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Assessment of Wood Photodegradation by Microtensile Testing

Određivanje fotodegradacije drva mikroispitivanjem vlačne čvrstoće*

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ABSTRACT • *The susceptibility to weathering of wood surfaces and their consequential high maintenance demands discourage the exterior use of wood and highlight the need for methods of enhancing the resistance of wood to photodegradation. Weathering processes in the surface layers of wood have been studied by measurement of the tensile strength changes occurring in 75 μm thick softwood strips during exposure to natural weathering or several regimes of artificial weathering. Microtensile testing at zero and 10 mm span enabled the relative changes in cellulose microfibril strength and the lignin-dependent properties of the matrix to be distinguished. The technique was found to offer a rapid, accurate and reproducible means of evaluating the chemical and structural changes involved in the weathering of wood and coated wood surfaces during weathering.*

Tensile strength curves indicated three phases in the degradation process. The initial phase was characterised by a slow rate of strength loss, and at high humidity levels even an increase in strength. During the second and third phases believed to be associated with the successive degradation of lignin and cellulose, strangth losses were more rapid. Differences in the weathering behaviour of three softwood species were distinuished, and temperature, moisture and radiation source shown to exert strong influences on degradation rate. Artificial weathering was found to provide a valid alternative to natural weathering in systematic investigation of degradation mechanisms.

SEM studies revealed that structural changes in the wood are associated with the early stages of photodegradation. Fractography showed that the progression of degradation involves the development of brittleness and reduction of stress transfer capabilities through lignin degradation, followed by reductions in microfibril strength resulting from cellulose degradation.

Key words: *softwoods, photodegradation, tensile strength, SEM, fractography.*

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SAŽETAK • *Podložnost površina drva prirodnom propadanju i primjereni visoki zahtjevi za obnavljanjem obeshrabruju upotrebu drva u vanjskom prostoru i naglašavaju potrebu uvođenja metoda poboljšanja postojanosti drva na svjetlosnu razgradnju. Proces starenja površinskih slojeva drva proučavan je mjerenjem promjena vlačne čvrstoće 75 µm debelih odsječaka drva četinjača tijekom prirodnog izlaganja te izlaganja nekolicini umjetnih klimatskih režima. Mikroispitivanje vlačne čvrstoće pri razmaku hvatišta od 0 i 10 mm omogućuje razlikovanje relativnih promjena čvrstoće celuloznih mikrofibrila i čvrstoće cjelokupne drvne strukture na koju poglavito utječu ligninske komponente. Ta se tehnika pokazala brzom, točnom i ponovljivom metodom za procjenu kemijskih i strukturnih promjena koje se zbijaju tijekom starenja drva i površinski obrađenih drvenih površina.*

Krivulje promjena vlačne čvrstoće upućuju na tri faze u procesu razgradnje. Početna je faza karakterizirana malim gubitkom čvrstoće, pri visokoj vlažnosti čvrstoća se može čak i povećati. Gubitak čvrstoće izrazitiji je tijekom druge i treće faze, za koje se vjeruje da su povezane sa susljednim razdobljima pretežno ligninske, a zatim celulozne razgradnje. Uočene su razlike u ponašanju tokom izlaganja triju vrsti četinjača. Pokazalo se da temperatura, uvjeti vlažnosti i vrsta zračenja izrazito utječu na intenzitet razgradnje. Utvrđeno je da umjetno klimatsko izlaganje osigurava valjanu zamjenu za prirodno izlaganje za potrebe sustavnog ispitivanja mehanizama razgradnje.

Istraživanje elektronskim mikroskopom (SEM) otkrilo je da su strukturne promjene drva povezane s ranim fazama svjetlosne razgradnje. Analiza lomne površine pokazala je da tijek procesa degradacije obuhvaća razvoj krtosti zbog razgradnje lignina, a time i smanjenje sposobnosti prijenosa naprezanja. Nakon toga slijedi i smanjenje čvrstoće mikrofibrila zbog razgradnje celuloze.

***Ključne riječi:** četinjače, svjetlosna razgradnja, čvrstoća na vlak, SEM, fraktografija.*

1. INTRODUCTION
1. Uvod

Exterior wooden joinery has experienced a marked decline in market share in the last 10 years due to poor performance of paints and a perceived susceptibility to rot. Wood remains nonetheless the only natural, renewable and energy-efficient construction material available to man and offers major economic, technical and environmental advantages over alternative materials. The successful re-establishment of wood for external joinery depends in large part upon exploiting the results of research to improve the weather resistance and durability of wood as a substrate and to extend the service life of decorative and protective exterior wood coatings.

All unifinished timber building components and those finished with semi-transparent and transparent wood coatings suffer surface degradation from the effects of sunlight. Although the reactions, manifested as discolouration and erosion, are restricted to a shallow surface layer and do not affect the basic properties of the wooden component, they seriously impair the performance of surface coatings and lead to increased maintenance demands.

Early work at the BRE (Building Research Establishent, UK) indicated that the measurement of tensile changes in thin wood strips (which represent the sections of the wood surface layer) could be used for investigation of the wood photodegradation phenomenon (Derbyshire, Miller 1981). The technique has been extensively applied by other workers in studies of the weather degradation of wood surfaces (Evans, Banks 1988, Evans 1989, Evans et al. 1992). Subsequent work at BRE (Derbyshire et al. 1995 a) has established the benefits to be gained from the use of short-span tensile testing for monitoring degradation, and has shown that the method offers a rapid, accurate and reproducible means of evaluating the chemical and structural changes involved in the weathering of wood and coated wood surfaces.

SPECIES a) *Vrsta drva* a)	DENSITY at *Gustoća pri* 20 °C 60% r.h. (g/cm³)	No of latewood bands per 10 mm *Broj zona kasnog drva na 10 mm*	ULTIMATE TENSILE LOAD *Vlačno opterećenje kod loma* (N)	
			SPAN BETWEEN THE JAWS *Razmak hvatišta*	
			Zero span (0mm)	10 mm span
SPH	480±10	3-4	73.0	60.8
SPS for artif. weathering *za umjetno izlaganje*	440±10	3-4	70.4	39.7
SPS for nat. weathering *za prirodno izlaganje*	540±20	4-5	72.8	51.4
NS	340±10	3-4	66.6	47.0
WRC	340±10	15-20	31.4	19.5

Table 1. *Relevant characteristics of the tested timber species after conditioning at 20±2 °C, 60±5% r. h.* • *Osnovne značajke ispitivanih vrsta drva nakon kondicioniranja kod 20±2 °C, 60±5% r. v. z.*

a) SPS, SPH - Scots pine (bijela borovina) - *Pinus silvestris;* SPS - sapwood (bjeljika), SPH - heartwood (srž)
NS - Norway spruce (smrekovina) - *Picea abies;*
WRC - Western red cedar (tujovina) - *Thuja plicata.*

This paper reviews the essential features of the thin strip method for assessing photodegradation of wood and presents results from a study of the influence of moisture on the degradation of several wood species during natural and artificial weathering. Also included are results of SEM investigations on weathered strips which illustrate the nature of the structural changes associated with the deterioration in strength properties. The influence of coatings will be referred to in subsequent papers.

2. MATERIALS AND METHODS
2. Materijal i metode

2.1 Thin strip preparation
2.1 Priprema tankih odsječaka

The essence of the method is the exposure of thin radial wood sections to natural or artificial weathering. Degradation of the wood is assessed from changes in the tensile strength of batches of strips withdrawn at regular intervals during the weathering period.

The careful preparation, selection and batching of the thin strips in crucial to minimizing variability and ensuring reliable results. Full details of the procedures developed at BRE have been reported by Derbyshire et al. (1995a).

In these trials three species were used: Scots pine (*Pinus sylvestris* L.) assessed as heartwood and sapwood; Norway spruce (*Picea abies* L.) and Western red cedar (*Thuja plicata* Don.). General material properties as determined on at least 10 replicates per measurement are given in Table 1. Three end- matched blocks of each species were selected and sectioned to give radial strips measuring 100 mm (longitudinal) x 10 mm (radial) with a nominal thickness of 80 μm.

2.2 Weathering
2.2 Klimatsko izlaganje

For natural weathering the strips were mounted on aluminium frames, backed with white filter paper and exposed horizontally at the BRE site (South-East England, 52°N, 70 m above sea level) between August and November 1993.

Artificial weathering was carried out in the QUV (Q-Panel Co) fitted with eight UVA-340 fluorescent lamps. The spectral output of these lamps is concentrated in the ultraviolet region of the spectrum between 300 and 400 nm with peak output at 340 nm.

Thin strips were fixed to aluminium panels suitable for mounting in the QUV apparatus. The QUV was operated to give a range of moisture conditions as follows:

QUV1 **Constant dry conditions** (stalni suhi uvjeti): 57±2 °C, 29± 3% relative humidity

QUV2 **Cycling between dry and wet conditions** (izmjena suhih i vlažnih uvjeta): QUV1 for 2 hours 30 minutes followed by 30 minutes condensation with the lamps off (30±3 °C, 100% relative humidity)

QUV3 **Constant high humidity conditions** (stalni uvjeti visoke vlažnosti): 57± 2 °C, 90 ± 5% relative humidity

QUV4 **Constant wet conditions** (stalno mokro izlaganje): permanent condensation with strips kept fully wet, 57± 2 °C, 100% relative humidity.

2.3 Tensile testing
2.3 Ispitivanje vlačne čvrstoće

Tensile tests were carried out using a Pulmac short span tensile tester. The ultimate breaking load of the strips was determined at zero and 10 mm span. In the zero span test where the jaws are initially set in contact, all the microfibrils in the cross section bridge the gap between the jaws and the test is basically a measure of microfibril, essentially cellulose, strength. The 10 mm span test measures matrix properties and the strength is to a greater extent determined by the strength of the lignin intercellular material and the degree of fibre bonding.

Normally two zero span and two 10 mm span tests were carried out on each strip, and mean values of 10 measurements were calculated for the batch.

2.4 SEM examination
2.4 Mikroskopsko (SEM) ispitivanje

After being tested for tensile strength some samples were randomly chosen for SEM examination in preparation for which they were vacuum coated with a layer of platinum. The field-emission scanning electron microscope (FE-SEM) used was a JEOL JSM 6300 F located at EMPA, which offered the advantages of high magnification at an accelerating voltage of 5 kV, low enough to avoid damage to the wood tissue.

3. RESULTS
3. Rezultati

3.1 Comparison of photodegradation during natural and artificial weathering
3.1 Usporedba fotodegradacije tokom prirodnog i umjetnog izlaganja

Figures 1 a and 1 b show the strength loss of pine sapwood for natural weathering and for exposure in the QUV apparatus at high humidity (QUV3).

The similarity in the shape of the two curves shows clearly that artificial weathering reproduces the changes which occur during natural weathering but at an accelerated rate. For the graphs shown in Figures la and 1b the approximate acceleration factor was calculated to be 2.5.

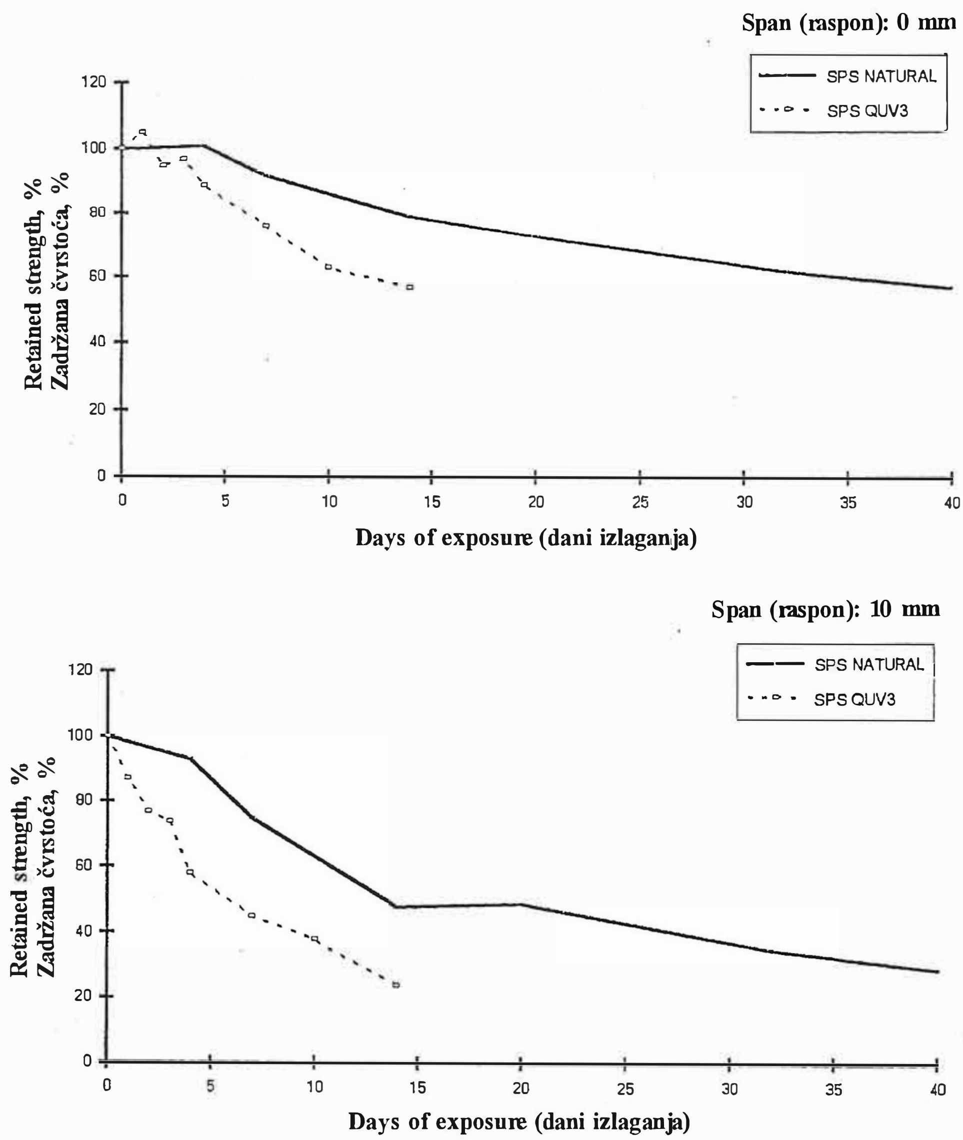


Figure 1
Zero span (fig. 1a) and 10 mm span (fig. 1b) tensile strength loss of Scots pine sapwood strips in natural and artificial weathering trials • Gubitak vlačne čvrstoće kod raspona hvatišta 0 mm (sl. 1a) i 10 mm (sl. 1b) listića bjeljike bijele borovine kod prirodnog i umjetnog izlaganja

3.2 QUV exposure of different species under low humidity conditions
3.2 QUV izlaganje različitih vrsta drva pri uvjetima niske vlažnosti

Figures 2a and 2b present the results of the QUV exposure trial at very low humidity (QUV1) conditions for the three softwood species. It will be evident that the strength loss curves for the 10 mm span tests show greater initial slope than the curves in the zero span tests. This is interpreted as the more rapid degradation of the lignin component in the early stages of weathering.

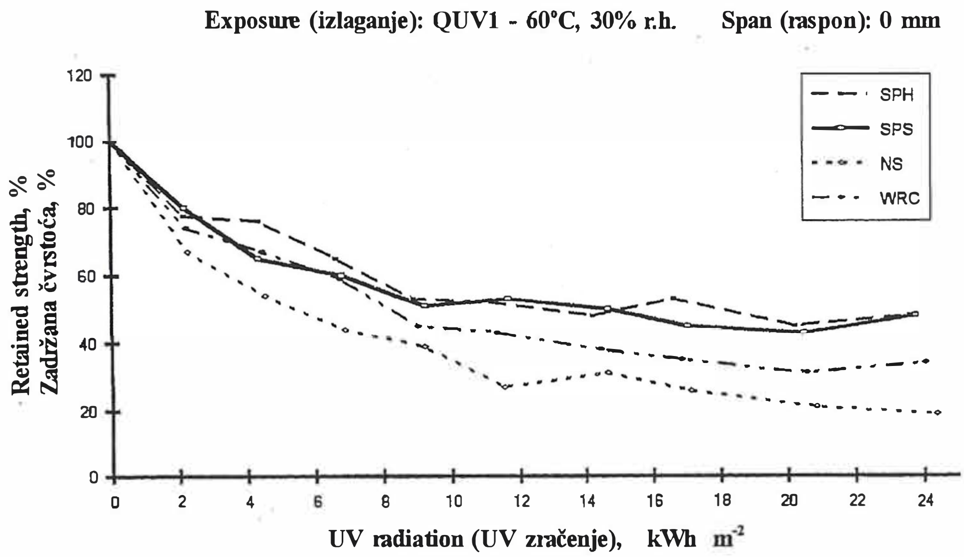
It is also clear from Figures 2a and 2b that the method can discriminate the weathering resistance of the different species. It was found that the species were ranked consistently in the same order, with pine sapwood showing more rapid degradation than pine heartwood.Western red cedar showed more rapid degradation than pine but the highest degradation rates of all were consistently shown by Norway spruce.

3.3 Influence of moisture on degradation rates
3.3 Utjecaj vlažnosti na intenzitet razgradnje

Figures 3a and 3b show the effect of moisture on photodegradation rates for the specific case of pine sapwood. Weathering regimes QUV1 to QUV4 provided successively higher levels of moisture content in the strips. It can be seen that in dry conditions (QUV1) the strength loss took place continuously but very slowly, strength tending to level out in the final stage of the test.

The introduction of short intermittent periods of condensation (QUV2) caused strength to decrease more rapidly and there was a corresponding reduction in the final value. In some instances in zero span tests, this more rapid strength loss was preceded by a short period at the start of the exposure when strength changed very little and the curve showed a slight "shoulder".

When the level of moisture was further increased by exposure to 90 % r. h. (QUV3) or to



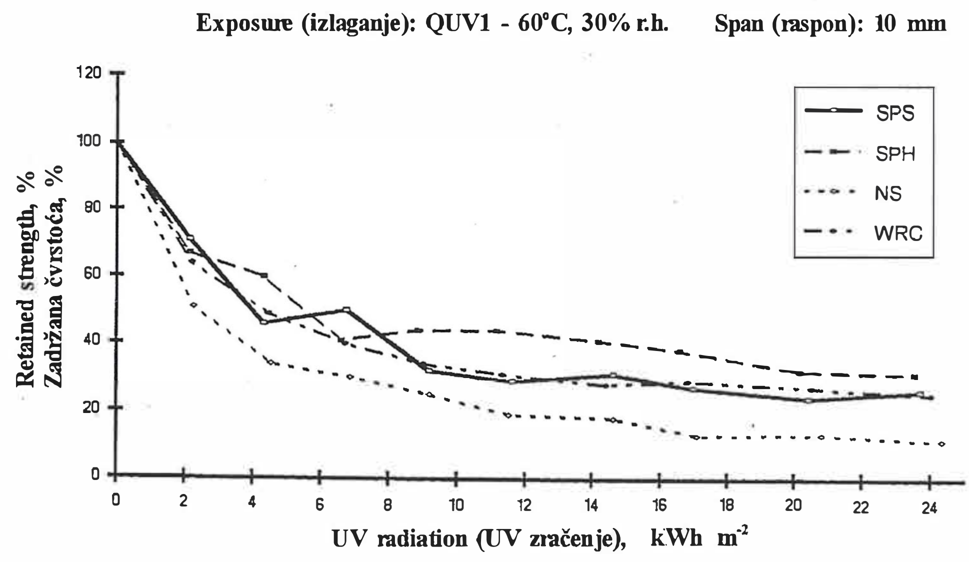


Figure 2
Zero span (fig.2a) and 10 mm span (fig. 2b) tensile strength loss of thin strips during QUV 1 exposure. • Gubitak vlačne čvrstoće kod raspona hvatišta od 0 mm (sl. 2a) i 10 mm (sl. 2b) tankih odsječaka tokom QUV 1 izlaganja.
SPS - Scots pine sapwood - bjeljika bijele borovine
SPH - Scots pine heartwood - srž bijele borovine
NS - Norway spruce - smrekovina
WRC - Western red cedar - tujovina

liquid water (QUV4) these trends developed. The shoulder in the strength change curve increased and was followed by a more rapid strength loss. The phenomenon was evident in pine heartwood and sapwood, less evident in Norway spruce and was absent in Western redcedar. This behaviour was usually observed in the zero span tests but was only shown by pine at high levels of moisture in the 10 mm span tests.

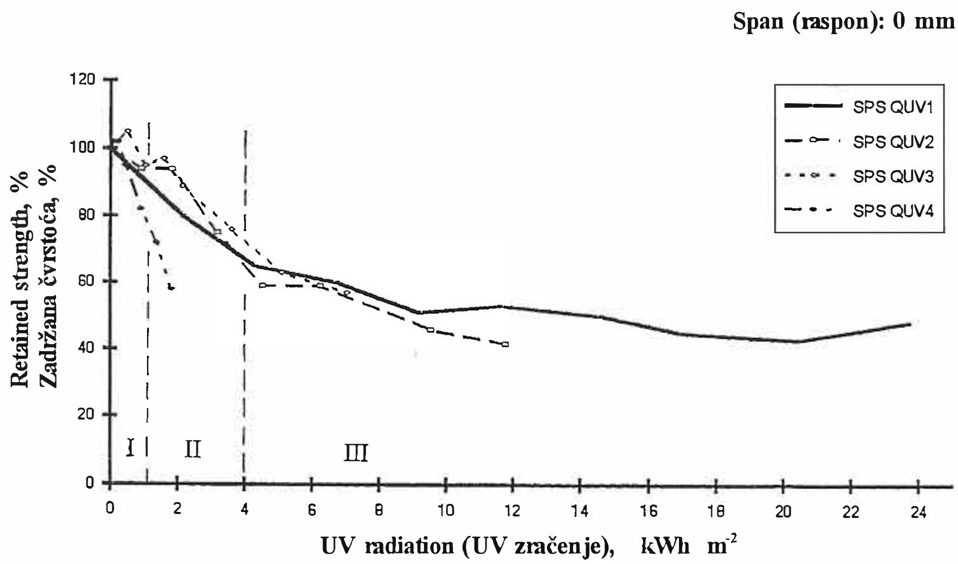
4. DISCUSSION OF STRENGTH CHANGES
4. Diskusija o promjenama čvrstoće

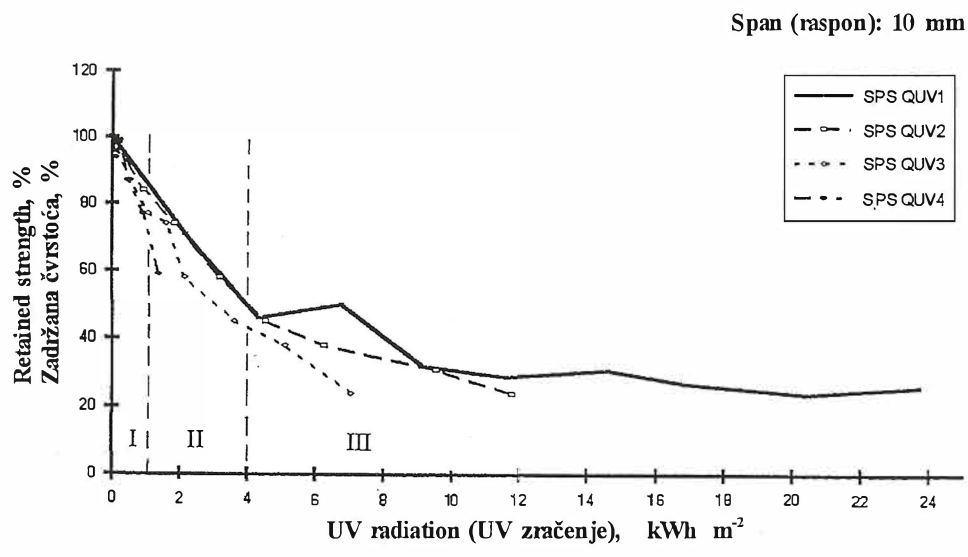
The strength changes described above reflect the complex chemical changes that occur during photodegradation in wood when water molecules penetrate the cell wall. The results suggest that two competing reactions occur in the initial stages of weathering, one resulting in a decrease in tensile strength due to chain scission and weakening of interfibre bonding, and the other resulting in an increase in tensile strength. The second process could be some form of crosslinking. The fact that the shoulder is more frequently observed in zero span tests suggests that this second process has a strong influence on microfibril cellulose strength. It would appear that the more rapid strength loss associated with breakdown of the lignin-rich middle lamella and outer layers of the cell wall is the predominant influence in the 10 mm span tests since in these tests the shoulder is rarely observed.

The strength changes suggest three phases in the photodegradation process. Behaviour in the initial phase is seen to be affected by exposure conditions and also differs according to timber species. Strength may be observed to increase, desrease or change very little as described above.

The consistent strength losses which follow the initial phase appear to occur in two phases, with a higher rate of degradation in the second phase and a lower rate in the final

Figure 3
Zero span (fig. 3a) and 10 mm span (fig. 3b) tensile strength loss of Scots pine sapwood (SPS) strips at various humidity levels in QUV exposures • Gubitak vlačne čvrstoće kod raspona hvatišta 0 mm (sl. 3a) i 10 mm (sl. 3b) listića bjeljike bijele borovine kod QUV izlaganja pri raznim uvjetima vlažnosti





phase. This could reflect the presence of two components in the wood, one being more photo-susceptible than the other. It is possible that these two components could be associated with earlywood and latewood regions, since earlywood is known to be more photo-susceptible than latewood. However, the differences in the zero and 10 mm span tests suggest that the two components are more likely to be represented by the crystalline cellulose microfibrils and the surrounding sheath of hemicellulose and lignin, the latter being the more photo-susceptible material.

5. SEM INVESTIGATIONS
5. Sem mikroskopska ispitaivanja

Scanning electron microscopy of tansverse fracture surfaces has provided insight into changes in the anatomical structure of wood occurring during weathering. The best results have beenobtained from strips tested at 10 mm span, which are unaffected by the clamping pressure imposed by the jaws.

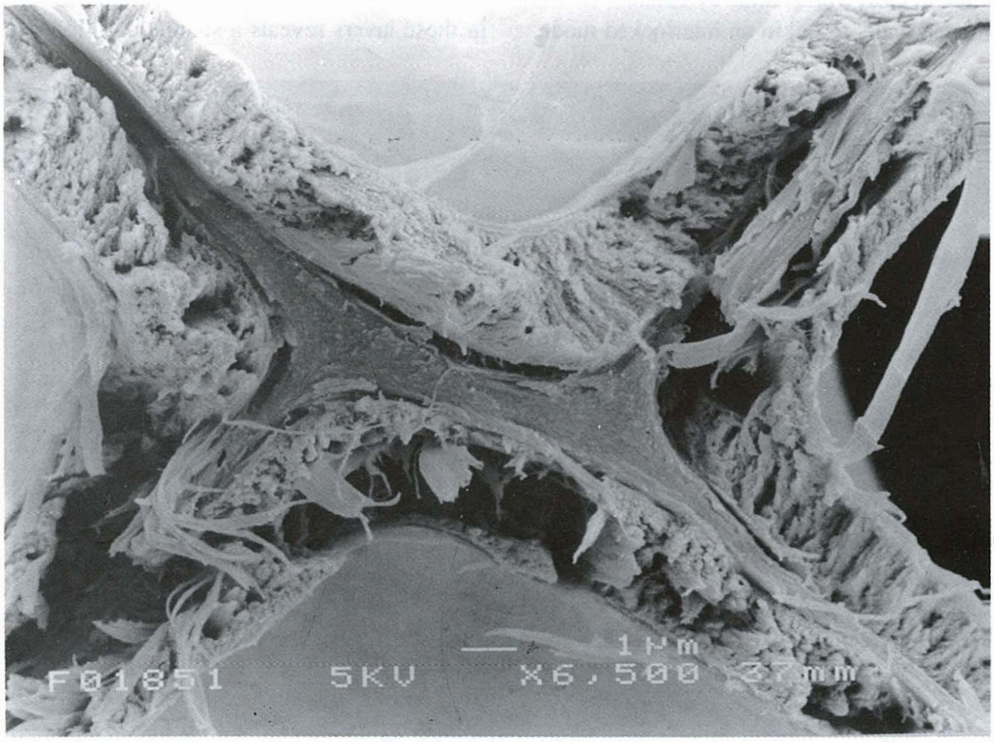


Figure 4
Spruce earlywood tracheids, unweathered (initial strength). Mag. 6.500:1 • Traheide ranog drva smrekovine, neizložene (početna čvrstoća). Pov. 6.500:1

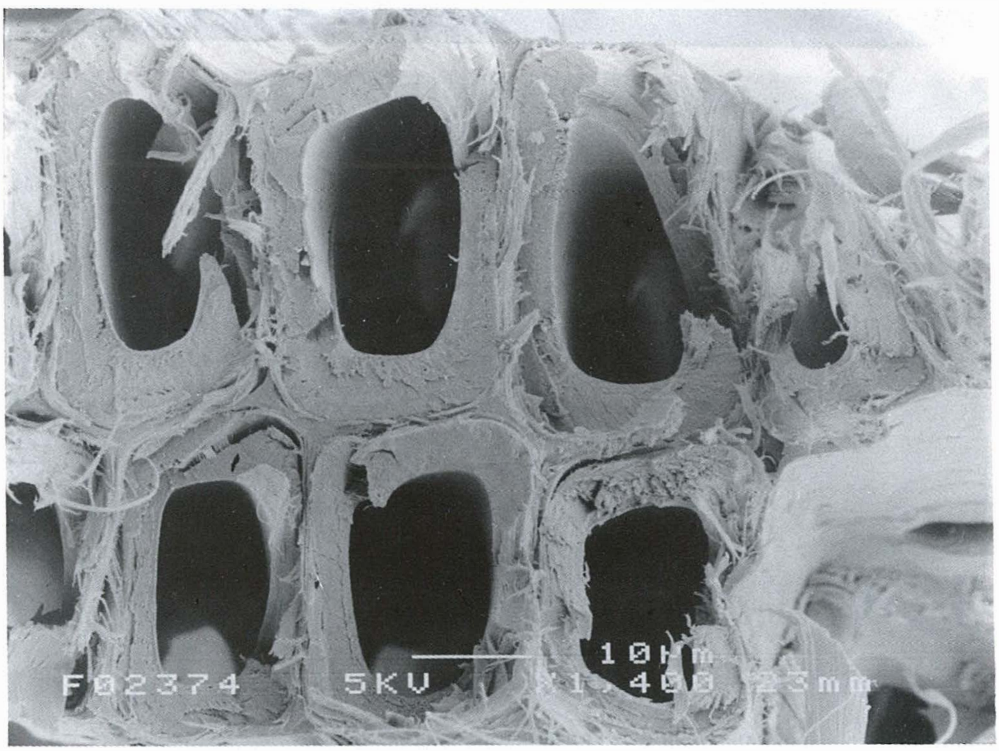


Figure 5
Spruce latewood tracheids, unweathered (initial strength). Mag 1400:1.Sl • Traheide kasnog drva smrekovine, neizložene (početna čvrstoća). Pov. 1400:1

Typical results are illustrated in Figures 4-9.

In general unweathered material tested in tension exhibits interlocked type of failure. However, in certain regions it seems that the failure of the unweathered wood is initiated in the weakest points in the latewood, from where it spreads perpendicular to the load axis, leaving crack surfaces smooth and "brash-like", as shown in Figure 5. As the crack develops in a stepwise fashion and the critical stress is released, microfibril agglomerations are torn apart. Progression of the crack in earlywood bands by contrast causes the cell walls to fail in an interlocked mode, without smooth crack surfaces (Figure 4). Radial agglomerations of microfibrils in the S2 layer can be seen and removal of some of these bundles results in voids in the cell wall.

Delamination due to elastic deformations and rapid and intense stress relaxations regularly occurs in both earlywood (Fig. 4) and latewood (Fig.5) between the middle lamella (ML) and the primary wall (P) or between the P and the S1 layers. P and S1 layers exhibit interlocked characteristics and are often torn out in woolly fibrous bundles. The bond between the less inclined microfibrils in these layers reveals a sound condition of

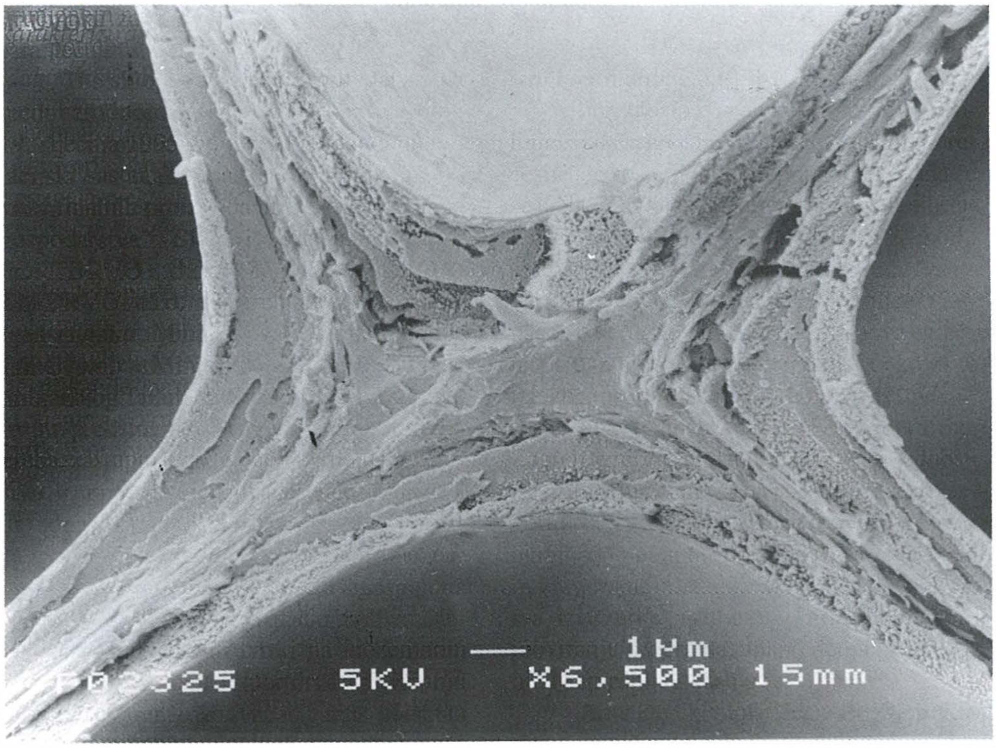


Figure 6
Pine sapwood earlywood tracheids, weathered in QUV 3 for 72 hrs: 56 % retained initial strength. Mag. 6.500:1. • Traheide ranog drva bjeljike borovine izlagane 72 h u QUV3 režimu: 56 % početne čvrstoće. Pov. 6.500:1

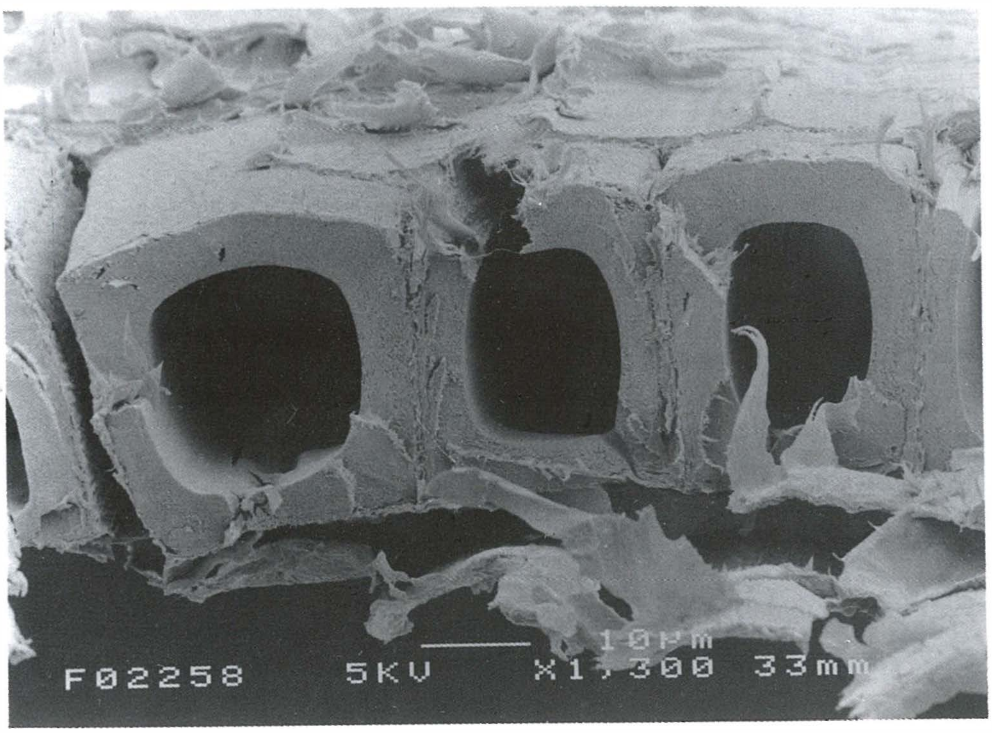


Figure 7
Pine latewood tracheids, weathered naturally for 41 days, 40 % retained initial strength. Mag. 1300:1. • Traheide kasnog drva borovine, prirodno izlagane 41 dan, 40 % početne čvrstoće

the lignin and hemicellulose components, the concentration of which is much higher here than in the S2 layer. These fractographic observations support recent detailed investigations of transverse tensile fractures of tracheids reported by Zimmermann et al. (1994) and indicate that the mechanical failure of thin strips in tension does not differ from that of solid wood.

The consequences of weathering on structure are presented in Figs 6 & 7. It seems that at 50-60 per cent strength loss, corresponding to the transition from the second to the third degradation phase, lignin breakdown is well advanced. The middle lamella is badly degraded and partially lost (Fig.7). The contraction of the wood substance following lignin loss is particularly obvious from the brittle failure and smooth crack surface evident in earlywood cell walls (Figure 6).

Values of strength loss of over 60 per cent are associated with the third phase of degradation. Since rates of strength loss at zero and 10 mm span are similar it is assumed that interfibre bonding plays a minor role and that strength changes are associated predomi-

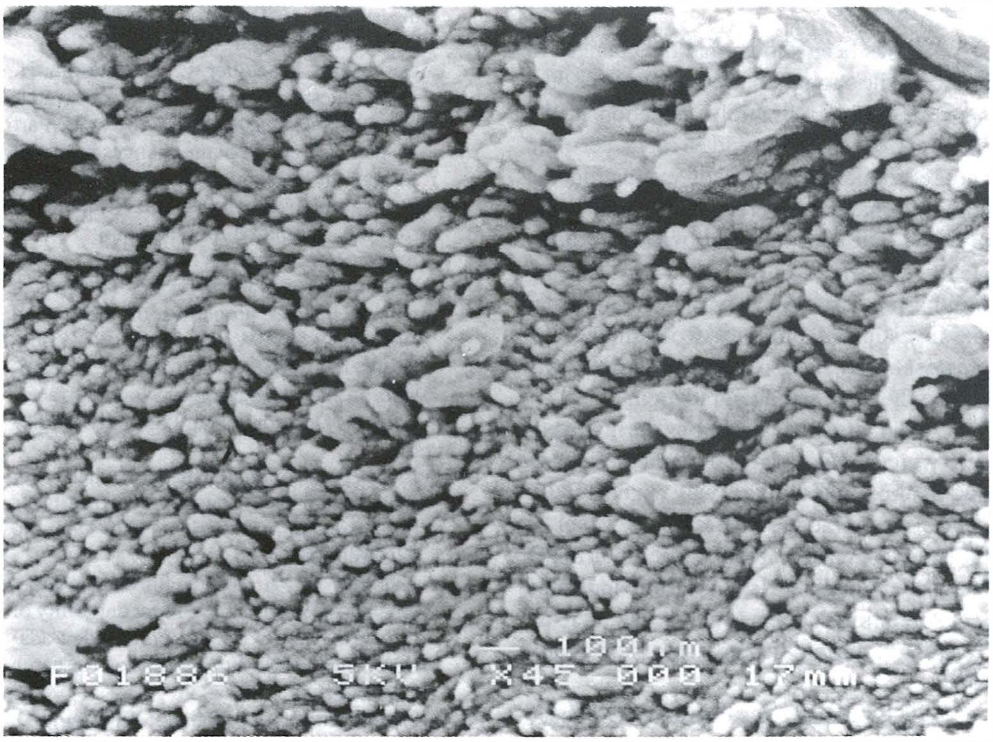


Figure 8
Pine latewood tracheid, S2 layer, inweathered. Mag. 45.000:1 • S2 podsloj traheide kasnog drva borovine, neizlagano. Pov. 45.000:1

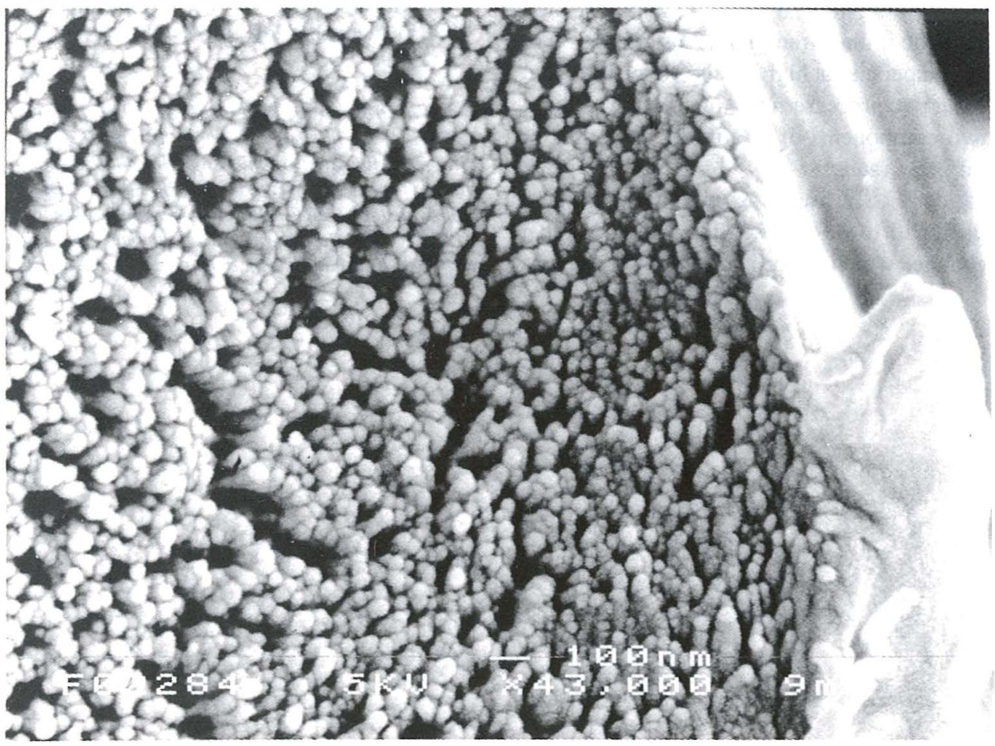


Figure 9
Pine latewood tracheid, S2/S3 layers, weathered naturally for 41 days (40 % retained initial strength). Mag. 43.000:1 • Traheide kasnog drva borovine (S2/S3 podsloj), prirodno izlagane 41 dan, 40 % početne čvrstoće

nantly with cellulose breakdown. Comparison of the unexposed latewood S2 cell wall layer (Fig.8) and of that which has suffered 60 per cent strength loss (Fig.9) shows that destruction of the lignin matrix results in micro-voids between single microfibrils. The microfibrils also exhibit more brittle failure, in that they are rarely bound to each other and also exhibit blunt tips (Fig.9). This supports the conclusion of more intensive cellulose degradation in the final stages of weathering.

6.CONCLUSIONS
6. Zaključci

It has been shown that the changes in microtensile strength of thin wood strips during exposure to ultraviolet radiation in the QUV apparatus can provide a rapid, accurate and reproducible means of evaluating the complex changes involved in the weathering of wood. The method has proved to be sufficiently sensitive to distinguish the differing weathering resistance of the softwood species investigated. Pine heartwood showed the greatest weathering resistance and Norway spruce the most rapid degradation.

The moisture conditions during exposure were shown to have a marked effect on degradation rates; there was a general increase in degradation rates as the level of moisture increased. Tests carried out under exposure to high levels of moisture indicated that some timber species exhibit an increase in strength during the early stages of weathering.

The strength loss curves were consistent with three simultaneous weathering processes. The first process was associated with the initial strength increase observed in some spepcies at high levels of moisture. The other two processes were interpreted as being two components of the timber degrading at different rates.

FE SEM analysis was shown to be a powerful tool for observing the anatomical changes which underlie the strength changes and has considerably increased the information to be gained from investigations of photodegradation using thin wood strips.

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