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SEM Micrographs of Spruce Wood Impregnated with Imersol-Aqua and Acrylic Varnished

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Abstract: The aim of this study is to understand the mechanism of change in color of wood by impregnation and varnishing processes with SEM micrographs. Even tough the wood has many advanced properties; humidity is an important disadvantage for wood in use. Wood is impregnated and varnished with some special chemicals to overcome these disadvantages. In impregnation process, the impregnation material is placed to the wood cell and shows a keeping impact. In varnishing, the surface of wood is covered with the varnishing chemicals to keep the wood from external impacts. Some chemical and physical properties of wood are developed by those processes. So, to understand the mechanism this interaction is very important. Impregnation and varnishing changes the yellow color tone of wood. Use of these materials more than needed will cause to increase in production costs and also will create some environmentally bad results. In this study, cell structure of Oriental spruce (*Picea orientalis* Link.) wood impregnated and varnished is observed by scanning electron microscopy. The graphs taken by SEM are discussed to understand the mechanism of change in color. It is understood that the change in color of wood by impregnation and varnishing is due to the cypermethrin in Imersol-aqua. So, SEM micrograph technique may be used in analyzing the reasons of change in physical and mechanical properties of woods.

Key words: Oriental spruce, impregnation, acrylic varnishing, yellow color tone, scanning electron microscopy

INTRODUCTION

The wood has many advanced properties, but humidity is an important disadvantage for wood in use. Wood is impregnated, dried and varnished with some special chemicals to overcome these disadvantages (Rowell and Konkol, 1987; Feist, 1990). Drying of wood may lead to readily observable impacts on wood like macro scale cracks and decrease of mechanical properties (Laura *et al*., 2007). In a study of Thuvander *et al*. (2001) the tensile strength parallel to the grain for wood impregnated in the green state was compared with that for ordinary dried wood and for wood impregnated after drying. Data demonstrate significantly higher strength for wood impregnated in the green state. It is postulated that this is due to damage in the cell walls of non-impregnated wood where the damage is induced by the drying stresses. Support for this hypothesis is also presented in the form of fractography results taken at SEM (scanning electron microscopy). This study is very important that cell structure had been started to be studied by SEM. Wallström and Linberg (1997) studied the penetration of bulking chemicals like glycerol, Poyethylene glocal PEG 200, PEG 1500 and pentaerythritol to the cell wall by SEM technique. According to the SEM micrographs, the cell thickness of wood showed a greater cell wall bulking.

In another study done by Atar *et al*. (2007) the effects of impregnation with Imersol-aqua on yellow color tone of Scotch pine (*Pinus sylvestris* L.), Uludağ fir (*Abies bornmuelleriana* Mattf.) and Oriental spruce and varnishes were searched. According to the results of that study impregnation process, impregnation period and varnishes applied to wood showed an increasing impact on yellow color tone value of wood materials. The impact of impregnation with Imersol-aqua on yellow color tone of Oriental beech (*Fagus orientalis* Lipsky) and European oak (*Quercus petrea* Liebl.) was studied by Çolakoğlu (2006). Keskin and Atar (2007) studied the effects of impregnation with Timbercare Aqua on the red and yellow color tone of Oriental beech, European oak, Scotch pine, Oriental spruce and Uludag fir woods and some varnishes. After impregnation, wood surfaces have been coated by Sayerlack parquet varnish (Sp), Sayerlack interior varnish (Si) and Sayerlack exterior varnish (Se) and the red and yellow color tone of samples after varnishing process was determined. As a result, the value of red color tone was the highest in Oriental beech and the lowest in Uludag fir. For the interaction of wood material, impregnation material and varnish, the red color tone value was the highest in Oriental beech + Tc + Sp but, the lowest in Uludag fir + Tc + Si. The value of the yellow color tone was the highest in Scotch pine and the lowest in Oriental beech. For the wood material, impregnation material and varnish interaction, the yellow color tone value was the highest in Oriental spruce+Tc +Sp and the lowest in Oriental beech+Tc+Si. This effect may be due to the impacts of impregnation chemical on wood extractives and color pigments in varnish. Jörg *et al.* (2003) studied the lignin distribution in cell walls of spruce and beech wood by high-voltage Transmission-Electron-Microscopy (TEM) in sections stained with potassium permanganate as well as by Field-Emission-Scanning-Electron-Microscopy (FE-SEM) combined with a back-scattered electron detector on mercerized specimens. The SEM is a new technique based on the mercerization of lignin and the concomitant visualization of mercury by Back-Scattered Electron Microscopy (BSE). Due to this combination it was possible to obtain a visualized overview of the lignin distribution across the different layers of the cell wall. This combined method was used the first time to analyze the lignin distribution in cell walls. In agreement with previous work the highest lignin levels were found in the compound middle lamella and the cell corners. Back-scattered FE-SEM allows the lignin distribution in the pit membrane of bordered pits as well as in the various cell wall layers to be shown. In addition, by using TEM as well as SEM we observed that lignin closely follows the cellulose micro fibril orientation in the secondary cell wall. From these observations, it was conclude that the polymerization of monolignols is affected by the arrangement of the polysaccharides which constitute the cell wall. Bariska and Pizzi (1986) studied the interaction of polyflavonoid tannis with wood cell walls by SEM. It was observed that the overall shrinkage was reduced and the damages due to drying were lessened.

In this study, spruce wood impregnated with Imersol-aqua by short, medium and long term dipping and acrylic varnished has been observed at cell level by SEM. The aim of this study is to try to understand the mechanism of change in yellow color tone by impregnation and varnishing through cell micrographs taken by SEM.

MATERIALS AND METHODS

This study is conducted at Gazi University Furniture and Decoration Department Laboratory and Erciyes University Technology Research and Application Center SEM Laboratory in 2009.

Wood material: The wood of Oriental spruce was chosen randomly from timber merchants of Ankara, Turkey. Special emphasis is given for the selection of the wood material. Accordingly, non-deficient, proper, knotless, normally grown (without zone line, without reaction wood and without decay, insect mushroom damages) wood materials were selected. Test samples are kept at 20±2°C and 65±3% relative humidity conditions up to reaching to 12% humidity ratio according to Turkish Standard TS 345 (1974) and TS 4176 (1984). Later on, the samples are dried at a maximum temperature of 50°C until reaching to the humidity ratio as defined in TS 2472 (TS 2472, 1976). The densities of wood samples measured according to TS 2472 for different drying and impregnation methods are given in Table 1 (Atar *et al.*, 2007).

Table 1: Densities of wood material

Type	Impregnation method	Density (g cm^{-3})
Oven	Control	0.405
	Short-term dipping	0.408
	Middle-term dipping	0.409
	Long-term dipping	0.414
Air	Control	0.420
	Short-term dipping	0.428
	Middle-term dipping	0.437
	Long-term dipping	0.440

Impregnation material: Imersol-aqua used as an impregnation material in this study was supplied from Hemel Hickson Timber Products, Istanbul. Imersol-aqua is a nonflammable, odorless, fluent, water-based, completely soluble in water, non-corrosive material with a pH value of 7 and a density of 1.03 g cm^{-3}. It is available as a ready-to-use solution. It contains 0.5% w/w tebuconazole ($C_{16}H_{22}ClN_3O$), 0.5% w/w propiconazole ($C_{15}H_{17}Cl_2N_3O_2$), 1% w/w 3-Iodo-2-propynyl-butyl carbamate ($C_8H_{12}INO_2$) and 0.5% w/w cypermethrin ($C_{22}H_{19}Cl_2NO_3$). Tebuconazole and propiconazole are triazole group of fungicides used to treat plant pathogenic fungi. 3-Iodo-2-propynyl-butyl carbamate is a water repellent fungicide. Cypermethrin is a synthetic compound used as an insecticide. Before the application of Imersol-aqua on the wood material, all kinds of drilling, cutting, turning and milling operations should be completed and the relative humidity should be in equilibrium with the test environment. In the impregnation process, dipping duration should be at least 6 min. The impregnation pool must contain at least 15 L of impregnation material for 1 m^3 of wood. The impregnated wood should be left for drying at least 24 h. The wood material can be painted, varnished or glued after it is fully dried (Hickson's IA Datasheet, 2000).

Oriental spruce wood was impregnated with Imersol-aqua by short, medium and long term dipping method according to ASTM D 1413 (1976). Retention amounts of impregnation material by wood for different dipping durations are given in Table 2 (Atar *et al.*, 2007).

Table 2: Retention amounts of wood materials

Impregnation method	Dipping duration	Retention amount (kg m^{-3})
Short-term dipping	6 min	32.785
Middle-term dipping	2 h	51.285
Long-term dipping	7 days	156.915

Table 3: Some properties of acrylic varnish

Properties	Value
pH (filler layer)	4.30
pH (finishing layer)	4.60
Density-filler layer (g cm^{-3}) at 20°C	0.95
Density-finishing layer (g cm^{-3}) at 20°C	0.97
Viscosity (sn DINCup/4 mm)	18.00
Amount applied (g^{-2})	120.00
Nozzle gap (mm) in application	1.80
Air pressure (bar) in application	2.00

Table 4: Yellow color tones of impregnated and varnished spruce wood

Material	Yellow color tone
Spruce wood	29.53
Spruce wood + Short term impregnation	43.81
Spruce wood + Medium term impregnation	34.64
Spruce wood + Long term impregnation	35.54
Spruce wood + Short term impregnation + Ac varnished	45.10
Spruce wood + Medium term impregnation + Ac varnished	23.28
Spruce wood + Long term impregnation+ Ac varnished	36.49

Acrylic varnish: Impregnated test specimens were varnished with Dewilux acrylic varnish ($C_{13}N_3H_{12}O_2$) according to ASTM D 3023 (1981). Some properties of acrylic varnish are given in Table 3 (Dewilux Technical Bulletin, 2009). The varnish layer thickness was measured as 92.14 µm (Atar *et al*., 2007).

Yellow color tones: Yellow color tones of impregnated and varnished wood samples measured by Atar (2007) are given in Table 4 according to ASTM D 2244-094u (2003). As shown in the table, the highest yellow color tone was obtained by short-term impregnation and varnishing (45.10). In medium-term impregnation, yellow color tone decreases (23.28). It increases again in long-term impregnation (36.49) but not reaching to short-term dipping level. Varnishing with acrylic varnish increases the yellow color tone of spruce wood (Atar *et al*., 2007).

Impregnation of Oriental beech and European oak with Imersol-aqua and varnishing with acrylic, polyurethane or synthetic varnishes showed the similar impact on yellow color tone of wood samples (Çolakoğlu, 2006).

Scanning electron microscopy: In this study, scanning electron microscopy model Leo 440 at Erciyes University Technology Research and Application Center was used. SEM works with electron diffraction method. The micrographs are taken with 250 to 40000 magnifications. The dimension at those magnification intervals is in between 1 to 100 µm. High Temperature (HT) value is 20.00 kV and detector area is 10 mm^2. The tube of SEM is Oxford 7060 model with a resolution of 138 eV to 5.9 keV. The samples studied in SEM are prepared with scattering method by covering 80% Au + 20% palladium with a thickness of 10 nm as maximum in Poloran SC7620 Mini Sputter Coater. The test samples for SEM were cut with Struers Minitom at 200 rpm.

Method of testing: It is observed in literature that, impregnation and varnishing have a positive impact on physical and mechanical properties of wood. Those properties are studied generally by physical and mechanical testing methods, but not studied at cell level. So, in this study the following micrographs of wood cell are taken by SEM:

- Micrographs of wood cells vertical to fibers without any chemical process
- Micrographs of wood cells parallel to fibers without any chemical process
- Micrographs of wood cells impregnated by short term dipping and varnished
- Micrographs of wood cells impregnated by medium term dipping and varnished
- Micrographs of wood cells impregnated by long term dipping and varnished
- Surface micrographs of thin layer varnishing
- Surface micrographs of thick layer varnishing
- Energy Dispersive (EDX) micrographs of varnish layer and impregnated wood cells parallel to fibers

The EDX X-ray analysis is a technique used for identifying the elemental composition of a specimen, or an area of interest as an integrated feature of a SEM. During EDX analysis, the specimen is bombarded with an electron beam inside SEM. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. In doing so, however, the transferring outer electron must give up some of its energy by emitting an X-ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

RESULTS AND DISCUSSION

Some SEM micrographs of spruce wood cells taken at Leo 440 are given. As working with SEM the surfaces must be smooth so to be furnished, but due to the properties of wood it was impossible. The polishing operation would cause to destroying the varnish layer and wash out the impregnation materials. So we tried to cut the test samples with minitome at low rpm.

In Fig. 1, the micrographs of control sample wood cells perpendicular to fibers without any process are given. The micrographs are taken by SE - Secondary Electrons detector. As shown in micrographs, there is no chemical material of impregnation and varnishing. The dimensions of cells can be estimated with the scale given under the micrographs. The dimensions of cells are approximately 15 to 25 μm which is compatible with the literature.

In Fig. 2, the micrographs of wood cells parallel to fibers without any chemical process are given. The fibers with no chemicals of impregnation or varnishing are also observed very clearly in those micrographs.

In Fig. 3, the micrographs of wood cells impregnated by short term dipping and than varnished with acrylic varnish are given. In the micrographs placed at the top, the thicknesses of varnish layers are shown. According to this, the thicknesses of thin and thick layers are 36.87 and 93.49 μm at the measured points. The boundaries of varnish layers can be observed in micrographs if there is more than one layer. So, the thickness in thick layer is approximately 3 times of thin layer. Impregnation material particles can be observed as imbedded in the upper parts of varnish layer. The retention amounts in short term dipping is 0.032785 g cm^{-3}, in medium term dipping 0.051285 and 0.156915 g cm^{-3} in long term dipping. This means that in long term dipping the amount of retention of impregnation material by wood is approximately 3 times of medium term and 5 times of short term dipping. The dimension of impregnation material particles are around 2 μm. They are defined by the EDX analysis according to the Cl existing in tebuconazole, propiconazole and cypermethrin and Iodo existing in 3-Iodo-2-propynyl-butyl carbonate of Imersol-aqua.

In Fig. 4, the micrographs of wood cells impregnated by medium term dipping and varnished are given. The concentration of impregnation particles embedded in varnish layer and wood cells is more than the short term dipping one.

In Fig. 5, the micrographs of wood cells impregnated by long term dipping and varnished are given. The thickness of varnish layer in this sample is 88.33 μm as shown in the micrograph with a 250 magnification at 20 kW EHT with QBSD-Quadrant Back Scattering Detector. The concentration of impregnation particles

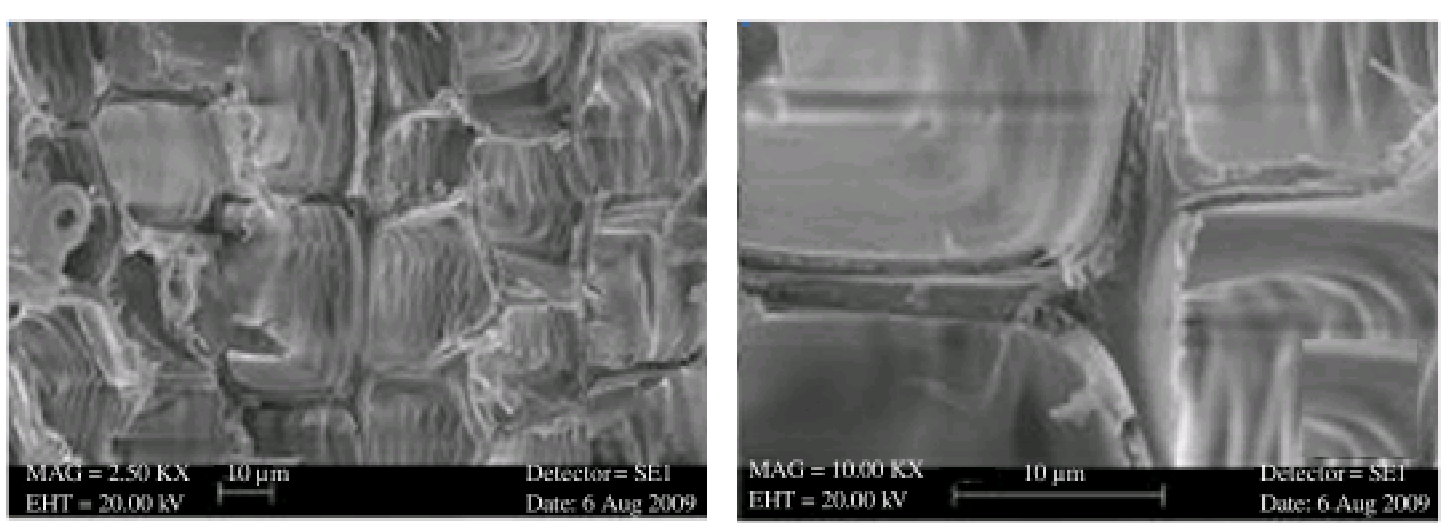

Fig. 1: Micrographs of wood cells vertical to fibers without any chemical process

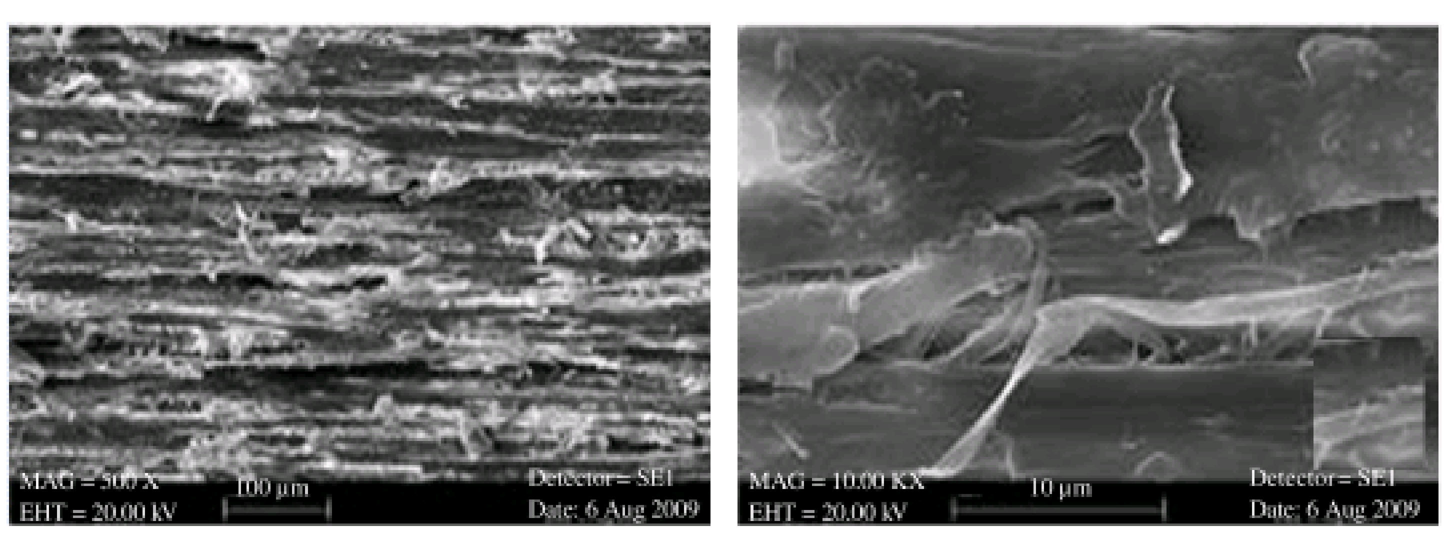

Fig. 2: Micrographs of wood cells parallel to fibers without any chemical process

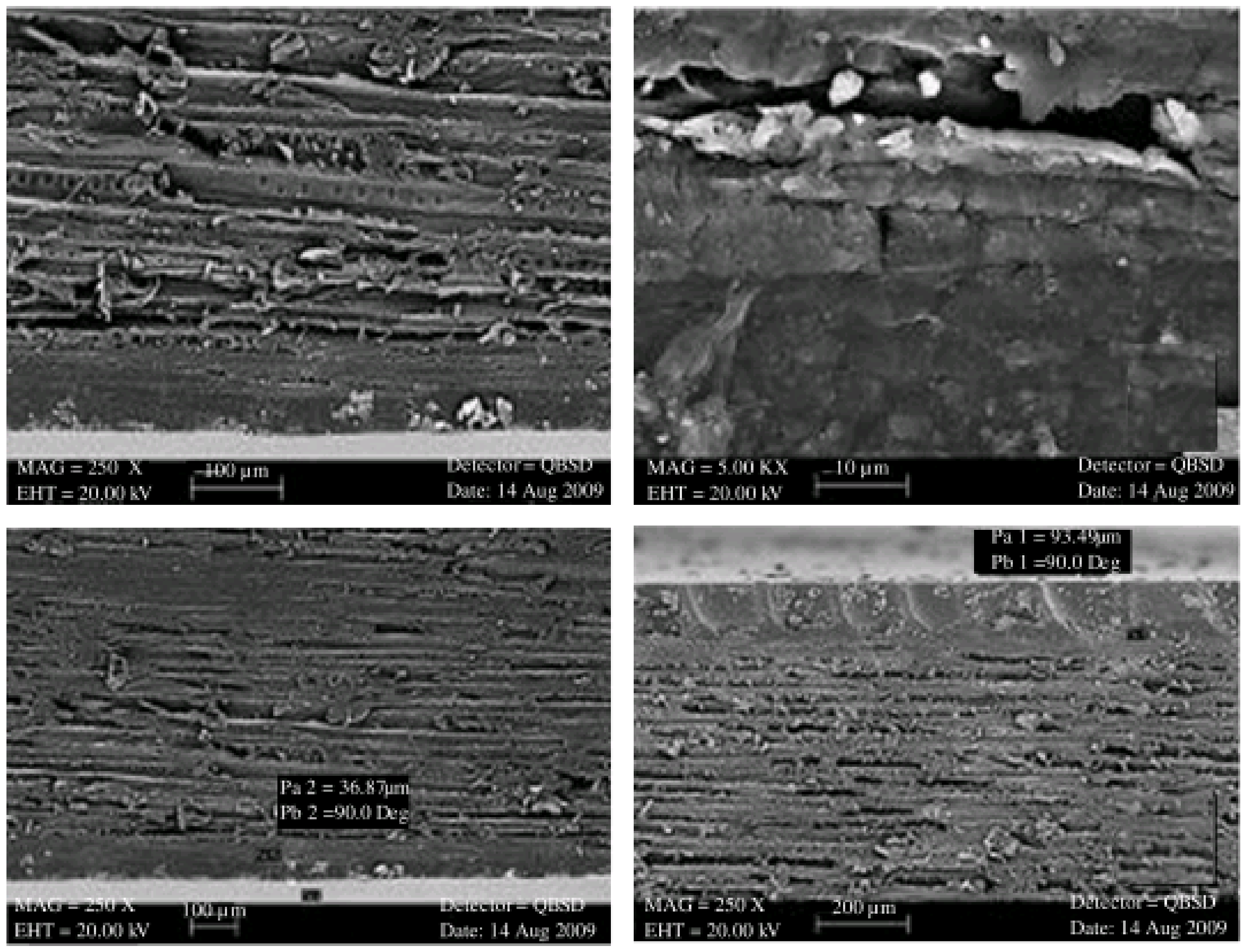

Fig. 3: Micrographs of wood cells impregnated by short term dipping and varnished

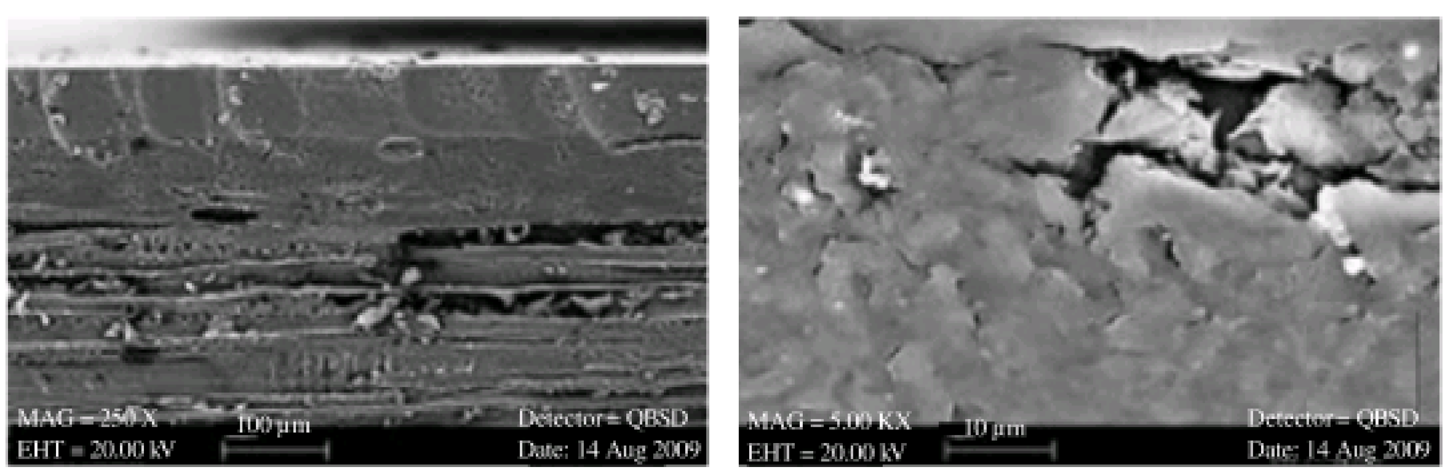

Fig. 4: Micrographs of wood cells impregnated by medium term dipping and varnished

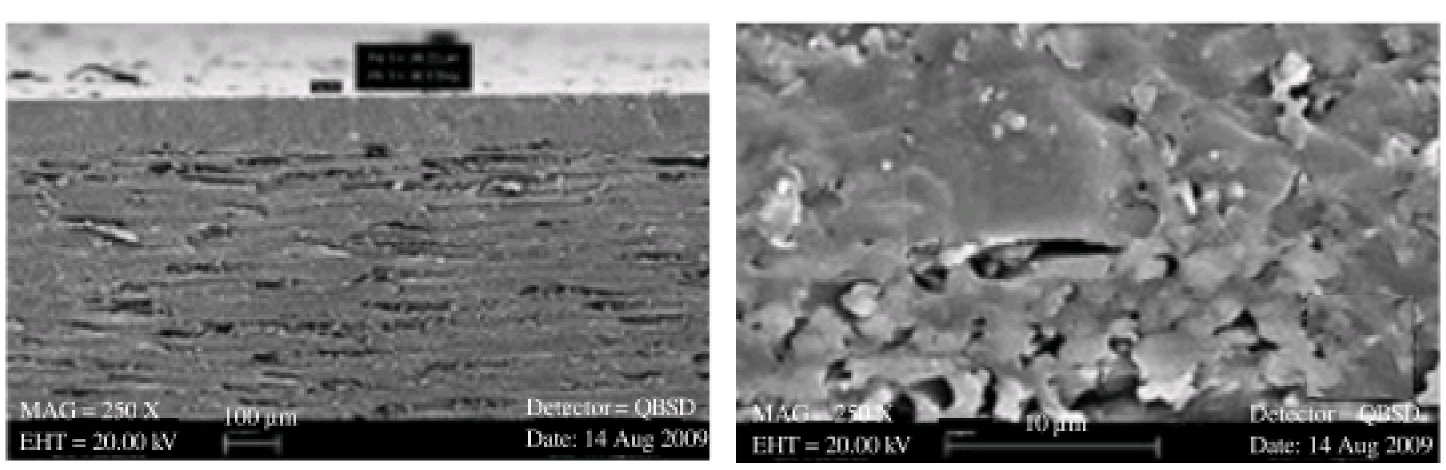

Fig. 5: Micrographs of wood cells impregnated by long term dipping and varnished

embedded in varnish layer and wood cell is higher than that of short and medium terms dipping.

In Fig. 6, the surface micrographs of thin layer varnishing are given. The layers of varnishing materials are shown very clearly in those micrographs. The particles shown at surfaces are not impregnation material but dirty. This case shows the importance of a clear medium in varnishing process.

In Fig. 7, the surface micrographs of thick layer varnishing are given. The varnishing chemical tries to

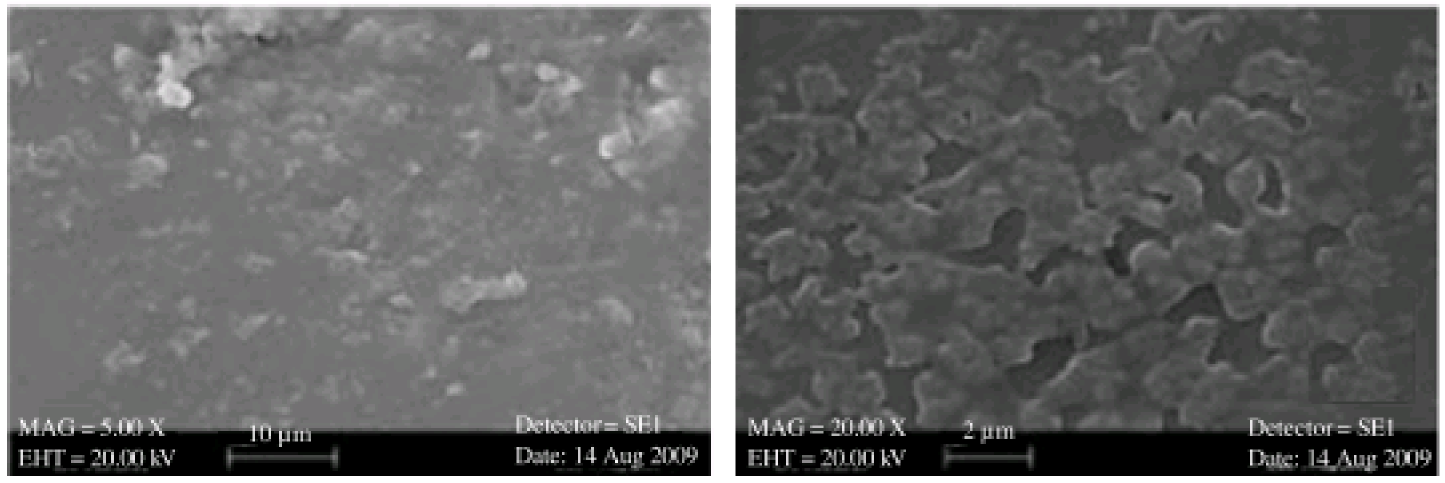

Fig. 6: Surface micrographs of thin layer varnishing

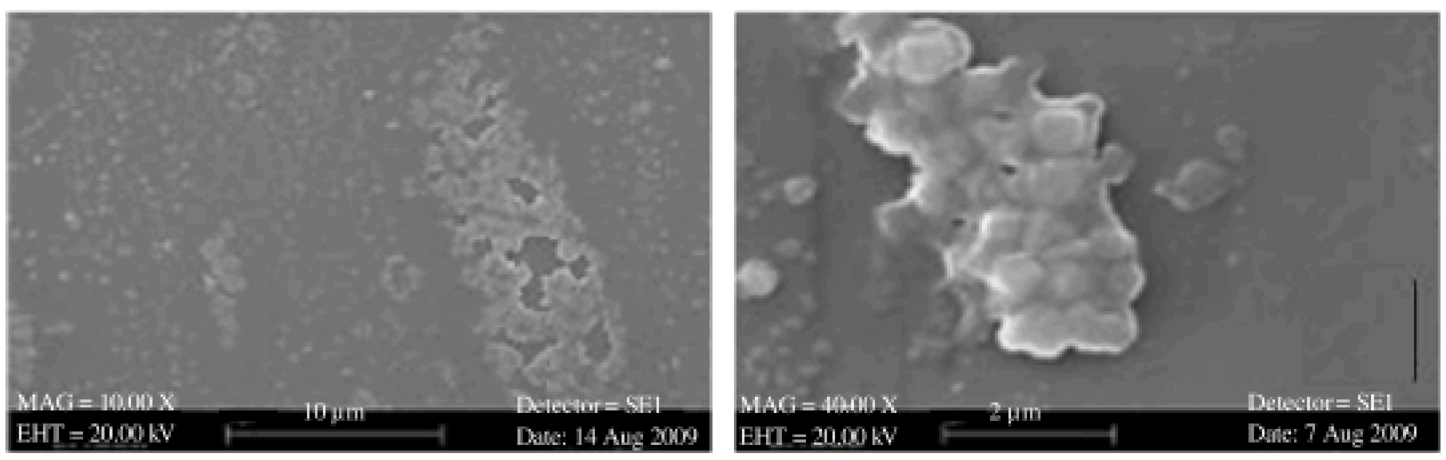

Fig. 7: Surface micrographs of thick layer varnishing

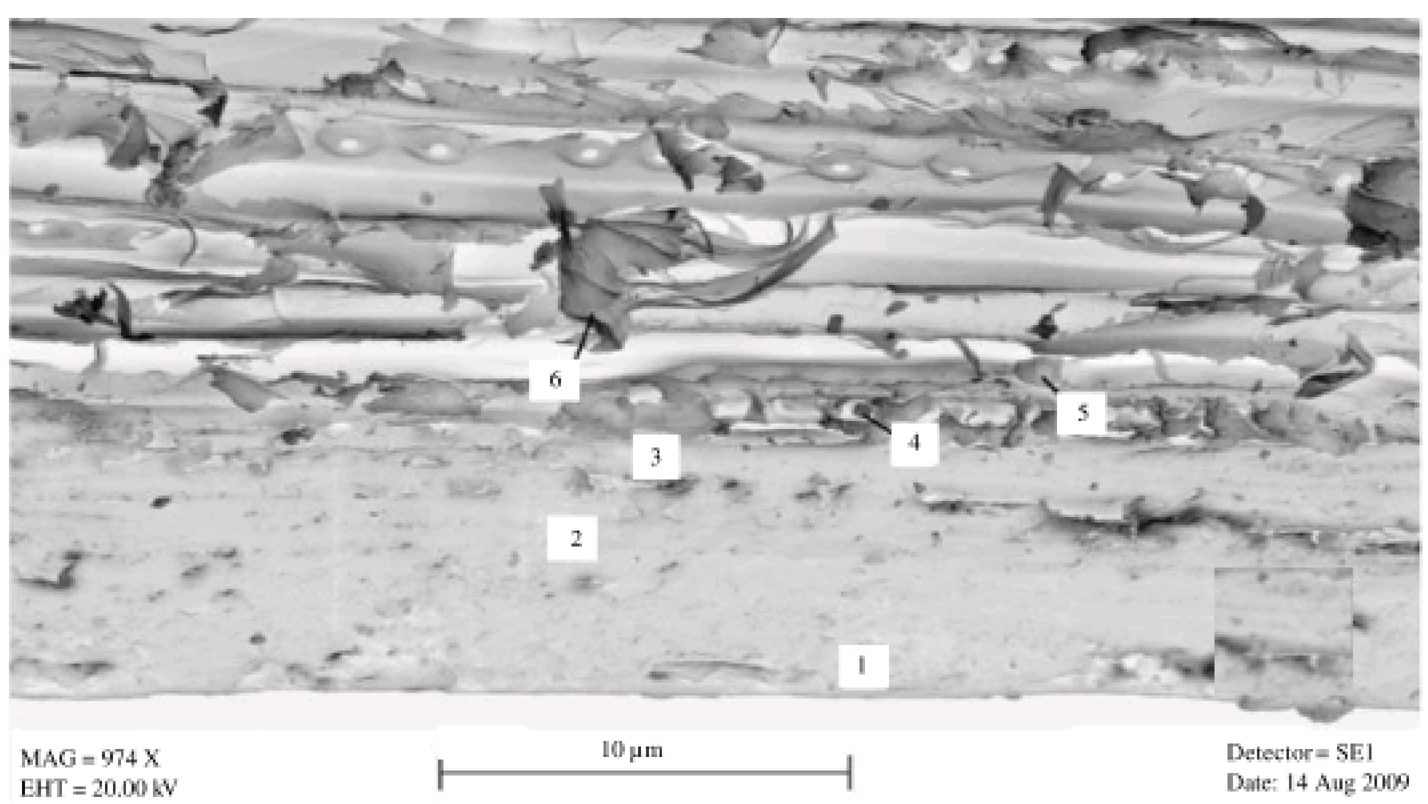

Fig. 8: EDX micrographs of varnished and impregnated wood cells parallel to fibers

create a single cover over the wood but in some parts it is impossible as shown at the micrograph with 40 KX magnifications.

In Fig. 8, EDX micrographs of varnished and impregnated wood cells parallel to fibers are given. As shown in the micrographs, the points 1, 2 and 3 are the varnish layers, points 4 and 5 are the examples of some of the impregnation material particles and point 6 is the wood fiber. According to EDX analysis, a very small amount of Na from the wood exists at points 1 and 2, but not detected at point 3. Cl is defined at point 4 and point 5. Cl is the element existing in tebuconazole and propiconazole of Imersol-aqua. Iodo also exists in Imersol-aqua and it is defined at point 5, but not defined at point 4. The impregnation material can be placed inside the cell or between the fibers. At point 6 which is the wood fiber, Cl and I are defined.

Those micrographs showed that SEM technology can be used to study the wood at cell level to understand the impact of impregnation materials and varnishing process on the physical and mechanical properties of wood.

CONCLUSIONS

As shown in SEM micrographs, impregnation material is diffused into the wood. Cypermethrin has a yellow color. It combines the other three azole group of elements. The reason for the change in yellow color tone of wood impregnated with Imersol-aqua is cypermethrin. Azole group of compounds have a cross resistance property, so the yellow color tone of wood do not increases linearly with the increase in the amount of retention of impregnation material. This increase is not linear with the amount of retention of impregnation material by wood due to the cross resistance properties of azole group of compounds. Varnishing also cause to an increase in yellow color tone but it is very small as compared with impregnation process. The chemical analysis of impregnated wood with FT-IR possibly will give us more information about the mechanism of change in yellow color tone.

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