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Work of adhesion as a criterion for determination of optimum surface tension in adhesives

Adhezijski rad kao kriterij za određivanje optimalne površinske napetosti adheziva

Izvorni znanstveni rad
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SUMMARY • *The article presents a new method for determination of the optimum surface tension in adhesives (glues and wood varnishes). The criterion employed is maximum work of adhesion. In view of the fact that work of adhesion depends, among other things, on the free surface energy of wood and the surface tension of the adhesive, and that the free surface energy changes in relation to roughness, this experiment was carried out on three groups of specimens of beech wood with radial surface. One group of specimens thus had a sanded surface, the second group consisted of planed pieces, while those in the third group had a surface worked out with a steel hand scraper. Work of adhesion can be good criterium for determination of optimum surface tension because it take into consideration adhesiv, adherent and their interaction. The roughness of wood surface was measured and expressed as the average arithmetic deviation of the surface roughness profile* R_a. *The wetting angle* θ *was also measured for nine liquids with different levels of surface tension. On the basis of the wetting angle and surface tension the critical surface energy of wood* (γ_c) *was calculated, as well as the work of adhesion* (W_a), *the optimum surface tension of the liquid wetting the wood surface in question* ($\gamma_{L.G.opt}$) *and the maximum work of adhesion* ($W_{a,max}$).
Key words: *wetting angle, work of adhesion, critical surface energy, roughness, optimum surface tension of adhesives*

SAŽETAK • *U radu je prikazana nova metoda za određivanje optimalne površinske napetosti adheziva (ljepila i lakova za drvo) koja kao kriterij koristi maksimalni rad adhezije. Budući da adhezijski rad pored ostalog ovisi o slobodnoj površinskoj energiji drva i površinskoj napetosti adheziva, a da se slobodna površinska energija drva mijenja sa hrapavošću pokus*

je rađen na površini bukovine (radijalne teksture) sa različitom hrapavošću. Jedna grupa uzoraka imala je brušenu, druga blanjanu, a treća, površinu obrađenu čeličnom postrugom. Adhezijski rad može biti dobar kriterij za određivanje optimalne površinske napetosti adheziva jer uzima u obzir adheziv, adherend te njihovu interakciju. Izvršena su mjerenja hrapavosti površine drva koja je izražena srednjim aritmetičkim odstupanjem profila R_a *i mejrenja kuta kvašenja* θ *za devet kapljevina (tekućina) različitih površinskih napetosti. Iz kuta kvašenja i površinske napetosti tekućine izračunata je kritična površinska energija* γ_c *rad adhezije* W_a *te optimalna površinska napetost tekućine* $\gamma_{L.G\ opt}$ *kod koje je rad adhezije maksimalan* $W_{a.max}$.
Ključne riječi: *kut kvašenja, adhezijski rad, kritična površinska energija, hrapavost, optimalna površinska napetost adheziva.*

1. INTRODUCTION
1. Uvod

Adhesion is of great relevance for various wood industry processes since it is due to adhesive forces that different materijals can stick fast in gluing and varnishing. Attempts to explain the phenomenon of adhesion have resulted in a number of theories, each of them, however, referring only to some phenomena and some particular material combinations, being inapplicable to other materials. The complexity of adhesion in wood is best illustrated by (Marra, 1972) with the "nine-link-chain", where each "link" stands for an interface and quoted by (Youngquist, 1987).

Adhesion depends on the strength of each link since it is at the weakest link that the chain will break. This fact suggests that each and every detail of wood working is highly important - from the preparation of wood surface to good process management as well as the quality and the features of the selected adhesive; they all bear on the final strength of the adhesive bond.

But not event with a most carefully conducted process can we achieve the theoretical maximum adhesion; working against us passive forces such as incomplete adherence at some of the potential points of connection, or residual stress in the bond due to microcracks etc.

Especially important for the quantification of adhesion is the work of adhesion, Wa, which can be defined as the work needed to separate two phases (a solid from a liquid one) connected through adhesion. Work of adhesion Wa depends on free energies in interfaces (Herceg, 1965) and can be described with the following eqation:

$$W_a = \gamma_{S.G} + \gamma_{L.G} - \gamma_{S.L} \qquad (1)$$

where $\gamma_{S.G}$ stands for free surface energy of the solid, $\gamma_{L.G}$ for the surface tension of the liquid, and $\gamma_{S.L}$ for the energy of the solid-liquid interface.

Since $\gamma_{S.G}$ and $\gamma_{S.L}$ are difficult to measure, it is rather difficult to calculate the work of adhesion by means of equation (1). It (W_a) is therefore usually worked out by means of equation (2), including the wetting angle and the surface tension of the wetting liquid. The wetting angle can be measured on the boundary of the three interfaces - the solid, liquid and gas one (Gray, 1962), as has been done here.

$$W_a = \gamma_{L.G}\,(1 + \cos\theta) \qquad (2)$$

Free surface energy has been measured according to the method introduced by (Zisman 1963), based on the measurement of the wetting angle for a number of liquids with different, but known values of surface tension $\gamma_{L.G}$. If $\cos\theta$ is presented as a function of $\gamma_{L.G}$, by extrapolating the line to the point where $\cos\theta = 1$, we can establish the parameter called critical surface energy γ_c, which provides a satisfactory approximation of free surface energy $\gamma_{S.G}$. Critical surface energy thus equals the particular surface tension of a liquid when the wood surface is fully wetted, that is to say when the condition $\gamma_{L.G} \leq \gamma_C$.

Zisman proved in his works that there is a linear relation between $\gamma_{L.G}$ and $\cos\theta$ for various liquids wetting a solid. The graph can be defined by equation (3):

$$\cos\theta = 1 + b\,(\gamma_C - \gamma_{L.G}) \qquad (3)$$

where b stands for the slope of the line, i.e. tg α.

Mechanical working of wood surface results in various degrees of roughness which bears on wetting and thereby adhesion (Bogner, 1991). The influence of roughness on wetting was first defined by Wenzel as early as in 1936. He has been quoted by numerous authors, such as (Collett 1972), (Voyutsky 1975) etc. Wenzel defined roughness as the ratio between the real area of a surface and its geometrical projection, which he presented by the foloowing equation:

$$r = A/a \qquad (4)$$

where r - roughness factor
A - real area of a surface
a - geometrical projection of a surface.

For ideally smooth surfaces roughness factors equals 1 (r=1), while for rough surfaces it holds that r>1.

By introducing roughness factor into Young's equation (5)

$$\cos\theta = (\gamma_{S,G} - \gamma_{S,L}) / \gamma_{L,G} \qquad (5)$$

we can work out the cosine of the wetting angle for rough surfaces, as is defined by equation (6):

$$\cos\theta' = r\cos\theta = r\,(\gamma_{S,G} - \gamma_{S,L}) / \gamma_{L,G} \qquad (6)$$

where θ' - wetting angle for a rough surface
θ - wetting angle for a smooth surface.

Equation (6) shows that roughness multiplies wetting, and thereby the surface energy of wood, so that the work of adhesion and adhesion itself get increased as well.

Derived from equation (6) is equation (7):

$$r = \cos\theta' / \cos\theta \qquad (7).$$

This paper describes a method for determining the optimum surface tension of a wood adhesive using the term "maximum work of adhesion" as a criteria. This criteria can then be further related to the optimum adhesive bonding of wood substrat.

2. MATERIAL AND METHODS
2. Materijal i metode

Specimens, sized 180x140x10 mm, were made of bech wood. all the measurements were taken at radial surfaces. The average ring width was 5.8 mm, density 730.79 kg/m^3. The specimens were conditioned to 10% water content. All the three specimens were first planed with a thicknessing machine. The first specimen was then sanded with a hand vibrator sander, sanding paper grit size 60; the second one was hand scraped, while the third specimen kept the planed surface.

Roughness measurement

The roughness of the surface of all the three specimens was measured and expressed as the average arithmetic deviation of the profile R_a. Measurement was performed at five different points on each specimen, always perpendicularly to the grain, with a TALYSURF 10 with low magnification pick-up profilograph, with the radius of the contact needle 12.5 μm.

Wetting angle measurement

On each specimen wetting angles for nine different liquids with varying surface tension were measured (Nguyen, 1978). For each liquid the angle was measured three times, at three different points, and the average value was subsequently calculated. The liquids and their respective surface tension are given in table 1.

Table 1
Kinds of liquid and their respective surface tension • Vrsta tekućine i njezina površinska napetost

Liquid	Ratio	Surface tension $\gamma_{L,G}$ (mN/m)
distilled water	-	72.400
glycerol	-	63.100
calcium chloride/water	5/95	70.001
calcium chloride/water	10/90	70.539
ethylene glycol/water	10/90	66.048
ethylene glycol/water	20/80	62.260
ethylene glycol/water	30/70	58.736
ethylene glycol/water	42.5/57.5	56.505
ethylene glycol/water	55/45	55.153

Surface tension of distilled water was measured with a capillary tube, while a stalagmometer was used for all other measurements.

Wetting angle measurement proceeded in the following way: a liquid was applied to a wood surface and the drop was then filmed, 20 times enlarged, with a video camera (Kalnins, 1988).

The liquids were applied with a microsyringe, in volume of 5 μl.

A 2-second recording was made, which was used later on to measure the width "a" and the height "h" of the drop, and on the basis of those values the wetting angle cosine was worked out.

3. RESULTS
3. Rezultati istraživanja

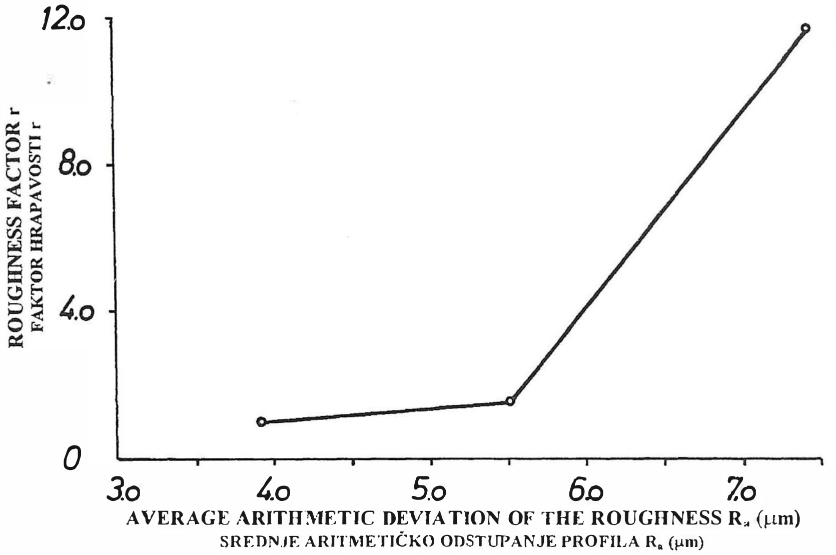
The values obtained through roughness measurement on the three specimens are presented in table 2 and figure 1.

Table 2
Roughness of wood surface and roughness factor • Hrapavost površine drva i faktor hrapavosti

	sanded No 60	planed	hand scraped
roughness R_a (μm)	7.4*	5.5	3.9
roughness factor r**	11.17	1.75	1.00

* the mean value for five measurements.
** the roughness factor r was calculated according to equation (7), cos θ being the one for surface worked out with a scraper (hand scraped), and for wetting angle measured by destilled water.

Fig. 1
Relation between the average arithmetic deviation of the surface roughness profile Ra and the roughness factor r for the sanded, planed and hand scraped surface • Odnos srednjeg aritmetičkog odstupanja profila R_a i faktora hrapavosti r za površinu drva obrađenu brušenjem, blanjanjem i postrugom



The results of the wetting angle measurement are presented in table 3.

Table 3
Wetting angle cosine for liquids with different surface tension on wood surfaces of different roughness • Cosinus kuta kvašenja za tekućine sa različitim površinskim napetostima na površini drva sa različitom hrapavošću

Surface tension of the liquid $\gamma_{L.G}$ (mN/m)	sanded No. 60	planed	hand scraped
	cos θ'	cos θ'	cos θ
72,400	0,659	0,103	0,059
70,539	0,773	0,049	0,130
70,001	0,727	0,054	0,254
66,048	0,903	0,486	0,459
63,100	0,880	0,602	0,627
62,260	0,948	0,665	0,566
58,736	0,993	0,787	0,706
56,505	0,996	0,837	0,764
55,153	0,996	0,903	0,787

The critical surface tension for all the three wood surfaces was established in the way already described. The results are presented graphically in figs. 2 - 4.

Figures 5-7 present the relation between the surface tension of a liquid $\gamma_{L.G}$ and the work of adhesion Wa for all the three wood surfaces researched, along with the calculation of the maxiumom work of adhesion Wa,max and the accompanying surface tension of the liquid $\gamma_{L.G.opt.}$ in text under figures.

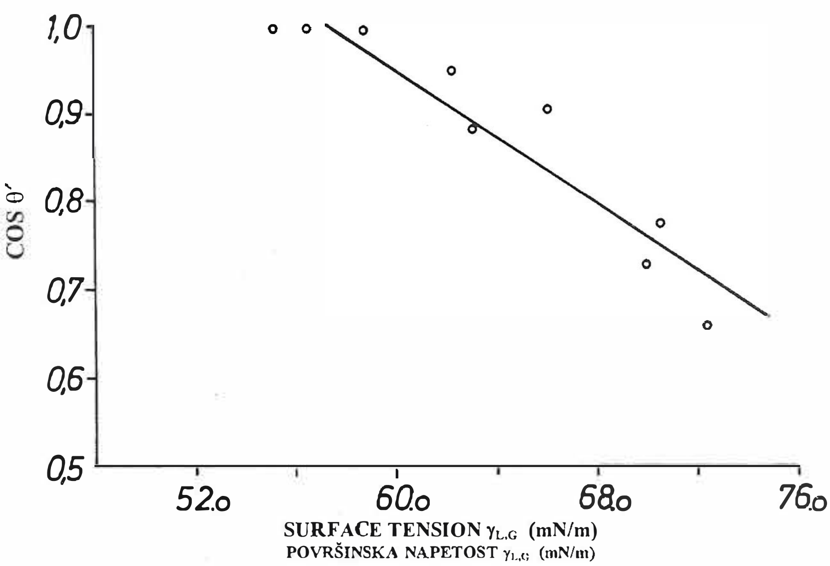
The maximum work of adhesion and the accompanying surface tension of the liquid can be worked out with the parabola equation for the given case. The maximum work of adhesion is described by equation (8), and the optimum surface tension of the liquid by equation (9):

$$W_{a,max} = (4ac - b^2)/4a \tag{8}$$

$$\gamma_{L.G.opt} = -b/2a \tag{9}$$

where a,b and c are constants of the parbola equation.

Fig. 2
Relation between surface tension $\gamma_{L,G}$ and cos θ' and the calculation of critical surface energy for the sanded surface; cos θ' = 2,0833 - 0,0189 $\gamma_{L,G}$; for cos θ' = 1, γ_C= 57,2 mN/m • Odnos površinske napetosti $\gamma_{L,G}$ i cos θ' uz proračun kritične površinske energije za površinu obrađenu brušenjem; cos θ' = 2,0833 - 0,0189 $\gamma_{L,G}$; for cos θ' = 1, γ_C= 57,2 mN/m



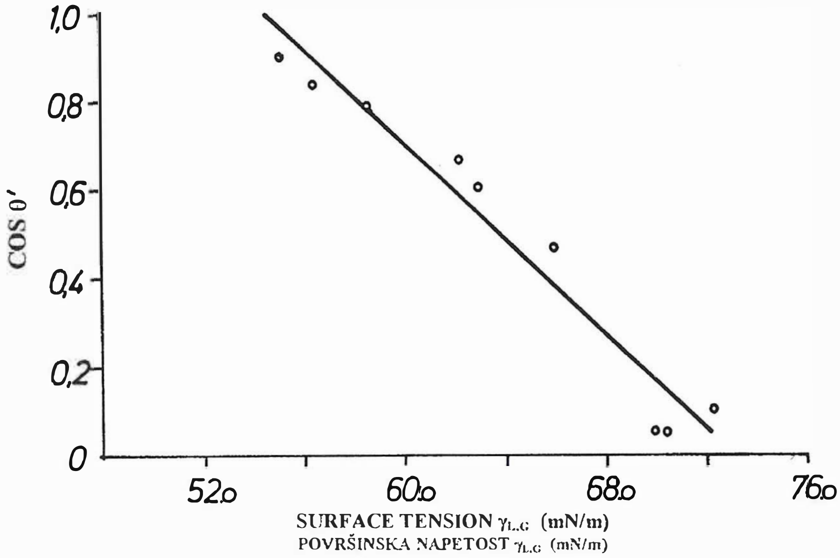


Fig. 3
Relation between surface tension $\gamma_{L,G}$ and $\cos\theta'$ and the calculation of critical surface energy for the planed surface; $\cos\theta' = 3{,}8983 - 0{,}0533\,\gamma_{L,G}$; for $\cos\theta' = 1$, $\gamma_C = 54{,}4$ mN/m • Odnos površinske napetosti $\gamma_{L,G}$ i $\cos\theta'$ uz proračun kritične površinske energije za površinu obrađenu brušenjem; $\cos\theta' = 3{,}8983 - 0{,}0533\,\gamma_{L,G}$; for $\cos\theta' = 1$, $\gamma_C = 54{,}4$ mN/m

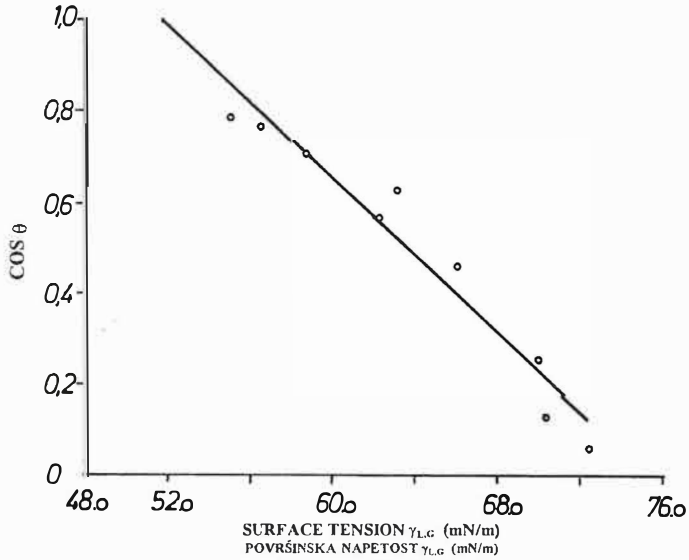


Fig. 4
Relation between surface tension $\gamma_{L,G}$ and $\cos\theta$ and the calculation of critical surface energy for the hand scraped surface; $\cos\theta = 3{,}1904 - 0{,}424\,\gamma_{L,G}$; for $\cos\theta = 1$, γ_C 51,6 mN/m • Odnos površinske napetosti $\gamma_{L,G}$ i $\cos\theta$ uz proračun kritične površinske energije za površinu obrađenu postrugom; $\cos\theta = 3{,}1904 - 0{,}424\,\gamma_{L,G}$; for $\cos\theta = 1$, γ_C 51,6 mN/m

Fig. 5

Relation between surface tension $\gamma_{L,G}$ and work of adhesion W_a for the sanded surface, and the calculation of maximum work of adhesion $W_{a,max}$ and optimum surface tension $\gamma_{L,G,opt}$ function equation: $W_a = -0{,}0885\ \gamma^2_{L,G} + 11{,}9414\ \gamma_{L,G} - 279{,}4$ vertex coordinates: $W_{a,max} = 123{,}40$ mN/m ; $\gamma_{L,Gopt} = 67{,}46$ mN/m • Odnos između površinske napetosti $\gamma_{L,G}$ i rada adhezije W_a, za brušenu površinu sa proračunom maksimalnog rada adhezije $W_{a,max}$ i optimalne površinske napetosti $\gamma_{L,G,opt}$ jednadžba funkcije: $W_a = -0{,}0885\ \gamma^2_{L,G} + 11{,}9414\ \gamma_{L,G} - 279{,}4$ koordinate vrha: $W_{a,max} = 123{,}40$ mN/m ; $\gamma_{L,Gopt} = 67{,}46$ mN/m

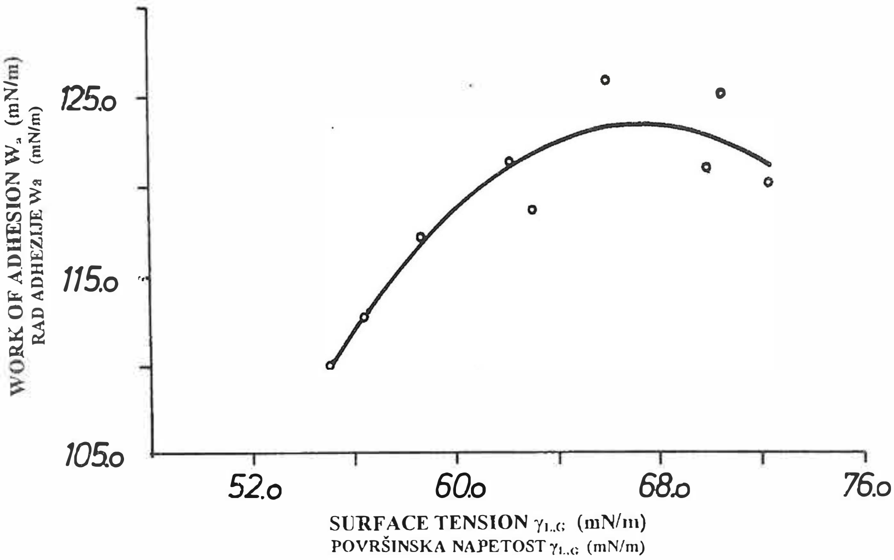
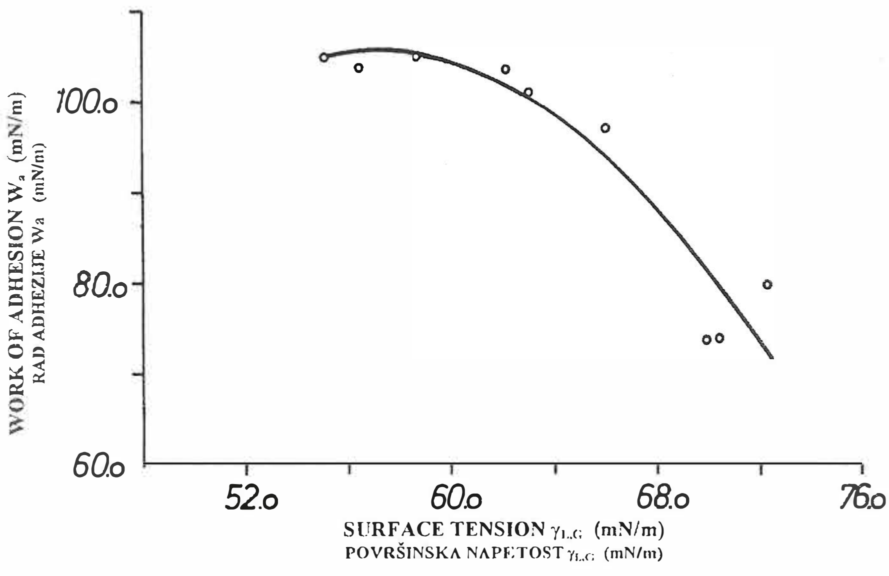


Fig. 6

Relation between surface tension $\gamma_{L,G}$ and work of adhesion W_a for the planed surface, and the calculation of maxiumom work of adhesion $W_{a,max}$ and optimum surface tension $\gamma_{L,G,opt}$ function equation: $W_a = -0{,}1409\ \gamma^2_{L,G} + 16{,}0467\ \gamma_{L,G} - 351{,}5$; vertex coordinates: $W_{a,max} = 105{,}39$ mN/m ; $\gamma_{L,G,opt} = 56{,}94$ mN/m • Odnos između površinske napetosti $\gamma_{L,G}$ i rada adhezije W_a, za brušenu površinu sa proračunom maksimalnog rada adhezije $W_{a,max}$ i optimalne površinske napetosti $\gamma_{L,G,opt}$ jednadžba funkcije: $W_a = -0{,}1409\ \gamma^2_{L,G} + 16{,}0467\ \gamma_{L,G} - 351{,}5$; koordinate vrha: $W_{a,max} = 105{,}39$ mN/m ; $\gamma_{L,G,opt} = 56.94$ mN/m



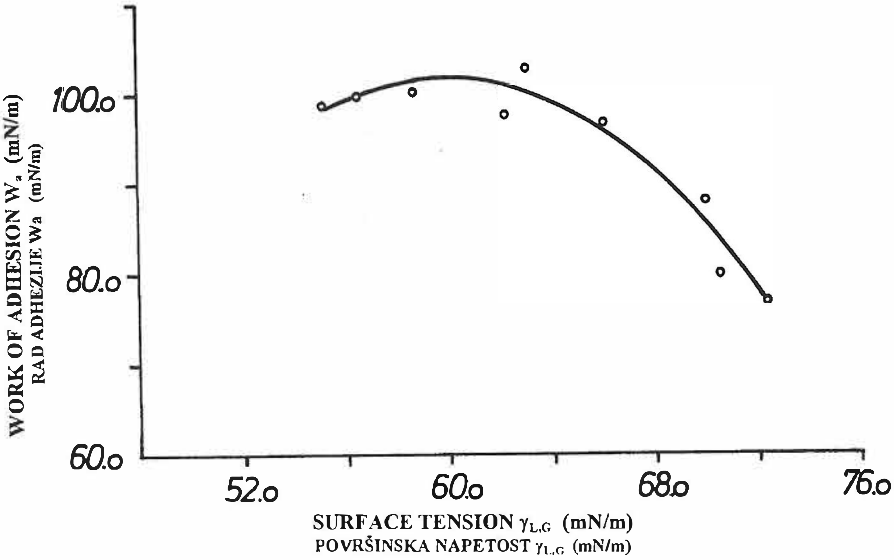


Fig. 7

Relation between surface tension $\gamma_{L,G}$ and work of adhesion W_a for the hand scraped surface, and the calculation of maximum work of adhesion $W_{a,max}$ and optimum surface tension $\gamma_{L,G,opt}$ function equation: $W_a = -0,1611\ \gamma^2_{L,G} + 19,2941\ \gamma_{L,G} - 476,3$ vertex coordinates: $W_{a,max} = 101,38$ mN/m ; $\gamma_{L,G,opt} = 59,88$ mN/m • Odnos između površinske napetosti $\gamma_{L,G}$ i rada adhezije W_a, za površinu obrađenu postrugom sa proračunom maksimalnog rada adhezije Wa,max i optimalne površinske napetosti $\gamma_{L,G,opt}$ jednadžba funkcije: $W_a = -0,1611\ \gamma^2_{L,G} + 19,2941\ \gamma_{L,G} - 476,3$; koordinate vrha: $W_{a,max} = 101,38$ mN/m ; $\gamma_{L,G,opt} = 59,88$ mN/m

4. DISCUSSION AND CONCLUSION
4. Diskusija i zaključak

An increase in the roughness of wood surface brings about an increase in roughness factor "r" (Fig. 1), which then has a positive influence on wetting and thereby on work of adhesion, and adhesion. In the experiment described here, it was a sanded surface of bech wood that had the highest roughness factor and that was the roughest. Further research on the impact of the roughness of various worked wood surfaces might provide solutions to a number of yet unanswered questions, such as what is the optimum roughness for a specific surface intended for gluing or varnishing, or what are the limits of the permissible roughness, or smoothness, that will not cause any considerable decrease in adhesion. We can by all means conclude that surface free energy of wood gets changed along with a change in roughness, and that in this experiment it increased whenever there was an increase in roughness.

This statement can be substantiated with critical surface energy values γ_C which indicate that the highest energy occurred with the roughest surface (i.e. the sanded one), the second highest with the planed surface, and that the lowest value was achieved with the scraped surface (c f. Fig. 2, 3 and 4).

Figures 5, 6 and 7 indicate that the realtion between surface tension $\gamma_{L,G}$ and the work of adhesion Wa has obtained the form of a parabola. If we, then, use the parabola equation to work out the coordinates of the vertex, we can establish the value for the surface tension of a liquid the shall result in maximum work of adhesion on the wood surface with specified characteristics (cf table 4).

Calculation of the vertex of the parabola, that is the relation between surface tension and work of adhesion, enables us to determine the surface tension of an adhesive. A method has been established that may result in the development of a procedure for maximizing the adhesion between wood speciments when an adhesive is used. However, while trying to achieve the optimum surface tension of an adhesive, we should bear in mind the rest of its characteristics and take care that they do not deteriorate.

Table 4

Maximum work of adhesion and optimum surface tension of the liquid • Maksimalni rad adhezije i optimalna površinska napetost tekućine

	sanded No 60	planed	scraped
Max work of adhesion $W_{a,max}$ (mN/m)	123,40	105,39	101,38
Optimum surface tension of the liquid $\gamma_{L,G,opet}$ (mN/m)	67,46	56,94	59,88

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