presented work deals with the influence of acidity of beech particles of different size on the hardening of the urea–formaldehyde adhesive. The pH value and the milliequivalents of soluble and total acids were determined upon the method published by Subramanian et. al. in 1983. The method is based on the reaction between acids in wood and the aqueous solution of sodium acetate, where the equivalent quantity of acetic acid is generated. The quantity of the generated acetic acid was determined by the titration and presents the total acids in wood. The acetate solution helps to extract the acids soluble and insoluble in water. We determined that the particle size does not influence the pH value of particles and the quantity of the extracted soluble acids, but does have the influence on the quantity of the extracted insoluble acids. We furthermore determined that the particle size influences the gel time of the urea–formaldehyde (UF) adhesive. The shortest gel time was determined at the finer particles.

Key words: beech particles, soluble wood acids, insoluble wood acids, adhesive gel time

Introduction

The acidity of wood has been investigated and measured by many workers.[1-4,6,7] The acidity of wood was interested because it influences the hardening of adhesive used to bind particles together. Because UF adhesives, which are the most common wood adhesives used in manufacture of particleboards, cure in acid environment wood acidity can affect the rate at which UF adhesives harden.

The effects of wood on hardening of urea–formaldehyde (UF) adhesive was investigated by Johns and Niazi.[2] They determined that pH value of wood and buffering capacity influences the hardening of UF adhesive and that gel time of UF adhesive correlates to the pH of the water soluble extract. Subramanian et al.[5] presented a different approach to determine acids presented in wood. They proposed a method in which total and water soluble acids and pH values could be determined. The same method for determining the pH value was used by Elias and Irle.[1] They determined that

fresh particles have lower pH value than particles that have been stored for a while. They noticed as well that particles derived from the sapwood have lower pH value than particles derived from the heartwood.

The knowledge of the pH value of wood is fundamental for the successful and effective use of wood during the processes where the adhesives and varnishes sensible to acidity or alkalinity of wood or wood based composites are used. For example: the UF adhesives need acid environment for their hardening; therefore it is senseless to expect them to be effective within almost neutral or even alkali environment.

From the literature, it is known, that different wood types have different pH value, which depends upon their chemical structure and the environment in which these trees grew. The most of the UF adhesive is consumed in the production where wood is in the first place separated into small pieces (particles or fibres), which are then blended and pressed together into a wood based composite (particle or fibre board). Therefore it is very important to ascertain whether the size of these pieces influences the pH value of particles and the speed of hardening of the adhesive. The purpose of this investigation was to determine how particle size from beech wood influences the pH value, acid content and hardening of UF adhesive.

Materials and Methods

Beech wood (*Fagus silvatica* L.) particles of three different sizes were used for determining the influence of the particle size on the pH value, namely:

Size A (thickness×width×length): 0.13 mm × 0.15mm × 0.92 mm
Size B (thickness×width×length): 0.18 mm × 0.20 mm × 2.85 mm
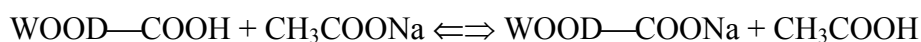Size C (thickness×width×length): 0.48 mm × 0.50 mm × 9.20 mm

Particles from fresh beech log were produced in the laboratory chipper. During the production of particles, the moisture of beech wood was between 60 and 65%. Beech wood particles were then dried to moisture content 10% approximately and then sieved to three different sizes.

Besides determining the pH value of particles, gel time was also determined. The gel time, as a factor that depends upon the type of the adhesive or the pH value of the adhesive mixture respectively and the pH value of particles, was determined in such a

manner that 10 g of hardener (20% solution of the ammonium sulphate) was added to 85 g of the adhesive resin. Instead of distilled water, the water extract of particles was used for the preparation of this hardener.

Determining the pH Value and the Acid Content of Particles

The pH value of particles was determined upon the Subramanian's method,[5] with which total acids, insoluble or "bound" acids and water soluble acids present in wood could be determined. The following form can simplify the reaction of the "bound" or insoluble wood carboxylic acids:

$$WOOD—COOH + CH_3COONa \Longleftrightarrow WOOD—COONa + CH_3COOH$$

The extraction was carried out within a mild environment (the pH value of 0.1 M sodium acetate solution was close to the neutral value) and at room temperature of 20 to 25 °C.

This method was chosen because of the determined correlation between the gel time of the adhesive and the share of the insoluble acids. The correlation between the share of the soluble acids and the gel time was merely 0.22, but the one between the share of the insoluble acids and the gel time was 0.82.[5]

Water extraction

The particles were oven dried at the temperature of 105 °C and then cooled to 20 °C. Then, 25 grams of dried and cooled particles is placed in the 800 mL beaker with 300 mL of distilled water. After 24 hours of extraction, the solution is filtrated. Particles are then washed four times, namely each time with 175 mL of distilled water. The filtrate and the washings are then diluted with distilled water to the total volume of 1000 mL.

Extraction with sodium acetate

The particles were oven dried at the temperature of 105 °C and then cooled to 20 °C. Then, 25 g of dried and cooled particles is placed in the 800 mL beaker with 300 mL of 0.1 M of sodium acetate solution. After 24 hours of extraction the solution is filtrated and washed four times, one time with 175 mL of 0.1 M sodium acetate solution

and afterwards three times with 175 mL of distilled water. The filtrate and the washings are then diluted with distilled water to the total volume of 1000 mL.

pH titration

200 mL of the aliquot is taken from the total volume of 1000 mL (the filtrate and the washings) and the pH value is measured. A known volume of 0.1 M of sodium hydroxide was than added to the solution with countinuous stiring. After two minutes the pH value of the solution is measured. The process is repeated as long as the pH value is not constant (the change is less than 0.5%).

Determining the equivalence point

The equivalence point is determined by calculating the ratio between the pH value change and the change of volume ($\Delta pH/\Delta V$), where the change of volume is equal to 0.1 mL. The equivalence point occurs when the slope of the titration curve is at maximum (Figure 1).
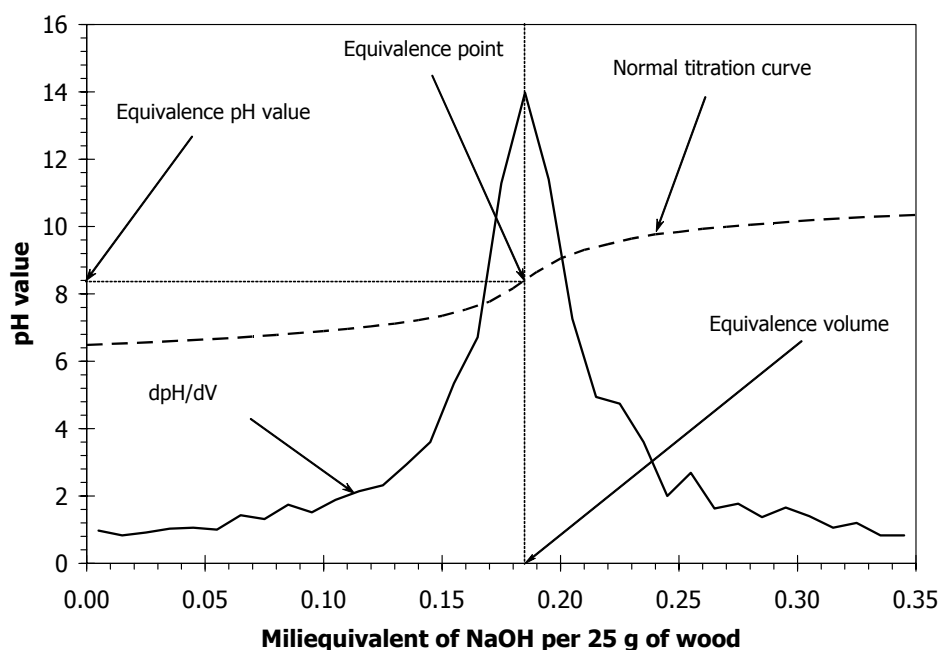

Figure 1. Determination of the equivalence point.

Results and Discussion

The pH value of particles is not dependant on the size of particles as could be seen in Table 1.

Table 1. pH value of the beech particles with regard to the size of particles.

Particle size	pH
Size A	6.30
Size B	6.30
Size C	6.20

The content of the extracted acids was determined by the pH titration. The results of the titration are presented in figures 2 and 3.
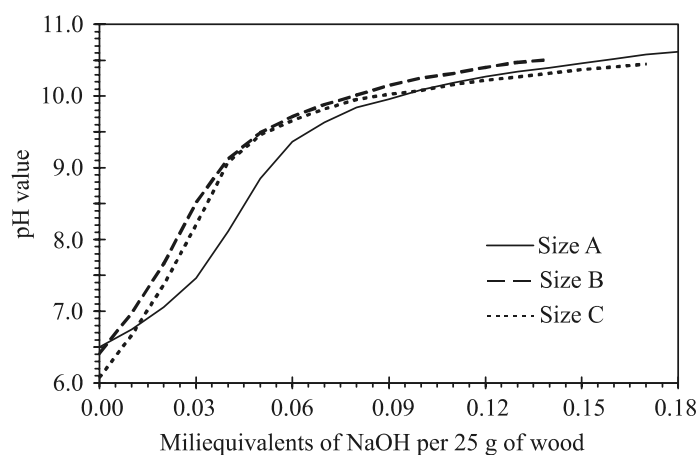

Figure 2. pH titration of extraction of beech particles with water, with regard to the size of particles.
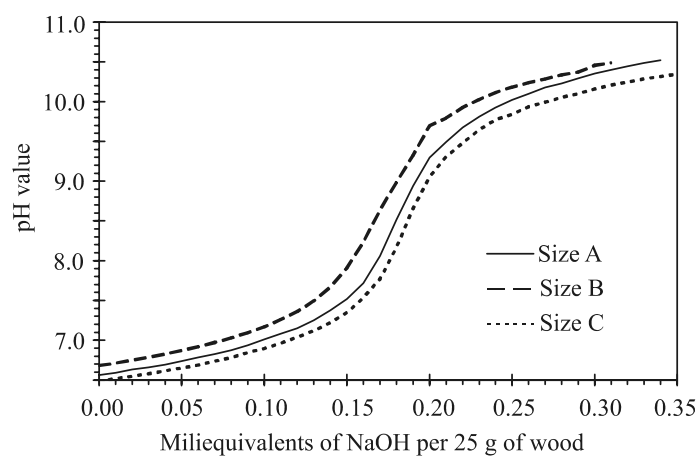

Figure 3. pH titration of extraction of beech particles with sodium acetate, with regard to the size of particles.

Miliequivalents of insoluble acids were calculated as the difference between the miliequivalents of total and the water–soluble acids (Table 2).

Table 2. Miliequivalent of the extracted soluble, insoluble and total acids with regard to the particle size.

Particle size	Soluble acids	Insoluble acids	Total
Size A	0.025	0.150	0.175
Size B	0.025	0.140	0.165
Size C	0.025	0.120	0.145

It was determined that the miliequivalent of the extracted soluble acids does not depend upon the size of particles, because the value ascertained was the same at all tree fractions. However, the values of the extracted insoluble acids are different. According to data presented in Table 2 it can determine that the increase of the particle size causes the decrease of the value of the extracted insoluble acids.

When the finer particles are exposed to the sodium acetate for 24 hours most of the water-insoluble acids are extracted, while in case of middle rough and rough particles lower share of these acids is extracted. According to our opinion, the sodium acetate is not penetrating fast enough into the middle of the particles to cause the extraction of all water-insoluble acids. Similar effect can be expected in the hardening of the adhesive during hot pressing. The pH value of wood is not so much important for the hardening of the UF adhesive, but it is more important what quantity of the water-insoluble acids could be used at the hardening reaction (Figure 4).
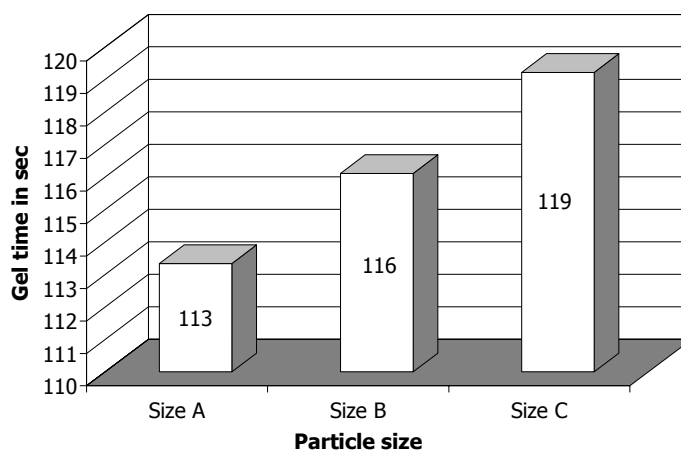

Figure 4. Correlation between gelation time and particle size.

When dealing with higher share of the finer particles it can be envisaged that bigger quantity of the insoluble acids will participate in the reaction than in case of higher share of rougher particles. When using the rough particles merely, only those water-insoluble acids that are on the surface or close to it will participate in the reaction, while those bound more in the middle of particles will have a passive role.

Conclusion

No differences between the pH values of beech particles with regard to their size was determined. The content of the extracted soluble acids and the size of particles were found to be in correlation with particle size used. The content of the extracted insoluble acids is higher at finer fractions (size A), where slightly shorter gel time was noticed as well.

The above – mentioned data strongly emphasise the meaning of the constant modification of the particle size structure, because it can be determined that a too big quantity of finer or bigger particles can cause a rapid or slow hardening of the UF adhesive, which negatively impacts mechanical properties of particleboards.

The application of bigger particles (size C) does not deteriorate the particleboards due to its unsuitable size merely (small slenderness and specific surface), but also due to slower hardening of the UF adhesive. However, even the application of finer particles does mean better characteristics, if the share of the finer particles is to high and the structure of the adhesive mixture is not changed properly, the adhesive will harden too quickly and the produced particleboards will once more have bad characteristics.

References

1. R. Elias, M. A. Irle, *Holz als Roh– und Werkstoff* **1996**, *54*, 65–68.
2. W. E. Johns, K. A. Niazi, *Wood and Fiber* **1980**, *12*, 4, 255–263.
3. D. F. Packman, *Holzforschung* **1960**, *14*, 6, 178–183.
4. H. Poblete, E. Roffael, *Holz als Roh– und Werkstoff.* **1985**, *43*, 1, 57–62.
5. R. Subramanian, K. N. Somasekharan, W. E. Johns, *Holzforschung* **1983**, *37*, 3, 117–120.
6. A. J. Stamm, *Forest Products Journal* **1961**, 310–312.
7. B. Wagner, E. Roffael, *Holz als Roh– und Werkstoff* **1996**, *54*, 56.

Povzetek

V prispevku je predstavljen vpliv kislosti bukovega iverja različnih velikosti na utrjevanje urea-formaldehidnega lepila. pH vrednost in miliekvivalnet vodotopnih in skupnih kisli v iverju bukve je bila določena po metodi, ki so je leta 1983 objavil Subramanina s sodelavci. Metoda temelji na reakciji med kislinami v lesu in vodno raztopino natrijevega acetata pri čemer se sprosti ekvivalentna količina ocetne kisline. Količina sproščene ocetne kisline je določena s titracijo in predstavlja skupne kisline v lesu. Z acetatno raztopino se namreč ekstrahirajo tako v vodi netopne, kot tudi v vodi topne kisline. Ugotovljeno je bilo, da velikost iverja ne vpliva na pH vrednost iverja in količino ekstrahiranih topnih kislin, medtem ko velikost iverja vpliva na količino ekstrahiranih netopnih kislin. Prav tako je bilo ugotovljeno, da velikost iverja vpliva na čas želiranja UF lepila. Pri finem iverju je bil ugotovljen najkrajši čas želiranja.