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PENETRATION OF UREA FORMALDEHYDE ADHESIVES IN WOOD TISSUE
Part II - Radial penetration of UF adhesives into Silver fir

Abstract: Penetration is the ability of the adhesive to move into the voids on the substrate surface or into the substrate itself. Wood's cellular nature allows significant penetration of the adhesive into the substrate. Objective of this work was the evaluation of the penetration and hence the distribution of urea-formaldehyde (UF) resins by means of microscopic detection of the penetration of such UF adhesives into the wood tissue. Tangentially cut 5 *mm* thick silver fir (*Abies alba* Mill.) plies, 100 *mm* long (parallel to the grain) and 30 *mm* width, were prepared for this study. Four types of UF resins with different degree of condensation were investigated in this research. Safranin was added to the resins and epi-fluorescence microscope was used for measuring the adhesive penetration. The UF adhesive mixes, consisting of the various resins, extender and hardener were applied to the surface of one ply. Two plies, one with applied adhesive mix and one without adhesive mix, were assembled with parallel grain direction. Samples were pressed in a hydraulic press at 120°*C* and 1.0 *MPa* for 15 minutes. Test-specimens of 20 μ*m* thickness were cut of each sample using a sliding microtome apparatus, exposing a bondline on a cross-sectional surface. The results show a significant correlation between the penetration behaviour and the degree of condensation (molecular sizes, viscosity) of the resins. The higher the degree of condensation, the lower the possibility for penetration, expresses as average penetration (AP) and as portion of filled tracheids on the whole cross section of interphase (filled interphase region FIR).

Key words: penetration, Silver fir (*Abies alba* Mill.), degree of condensation, urea-formaldehyde (UF) adhesive, fluorescence microscopy

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ПЕНЕТРАЦИЈА УРЕА-ФОРМАЛДЕХИДНОГ АДХЕЗИВА У ТКИВО ДРВЕТА

Део II: Радијална пенетрација УФ адхезива у дрво јеле

Извод: Пенетрација представља способност адхезива да улази у празнине на површини дрвета или у само дрво. Ћелијска природа дрвета омогућава значајну пенетрацију адхезива у ткиво дрвета. Предмет овог истраживања је процена пенетрације, а потом и дистрибуције уреа-формалдехидних (УФ) смола микроскопском детекцијом пенетрације одговарајућих УФ адхезива у ткиво дрвета. Тангенцијално резане дашчице (бочнице) дрвета обичне јеле (*Abies alba* Mill.) дебљине 5 *mm*, дужине 100 *mm* (паралелно са влакнима) и ширине 30 *mm* припремљене су за ово истраживање. У сврху овог истраживања коришћене су четири УФ смоле различитог степена поликондензације. У везива је додат сафранин пошто је за мерење дубине пенетрације адхезива коришћен епи-флуоресцентни микроскоп. УФ адхезиви, састављени од различитих смола, пуниоца и катализатора, нанешени су на површину једне плочице. Две дашчице, једна са и једна без адхезива, су слепљене у узорак тако да су им паралелна дрвна влакна. Узорци су пресовани у хидрауличној преси 15 *min* на температури од 120°*C* и притиску од 1,0 *MPa*. Попречни микротомски препарати, дебљине 20 μ*m* исечени су из сваког узорка на клизећем микротому. Резултати показују значајну зависност између пенетрације и степена кондензације (величине молекула, вискозитета) смоле. Што је већи степен кондензације, мања је могућност за пенетрацију, изражена као просечна пенетрација (ПП) и као удео испуњених трахеида у односу на целу зону лепљења (испуњеност зоне лепљења).

Кључне речи: пенетрација, обична јела (*Abies alba* Mill.), степен кондензације, уреа-формалдехидни (УФ) адхезив, флуоресцентна микроскопија

1. INTRODUCTION

Penetration is the ability of the adhesive to move into the lumens and cell walls. The filling of the lumens has long been one measure of penetration, but penetration can also involve the movement of the adhesive into the cell wall. Although it is generally known that proper penetration is important to strong bonds, it is not clear whether penetration into the lumens or the cell walls is more critical. Marra (1992) referred to penetration as a process of fluid movement. Mechanical interlocking, covalent bonding and secondary interactions have all been proposed as significant mechanisms (Marra, 1992, Wang, Yan, 2005). However, in each case adhesive penetration, and the associated intimate contact with internal surface, will play an important role. The penetration of adhesives into wood is most often examined at the cellular level. Some lumens have openings on the surface as a result of slope of grain so that the adhesive can flow into the lumen; this is more likely with larger diameter cells in softwood.

Factors that influence the filling of the lumens can be classified into those that are:

– Wood-related, such as diameter of the lumen and exposure on the wood surface;

– Adhesive-related, such as its viscosity and surface energy;
– Process-related, such as assembly time, temperature, pressure, moisture level.

In most bonding applications, adhesive penetration into the adherend does not occur to any great degree, but it is very important for wood. The proper degree of penetration influences both the formulation of the adhesive and the bonding conditions. The proper balance needs to be obtained in that poor bonds will result from either under- or over-penetration. In under-penetration, the adhesive is not able to move into the wood enough to give a strong wood-adhesive interaction. In contrast, with over-penetration so much of the adhesive moves into the wood that insufficient adhesive remains in the bondline to bridge between the wood surfaces, resulting in a starved joint. To solve these problems, the viscosity and composition of the adhesive can be adjusted (Frihart, 2005).

Though a large amount of information on resin penetration has been collected over the years using various techniques, the location of the penetrated resin under influence of resins with different levels of polycondensation is still largely unclear.

Former results concerning the penetration of urea-formaldehyde (UF) resins were reported by Scheikl and Dunky (1996, 1998), Brady and Kamke (1988) or others.

Despite of these existing results and experience, the lack of more exhausting research on the penetration of UF resins and adhesive mixes with different levels of polycondensation into wood tissue is evident and needs more attention, since these adhesive resins were the most important type of adhesives in the wood industry last 60 years (Miljković, 1993, Dunky, 2000).

Lumen penetration can be successfully examined by epi-fluorescence microscopy which is equipped with a three-component optical filter set. A high intensity, broadbend light source produces a wide spectrum of wavelength (Furuno, Saiki, 1988, Kamke, Lee, 2007). Typically, this type of technique involved adding a fluorescent marker into resin to make it visible.

Providing previously, the objective of this study was the evaluation of the penetration and hence the distribution of UF resins with different levels of polycondensation by means of microscopic detection of the penetration of such UF adhesives into the wood tissue.

2. EXPERIMENTAL

2.1. Materials

a) Samples and preparation of microtome sections

Tangentially cutted 5 *mm* thick silver fir wood (*Abies alba* Mill.) plies, 100 *mm* long (parallel to grain) and 30 *mm* width, were prepared for radial penetration. In order to have statistically representative results, silver fir plies were randomly selected. Before bonding, the wood plies were conditioned in standard climate conditions (T=20±2°C and φ=65±5%) causing moisture contents (MC) of 10%. The urea-formaldehyde (UF) adhesive was applied to the surface of one ply. Two plies (with and without adhesive) were assembled with parallel grain directions of two plies. Samples were pressed in a hydraulic press at 120°*C* and 1.0 *MPa* for 15 minutes.

After hot pressing, bonded samples were conditioned again in standard climate conditions. 20-μ*m*-thick microtome test specimens were prepared from different locations of each sample by a sliding microtome apparatus, exposing a bondline with a cross-sectional surface.

b) Urea-formaldehyde (UF) resins

Four types of laboratory UF resins with different degrees of condensation were provided for the investigations described here by DUKOL Ostrava, s r.o. (Ostrava, Czech Republic). The different degrees in condensation (DOC) were in progress from resin UF I (lowest DOC) to UF III (highest DOC). Resin UF IV had an equal degree of condensation as resin UF III, but urea was added at the end of the condensation step. The resins UF I, UF II and UF III had a molar ratio formaldehyde to urea (F/U) of 2.0, while for resin UF IV the molar ratio was F/U=1.45.

The resin mixes used in these investigations here and applied onto the various wood surfaces were prepared by addition of 10 mass % of wheat flour as extender and 0,05 mass % of safranin as marker (based on solid resin). The addition of ammonium sulphate as hardener was 0.5% for UF I and UF IV and 0.3% for UF II and UF III, both values expressed as solid ammonium sulphate on dry weight base.

Table 1. Characteristics of the resins and the prepared adhesive mixes UF I, UF II, UF III, and UF IV

Табела 1. Својства куповних и припремљених везива УФ I, УФ II, УФ III и УФ IV

№	Property Својство	Unit Јед. мере	Standard Стандард	Value Вредност							
				UF I		UF II		UF III		UF IV	
				A	B	A	B	A	B	A	B
1	Dry content Садржај суве супстанце	%	JUS H.K8.023	53.66	54.43	53.65	54.32	53.83	54.56	65.65	54.79
2	Brookfield viscosity (20°*C*) Вискозитет по Брукфилду (20°*C*)	*mPa*	JUS H.K8.022	218	545	281	745	555	1,644	2,052	460
3	Gel time Време желирања	*s*	JUS H.K8.025	58	59	59	60	58	59	59	61

Legend: A - resin, B - prepared adhesive mixes

Легенда: A - куповно везиво, B - припремљено везиво

For the experiments the same dry content and the same gel time of the prepared adhesive mixes were adjusted; this fact looked essential for the purpose of clear understanding and comparison of the penetration of the various adhesive mixes into wood tissue. The gel time was uniformed by addition of different quantity of the hardener, while the dry content was adjusted by addition of water (into UF IV only).

The prepared UF adhesive mixes were applied on the surface of one ply at a loading level of 200 $g{\cdot}m^{-2}$.

Table 1 shows the characteristics of both, the UF resins and the prepared adhesive mixes.

2.2. Methods

The interphase region of the adhesive bond is defined as the volume containing both, wood cells and adhesive (Brady, Kamke, 1988). The size of this interphase region was determined by measuring the depth of penetration of the adhesive. The average penetration (AP) was calculated as the mean value of individual penetration depths measured at 45 positions along the length (1,400 *μm*) of the bond line for each microtome slide section. The filled interphase region (FIR) was expressed as percentage of the ratio of the area covered by adhesive based on the total interphase region (including the unfilled lumen area).

Epi-fluorescence microscope (LEICA DM-LS) was used in this research for adhesive penetration measurement. The used set of optical filters consisted of 450 *nm* excitation filter, 510 *nm* dichromatic mirror, and a 515 *nm* emission filter. The image analysis system included a colour video camera (LEICA DC-300) and the image processor with analysis software (IM1000 by LEICA Microsystems, Heerbrugg, Switzerland).

3. RESULTS AND DISCUSSION

A silver fir structure representing the prosenchyma or fluid-conducting tissue which consists of the longitudinal tracheids, which make up the bulk of the structure (about 93%), and the parenchyma which includes mostly the ray parenchyma. The lumens of longitudinal tracheids are large enough to provide a good pathway for liquid-phase resin flow.

In this research dry content and gel time of the prepared adhesive mixes as well as loading level and press factors (press time, temperature, and pressure) were held constant.

The average depth of radial penetration as a function of viscosity (different degree of condensation) of the investigated UF adhesives is presented in Figure 1.

The degree of condensation increases from UF I (lowest degree) to UF III (highest degree). An indirect measure for this degree of condensation is shown as Brookfield viscosity (*mPa*) in Table 1. The viscosity of the prepared adhesive mixes rises from

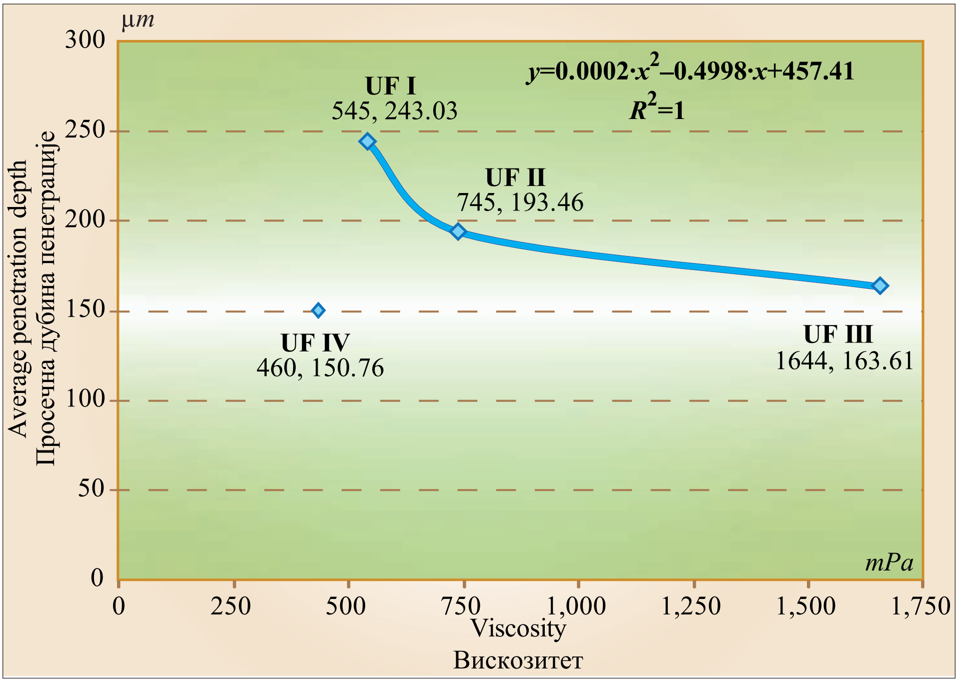

Figure 1. Average penetration depth (AP) as a function of viscosity (different degree of condensation) of the used UF adhesive

Слика 1. Просечна дубина пенетрације у зависности од вискозитета (различитог степена кондензације) УФ адхезива

545 *mPa* for UF I to 745 *mPa* for UF II and successively to 1,644 *mPa* for UF III. The higher the degree of condensation, the larger molecules are present in the resin and hence in the prepared adhesive mixes. The low molecular weight molecules of the adhesive should have penetrated deeper into the wood lumens, while high molecular weight molecules, or occlusions in the pits or lumens, may inhibit flow. Since it can be assumed that the penetration depends on the ratio of the average anatomical tracheid (lumen) diameters vs. the average size of resin molecules, the measured depths of penetration can be correlated with the viscosity of the resin. It is evident from Fig. 1

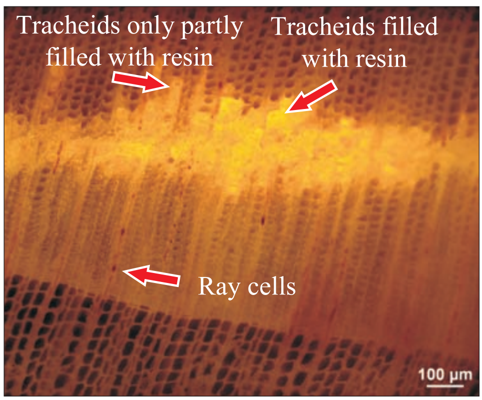

Figure2. Photomicrograph of UF I (with Safranin) bond line, using epi-fluorescence

Слика 2. Микрофотографија линије лепљења UF I са сафранином, помоћу епи-флуоресцентног микроскопа

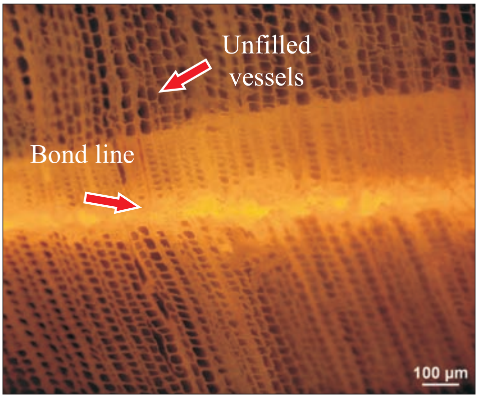

Figure 3. Photomicrograph of UF III (with Safranin) bond line, using epi-fluorescence.
Слика 3. Микрофотографија линије лепљења UF III са сафранином, помоћу епи-флуоресцентног микроскопа

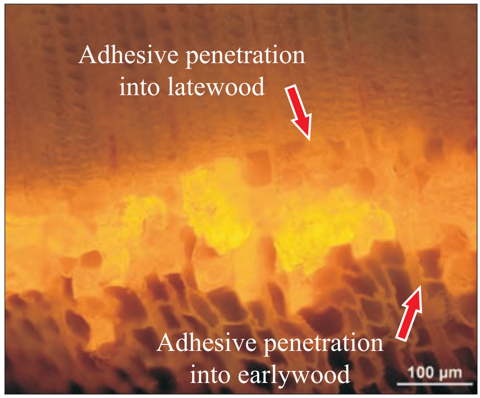

Figure 4. Photomicrograph of UF II (with Safranin) bond line, using epi-fluorescence
Слика 4. Микрофотографија линије лепљења UF II са сафранином, помоћу епи-флуоресцентног микроскопа

that the depth of penetration decreases with the increase of the viscosity, i.e. with higher degree of condensation and higher molecular sizes. It maybe speculated that the high molecular weight molecules of the adhesive induces pit aspiration, which occurs in softwoods because of theirs pits structure. This could be caused by capillary forses due to very small openings in the torus, which are generally invisible, but could exist as tortuous paths between the randomly oriented microfibrils of the torus. Since the openings are smaller than those in the margo, the resulting capillary force is greater and the dished torus aspirated pit.

The photomicrographs (Fig. 2 and Fig. 3) confirm the above mentioned results and show that the adhesive mixes fill the lumens of the tracheids.

Earlywood and latewood tracheids (with avarage diameter roughly from 40-60 µ*m* in earliwood and approximately half that size in latewood) are long, imperforated, narrow cells with tapered ends along the radial surfaces for a considerable portion of their lengths where they are in contact with other tracheids. Most of the intertracheid bordered pit pairs are situated along these tapered portions. Interconnecting pits are often adequate to permit resin flow, although the pit openings are very small in diameter compared with the lumens. The thickness of the pit membrane is an important dimension affecting flow resistance and the interpretation of flow data. Also there are half-bordered pit pairs permitting flow to adjacent ray parenchyma cells. Most of the radial penetration of adhesives is probably through the ray cells and between the longitudinal tracheids and rays (S i a u , 1984).

The photomicrograph (Fig. 4) shows greater penetration into earlywood than into latewood cells. It was expected since earlywood is generally of much lower density than latewood. The lumens are much larger and the cell-wall layers much thinner in earlywood. The radial diameter of tracheids is greatest in the earlywood, with the latewood

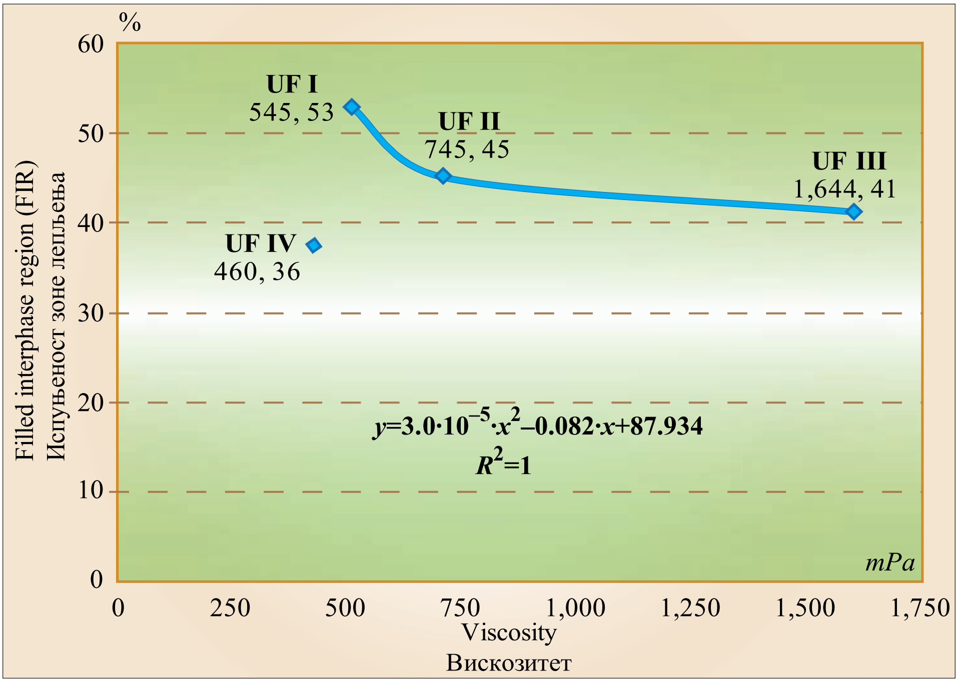

Figure 5. Percentage of filled interphase region (FIR) as a function of the viscosity (different degree of condensation) of the used UF adhesive

Слика 5. Процентуална испуњеност зоне лепљења у зависности од вискозитета (различитог степена поликондензације) УФ адхезива

having thicker-walled and narrow cells. There are smaller and fewer pits in latewood tracheids than in earlywood. The number of pits per tracheids varies from 50-300 in earlywood, while fewer in latewood.

The measured AP depth was nearly triple less into latewood; for UF I adhesive was 89,16 μ*m* and for UF II was 64,07 μ*m*.

The percentage of filled interphase region as a function of viscosity (different degree of condensation) of the used UF resins is illustrated in Figure 5.

The filled interphase region as well as the depth of penetration show a strict correlation to the degree of condensation and hence the viscosity of the investigated resins (Fig. 5). The filled interphase region decreases with increased viscosity, i.e. with a higher degree of condensation and higher molecular size.

Adhesive UF IV shows a different behaviour; FIR and AP are low (Fig. 1 and Fig. 5) since it differs in its composition from the other three adhesives. After dilution the viscosity of the adhesive mix based on resin UF IV was the lowest one in the row (460 *mPa*) although its degree of condensation is similar to resin UF III. Due to these differences a direct comparison of the results is not possible.

4. CONCLUSION

Epi-fluorescence microscopic was shown as a suitable technique for the determination of adhesive penetration into wood substance.

The depth of average radial penetration (AP) of urea formaldehyde (UF) adhesive mixes of different viscosity into fir tissue decreases with increasing of UF viscosity (degree of polycondensation). Penetration depends on the ratio of the average anatomical tracheid diameters vs. the average size of the adhesive molecules. It might be speculated that high molecular weight molecules of the adhesive induces pit aspiration. This was caused by capillary forses due to very small openings in the torus.

The average penetration (AP) depth was nearly triple less into latewood, since the latewood had thicker-wall and narrow cells with smaller and fewer pits of tracheids than earlywood.

The effect of adhesive penetration was expressed by the portion of partly or fully filled anatomical cells of wood tissues in the interphase region. On the basis of the results of this study, it might be concluded that the filled interphase region (FIR) also decreases with increase of adhesive viscosity. For the three analysed adhesives (UF I to UF III) AP and FIR show a clear correlation, whereas adhesive UF IV showed low AP and FIR because of its different composition from the other three adhesives.

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ПЕНЕТРАЦИЈА УРЕА-ФОРМАЛДЕХИДНОГ АДХЕЗИВА У ТКИВО ДРВЕТА
Део II: Радијална пенетрација УФ адхезива у дрво јеле

Резиме

Епи-флоресцентни микроскоп се показао да је одговарајућа техника за одређивање пенетрације адхезива у дрвно ткиво.

Просечна дубина радијалне пенетрације уреаформалдехидних адхезива различите вискозитета у ткиво јеле опада са порастом вискозитета (различити степен кондензације). Пенетрација зависи од односа пречника трахеида као анатомских елемената и средње величине молекула адхезива. Може се предпоставити да молекули адхезива велике масе изазивају аспирацију јамица због капиларних сила које се јављају услед веома малих отвора на порусу.

Просечна дубина пенетрације била је приближно три пута мања у касном дрвету зато што су трахеиде касног дрвета задебљалих зидова и уских лумена са много мање јамица простог типа у односу на рано дрво.

Ефекат адхезивне пенетрације је изражен као удео делимично и потпуно испуњених анатомских елемената дрвног ткива у зони лепљења. На основу резултата овог истраживања може се закључити да испуњеност зоне лепљења такође опада са повећањем вискозитета адхезива, док је адхезив УФ IV, због његове различите формулације у односу на остала три адхезива, показивао ниже вредности просечне пенетрације и испуњености зоне лепљења.