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Effect of duration of storage of MUF resin on the wetting angle on beech wood

Utjecaj trajanja skladištenja MUF smole na kut kvašenja bukovine

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SUMMARY • *If high-quality gluing of wood is to be achieved, it is necessary that the surface of the wood is suitably wetted and that the adhesive penetrates adequately into the wood. What degree of wetting is achieved depends mainly on the structure of the wood and the preparation of its surface, as well as on the type, composition and viscosity of the adhesive resins. One of the important factors relating to the surface of the wood is its geometry. Since the viscosity of adhesive resins increases with the length of time for which they are stored, longer storage times are also apt to cause a decrease in their wettability during gluing. Measurements of the wetting angle were performed on test specimens of beech (*Fagus sylvatica *L) in the form of peeled veneer of thickness 1,5 mm and in the form of solid wood of thickness 18 mm. Melamine-urea-formaldehyde (MUF) resins having different degrees of condensation and viscosity were used. In the research it was found that the influence of the surface of the wood was evident from the different initial and final wetting angles, and that ageing of the resin causes a greater increase in the wetting angle because of changed viscosity than that caused by under-condensation of the resin.*
Key words: *wetting angle, MUF adhesive, viscosity, beechwood*

SAŽETAK • *Da bi se postiglo visokokvalitetno lijepljenje drva, potrebno je osigurati dostatno kvašenje drvne površine i odgovarajuću penetraciju ljepila u drvo. Stupanj kvašenja koji je moguće postići uglavnom ovisi o strukturi drva i pripremi površine, ali isto tako i o vrsti, sastavu i viskoznosti smole ljepila. Jedan od važnih činitelja koji se odnosi na drvnu površinu jest njezina geometrija. S obzirom na to da se viskoznost smola ljepila povećava s trajanjem njihova uskladištenja, dulje vrijeme stajanja također pridonosi slabljenju svojstava kvašenja pri lijepljenju. Mjerenja kuta kvašenja načinjena su na uzorcima bukovine (*Fagus sylvatica *L.) u obliku 1,5 mm debelih ljuštenih furnira i na 18 mm debelim cjelovitim pločicama. Rabljena su melamin-urea formaldehidna ljepila različitih stupnjeva kondenzacije i viskoznosti. Istraživanjem je otkriveno da svojstva površine drva sigurno utječu na početne i završne vrijednosti kuta kvašenja. Duljina skladištenja smole uzrokuje veći porast kuta kvašenja zbog promjena viskoznosti nego što bi ga prouzročila potkondenzacija smole.*
Ključne riječi: *kut kvašenja, MUF ljepilo, viskozitet, bukovina*

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1. INTRODUCTION
1. UVOD

One of the conditions for the successful gluing of wood is the adequate wetting of its surface with the applied adhesive. Good wetting of the surface and penetration of the adhesive into the wood makes it possible to create a glued joint which is formed by the adhesive and the surface and subsurface of the wood. Poor wetting can be caused by numerous factors such as the structure and chemical composition of the wood, the anatomic direction of growth of the woo fibres , moisture content (MC), the hydrothermic methods used to process the wood, the preparation of the gluing surface, its contamination, etc. The individual factors are usually mutually interdependent, which means that studies of their effects are difficult, and the results frequently unreliable. Of course wetting also depends on the composition and method of preparation of the resin, and, in particular, on the latter's viscosity, which is influenced by, among other factors, its molecular mass and temperature. Since the viscosity of resins changes during their period of storage, longer storage periods present a problem because of the worsening of wettability during gluing.

The wettability of any liquid depends on its surface tension. Surface tension, or in the case of solid matter - surface energy, manifests itself most clearly on the boundary surfaces of various liquids or between liquids and solid matter and gases, whereas the forces inside the liquid or solid matter are neutralized. The forces due to surface tension tend to reduce the total surface areas of the different types matter. In the case of liquids surface tension usually results in the formation of droplets.

On a hard surface a droplet of liquid spreads out until a state of equilibrium is achieved between all the acting forces, so that the sum of the surface tension forces at the boundary between the solid and the liquid (s,l), at the boundary between the liquid and the gas (l,g), and at the boundary between the solid and the gas (s,g) is equal to zero (Bogner 1995). The angle which occurs between the solid surface and the liquid is known as the wetting angle (see Figure 1).

The droplet on the solid surface remains unchanged if the net sum of all three of the surface tension forces is equal to zero. This state of equilibrium can be written in the form of Young's Equation, from which the parameter can be calculated:

$$\sigma_{s,g} = \sigma_{s,l} + \sigma_{l,g} \cdot \cos\theta$$

$$\cos\theta = \frac{\sigma_{s,g} - \sigma_{s,l}}{\sigma_{l,g}}$$

If $\theta < 90°$ then it is considered that the liquid wets the surface, whereas if $\theta > 90°$ then the opposite is considered to be true. The liquid can be considered to absolutely wet the surface of solid matter if $\theta = 0°$. In this case the liquid spreads out completely over the solid surface, and only a thin layer of it is formed.

As has been mentioned above, wetting, e.g. of the surface of wood by a adhesive mixture, is affected not only by the properties of the adhesive but also by the characteristics of the wood and of the preparation of its surface. One such important factor is the geometry of the surface of the wood, since, if this surface is rougher, a greater surface energy will exist, which means better wetting. Peeled veneer, which,

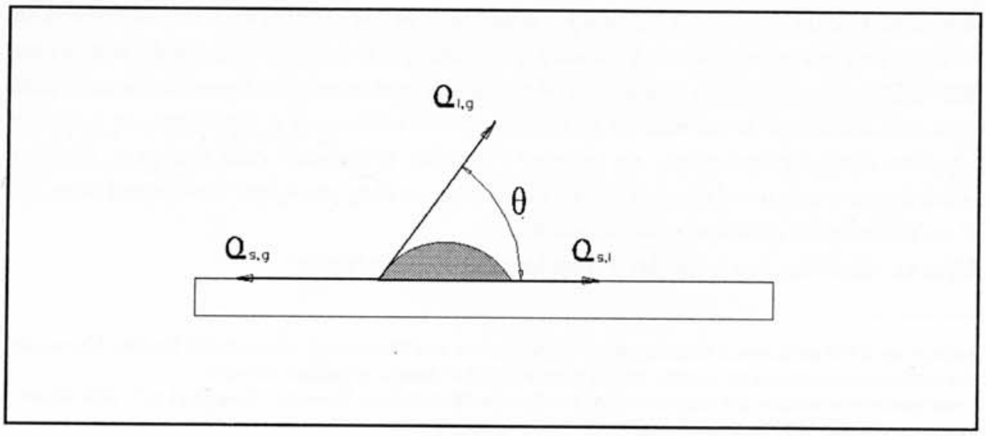

Fig. 1.
Schematic view of the acting forces and the wetting angle

Slika 1.
Prikaz djelujućih sila i kuta kvašenja

during its production, is exposed to aggressive hydrothermal processing and mechanical loading, is a special case regarding this factor. The surface of such veneer is usually cracked, torn or over-smoothed, with visible signs of collapse, and frequently it is also chemically changed.

In the text which follows are presented the results of an investigation into the influence of two very different types of surfaces of beech wood, and differently prepared MUF resins, on the wetting angle. Various different viscosities of the resin were achieved by (1) early concluded synthesis of the resin, (2) normally concluded synthesis, and (3) with artificial ageing of the prepared resin. In this way a storage duration of the studied adhesives were simulated.

2. LITERATURE REVIEW
2. PREGLED LITERATURE

Grey (1962) developed a technique for determining the surface tension of solid matter and a technique for calculating the free energy during wetting, and the energy of adhesion in the case of liquids. He found that any newly cleaned surface quickly becomes dirty, which has an effect on surface tension. By using a wetting model he found that suitable wetting of the surface is more important than suitable adhesion. Bogner (1991) studied the influence of the modification of beech and spruce wood on gluing with PVA adhesive. The surface of the wood was prepared by sawing and planing, and was suitably processed using a 10% solution of ammonium hydroxide. He investigated the dependence between the wetting angle and strength of the glued joint, and found that greater roughness of the surface and additional processing of the surface using a solution of ammonium hydroxide increases the wetting angle, the penetration of the adhesive into the wood, and the strength of the adhesive bond. He also found that better wetting results in a more uniform strength of the glued joint. Bogner (1993) defined the distinct wetting phenomena of adhesion, penetration and spreading. He also described conditions needed to obtain effective wetting. Boehme and Hora (1996) performed a study of the optimal gluing of lamellas. In their research they used two techniques for measuring the absorption of water. The research was performed on 40 different types of wood (tropical and European types of wood). The first technique used for the measurements involved the determination of the coefficient of absorption of water (Wt), whereas the second technique was based on the determination of the equivalent wetting angle of flowing water on the wood surface. The research concentrated on the dynamics of the wetting angle. The wood had a high permeability for water, as a result of which the wetting angle changed quickly with time. The permeability to water of wood also depends on the direction of the wood fibres, which is the result of the anisotropy of the wood. They determined the effect of the evaporation of water on measurements of the wetting angle, but, due to the short duration of the measurements (8 seconds), they neglected this effect. They found that the wettability of the wood surface does not depend on the specific gravity of the wood. They observed a degree of dependence between the content of water-soluble extracts in the wood and the wettability of the wood surfaces, but they were unable to prove it. Sheikl and Dunky (1998) investigated the effect of some parameters on the wetting of the wood surface. They performed a detailed investigation into the influence of the MC of the wood and the roughness of the wood surface. They found that the MC of the wood did not have a strong effect on surface tension, with the exception of some cases. They calculated surface tension according to the Zisman and Owens and Wendt method. They proved that roughness of the surface of the wood has a strong effect on the latter's wettability. This was confirmed by making studies of juvenile and adult wood of different types. Živanovći, Trbojević and Jaić (1998) studied the wetting characteristics of distilled water and coatings on fir and oak. They found that the surface of the oak test specimens wetted better with the coatings than with distilled water, whereas in the case of the test specimens made from fir the effect was the opposite. In general it was found that the wettability of the wood surfaces was better in the case of the coatings. They also investigated adhesion in connection with the wettability of surfaces. They found that the system consisting of two (top) coatings provided better adhesion than the system consisting of a prime coating and a top coating. These findings were not, however, in accordance with the results of measurements of wettability, since the prime coating provided better wettability than the top coating. They found that, in general, adhe-

Table 1. Data about the MUF resins used in the experiments
Tablica 1. Podaci o MUF smolama, upotrebljenim u eksperiementu

Data/Podaci	MUF1	MUF2	MUF3
Mole mass/molekularna masa	700	1000	1500
Viscosity/Viskoznost (mPa.s)	450	570	990
Dry matter/Suha tvar (%)	62.1	61.9	61.9

sion was better in the case of oak than in the case of fir. Gardner and Shi (2000) studied a wetting model which was developed for the description of the adhesion of wetting processes. The model was described on the basis of a number of different parameters, which were: two different resins (FF - phenol formaldehyde and PMDI - polydiphenylmethane diizocyanate resin), the direction of the wood fibres (lengthwise and transverse), the microlocations of the wetting (early and late wood), and different types of wood (Douglas fir, pine). The results of the investigation showed that the wetting model can be used for the accurate description of adhesion. A general finding was that the wetting angle changes as a function of time. They found that the direction of the wood fibres has an important effect on the wettability of the wood surface, since the wetting angle was smaller in the case of measurements which were performed in the direction of the wood fibres than in the case of those performed in the transverse direction. They also found that the type of wood and the microlocations of the wetting (early and late wood) did not have a significant effect on wettability, although changes in wettability were observed.

3. MATERIALS AND METHODS
3. MATERIJALI I METODE

Measurements of the wetting angle were performed on test specimens of beech wood (*Fagus sylvatica* L) in the form of peeled veneer of thickness 1.5 mm, and solid wood of thickness 18 mm. The veneer was produced industrially, whereas the solid wood was taken from the production of furniture. Before measuring the wetting angle, both types of test specimens were conditioned to a MC of 8 %. The solid beech wood had a mainly radial texture and medium-density growth, and its surface was planed. During the measurements the temperature of the wood was 20ºC.

Melamine-urea-formaldehyde (MUF) resins, having different degrees of condensation and viscosity, were used. The resin designated MUF1 was made in such a way that the synthesis was early concluded (and had a mole mass of about 700), whereas the resin designated MUF2 was prepared in the usual way (with a mole mass of about 1000). The resin designated MUF3 was artificially aged (with a mole mass of approximately 1500). Before the measurements were performed the resins were conditioned at a temperature of 20°C.

Measurements of the roughness of the wood surface were performed using a MITUTOYO Surfest 211 measuring device with a diamond sensor having a tip radius of 5 μm and an angle of 90º. The load which was applied through the sensor was 4 mN, and the speed of the sensor was 30 mm/min. Calculations were made of the arithmetical mean of the deviations from the absolute values (R_a) of the profile from the average value on the measurement path, and of the arithmetical mean of the maximum differences (R_z) between the peaks and troughs on five neighbouring measurement paths.

Measurements of the wetting angle were performed using a SONY 3CCD digital camera, with 10x optical magnification and a macro lens, by means of which it was possible to monitor the image at intervals of 0.5 sec. The camera was connected to an Intel Pentium III 800MHz computer with suitable hardware and software. The droplet of resin was applied by means of an injecting needle, 2 ml being applied in each case. For each resin six measurements of the wetting angle were performed, at time intervals of between 1 and 120 seconds. The digitalized images obtained were transferred intu the program AUTOCAD, which made possible measurements of the wetting angle of the droplet taking into account the different surfaces.

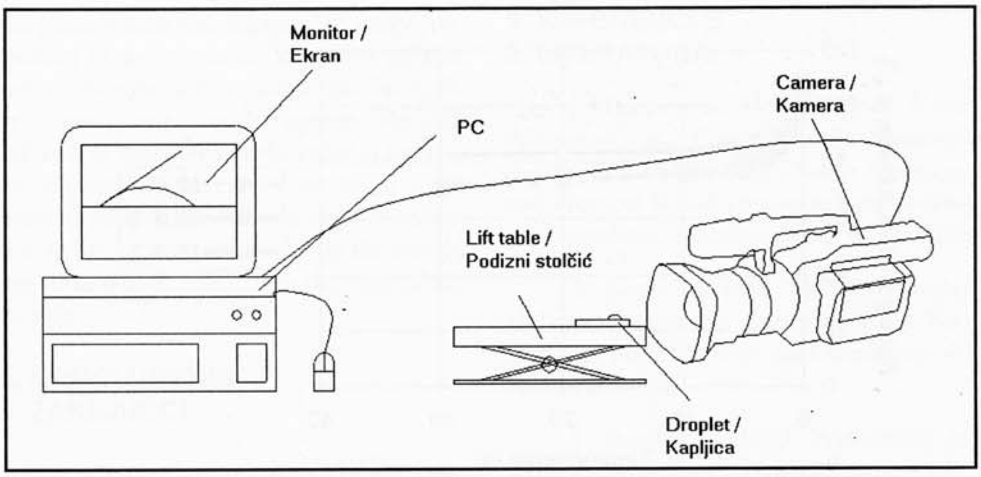

Fig. 2.
Diagram showing the test equipment set-up

Slika 2.
Sustav istraživačke opreme

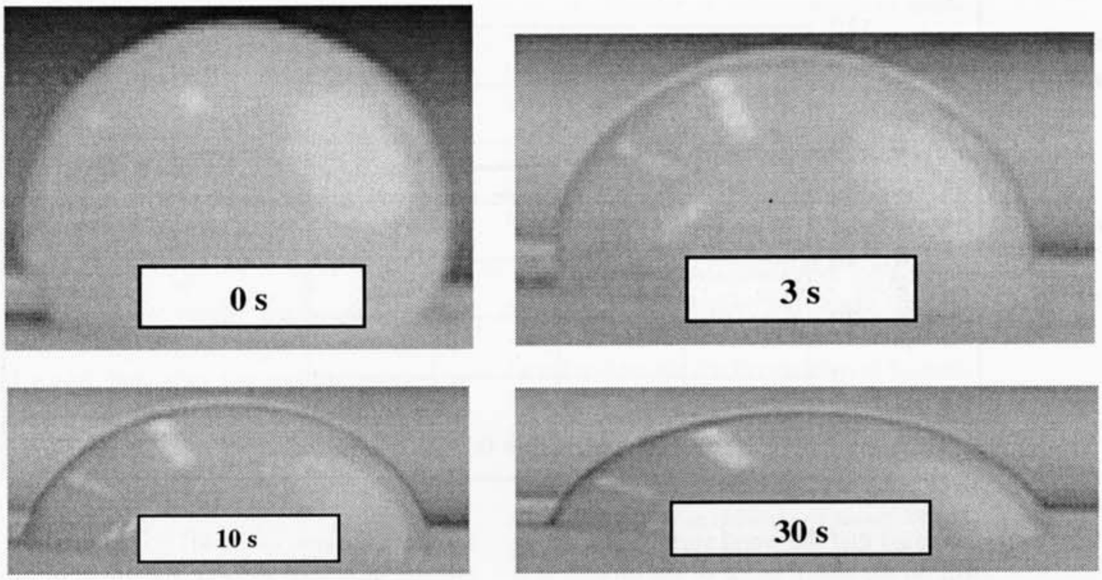

Fig. 3.
Dependence of the shape of the droplet of resin on time

Slika 3.
Zavisnost oblika kapljice o vremenu

4. RESULTS AND DISCUSSION
4. REZULTATI I DISKUSIJA

The results of the measurements of surface roughness (Table 2) confirmed the general expectation that the surface of the peeled veneer would be much rougher than that of the planed solid wood. In the case of beech veneer, the index of variation of the unevenness from the average value (R_a) was 2.35 greater than that for the solid wood , whereas the index of maximum variations of unevenness (R_z) was 2.21 greater. Of course these measurements did not take into account the microscopic cracks in the veneer and the damage to the wood fibres, which certainly must have had an effect on the wetting angle of the resin on such surfaces.

Measurements of the wetting angle of the investigated resins were performed over times ranging between 0 and 120 seconds. A comparison of the data obtained from these measurements showed that the wetting angle changed, in all cases, during the first 30 seconds of the measurement, whereas later changes were hardly noticeable, and could be neglected for all practical purposes. Because of this, in the text which follows only the results of the measurements of the wetting angle over the time period between 0 and 30 seconds are given.

The results of the investigation confirmed the general expectation that the wood surface has an important effect on the wetting angle. Thus, the results of the analysis of the data obtained from the measurements

Table 2.
Results of the measurements of surface roughness - arithmetical means

Tabela 2.
Rezultati mjerenja neravnoča površina - aritmetička sredina

SURFACE/POVRŠINA PARAMETER/PARAMETAR	R_z(µm)	R_a(µm)
Peeled veneer/Ljušten furnir	97,56	14,71
Viscosity/Viskoznost (mPa.s)	44,20	6,25

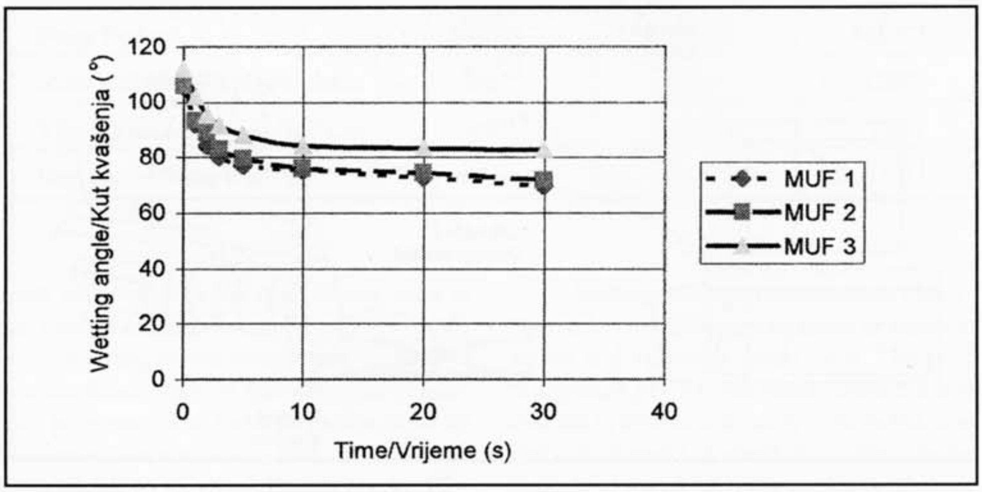

Fig. 4.
Dependence of the wetting angle on the type of resin - for the solid wood

Slika 4.
Zavisnost kuta kvašenja od tipa smole - za cjelovito drvo

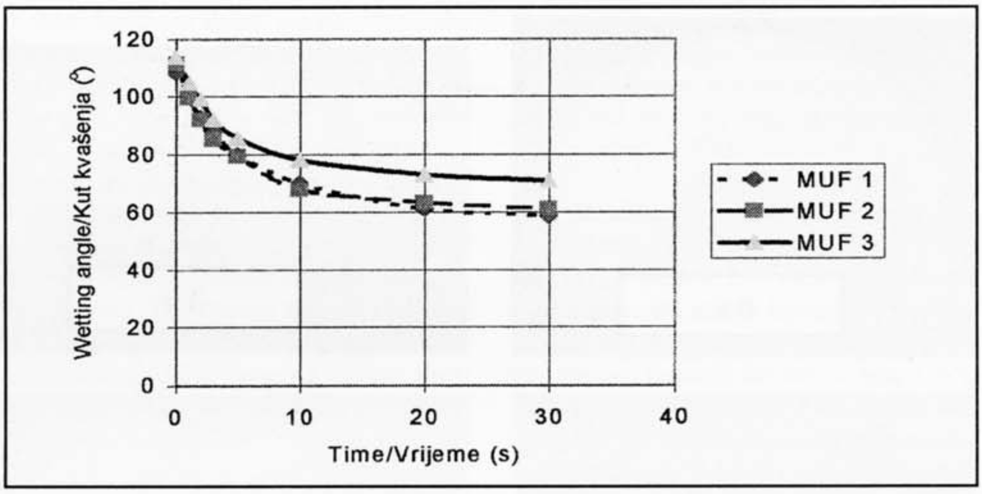

Fig. 5.
Dependence of the wetting angle on the type of resin - for the veneer

Slika 5.
Zavisnost kuta kvašenja od tipa smole - za furnir

indicated that the wood surface had an effect on the initial angle of the droplet at 0 seconds. In the case of all types of resins, the initial angle was greater in the case of the veneer than in the case of the solid wood, this difference amounting to 2.5° in the case of the MUF1 resin, 5.2° in the case of the MUF2 resin, and 1.5° in the case of the MUF3 resin. This larger initial angle in the case of the veneer can be attributed to its hydrothermic preparation, and particularly to the drying at a temperature of about 130°C, which causes chemical changes in the wood and the "swimming" to the surface of extracts. The much greater roughness of the surface of the veneer, and of course the presence of numerous micro-cracks, resulted in the more rapid spreading out of the droplet of resin on the veneer than on the solid wood. In their research into the effect of surface roughness on the wetting angle, Sheikl and Dunky (1998) also found that this effect was a large one. Changes in the wetting angle on both the solid wood and the veneer were first observed in the case of the MUF1 resin, where already after two seconds the angle of the droplet on the veneer was smaller than that on the solid wood, whereas in the case of the MUF3 resin this happened after three seconds. After 30 seconds the wetting angle of all three types of resin on the veneer was smaller by between 10.5 and 12°, and the type of resin used did not have a significant effect on this change. In comparison with the distilled water, which was used by Bogner (1991) in his experiments, the rate of change of the wetting angle was very similar for the investigated resins. In the case of distilled water, too, the greatest change in the wetting angle took place within the first three seconds, with the exception that the angles measured after 30 seconds were, in the case of water, 30 to 40° smaller. In the case of the research using artificialy aged resins, the 420 mPa.s greater than normal viscosity of the resin caused an increase in the wetting angle, after 30 seconds, of 11° on the solid wood, and 9.5° on the veneer. On the other hand, the lower viscosity of the resin, which was achieved by early conclusion of its synthesis, caused a smaller reduction in the wetting angle than the higher viscosity achieved by ageing. The 120 mPa.s less than normal viscosity of the resin, achieved by the early conclusion of the process of condensation, caused a reduction in the wetting angle of 2° in the case of the solid wood, and 2.5° in the case of the veneer.

5. CONCLUSIONS
5. ZAKLJUČCI

On the basis of the results of measurements of wetting angles, performed within the scope of in the investigation described in this paper, as well as comparisons and analyses of these results, the following conclusions can be drawn:

- the shape of the wood surface has a strong effect on the wetting angle, and this effect can be observed in the different initial and final wetting angles of the droplet of resin,
- on the veneer, the droplet of resin makes a larger initial angle than on the solid wood, but, after the wetting process is completed, the final angle is smaller in the case of the veneer,
- the increased viscosity of the resin, which is the consequence of ageing, has a greater effect on the wetting angle than the reduced viscosity of the resin due to under-condensation,
- the wetting angle of resins and its dependence on time depend on a large number of factors, and, due to the variability of wood, it is difficult to define this angle exactly.

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