Miro Tomažič, Borut Kričej, Matjaž Pavlič, Marko Petrič[1]

Modification of wood with dimethylol-dihydroxyethylenurea

Modifikacija drva dimetiloldihidroksietilenureom

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ABSTRACT • *Chemical modification of wood cell wall components has proven to have potentials to improve dimensional stability and durability of wood. Chemicals for wood modification are well known from other applications. One of them is the water-soluble resin 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone, usually known as dimethyloldihydroxyethyleneurea (DMDHEU). It is often used in the textile industry for improvement of resilience effects (wrinkle resistance) and dimensional stability of cellulose fibres. DMDHEU can crosslink the molecules in cellulose thus improving the quality of fabric. For the same reason it may be applied to wood modification. For successful modification of wood, various parameters are important: temperature, time, catalyst and wood species. Wood, treated with DMDHEU exhibits improved dimensional stability and increased resistance to wood pests. Mechanical properties of DMDHEU modified wood should be tested as well. Improved dimensional stability of the DMDHEU modified and surface coated wood could assure its longer durability in exterior conditions.*

Key words: *dimethyloldihydroxyethylenurea DMDHEU, modified wood, properties*

SAŽETAK • *Dokazano je da kemijska modifikacija komponenata stanične stijenke može poboljšati dimenzionalnu stabilnost i trajnost drva. Neke kemikalije za modifikaciju drva dobro su poznate iz drugih područja primjene. Jedna od njih je vodotopljiva smola 1,3-bis(hidroksimetil)-4,5-dihidroksi-2-imidazolidinon, poznata kao dimetiloldihidroksietilenurea (DMDHEU). Često se rabi u tekstilnoj industriji za poboljšanje otpornosti celuloznih vlakana prema gužvanju. DMDHEU se može umrežavati s molekulama pamuka poboljšavajući tako kvalitetu tkanine. Iz istog se razloga može primjenjivati i za modifikaciju drva. Za uspješnu modifikaciju drva ovom kemikalijom, važni su ovi parametri: temperatura, vrijeme, katalizator i vrsta drva. Drvo obrađeno DMDHEU-om pokazuje dimenzionalnu stabilnost i veću otpornost na drvne štetočine. Neka mehanička svojstva drva modoficiranoga DMDHEU-om ostaju nepromijenjena, a druga mogu biti poboljšana ili oslabljena. Poboljšana dimenzionalna stabilnost drva modificiranog DMDHEU-om trebala bi osigurati dulju trajnost vanjskih prevlaka na tako modificiranom drvu.*

Ključne riječi: *dimetiloldihidroksietilenurea (DMDHEU), modificirano drvo, svojstva*

[1]The authors are assistant, technical assistant, assistant and professor at the Biotechnical Faculty, Ljubljana University
[1]Autori su redom: asistent, tehnički asistent, asistent i profesor na Biotehničkom fakultet Sveučilišta u Ljubljani

1 INTRODUCTION
1 UVOD

Since decades, great efforts have been undertaken to chemically modify wood, in order to improve its absorption-, shrink- and swelling properties and its resistance to fungi and insects. The chemical modification, in this relation, means a chemical reaction between reactive parts in the wood's-cell walls and a chemical reagent, in which covalent amalgamations develop between the wood and the reagent (Rowell, 1975). Most commonly, chemical modification of wood involves reactions with the hydroxyl groups of the cellulose, the hemicellulose and the lignines, which can react with ethers, acetates, esters and other functionalities (Militz et al. 1997). Research in this area increased considerably in the past decade and many chemicals for modification of wood have been examined (Militz et al. 1997; Kumar, 1994; Rowell, 1983). Chemical modification of wood cell wall components has been proven to have potentials to improve durability and dimensional stability of wood. Application of several chemicals for wood modification has been well established in textile finishing sector. One of them is the water-soluble resin dimethyloldihydroxyethyleneurea (DMDHEU) (Kullman, 1978; Voncina et al. 2002).

Textile materials made of cellulose fibres have in addition to their well known favourable properties, a drawback of wrinkling and shrinking. In order to improve the quality and applicative value of cellulose based fabrics, in textile industries they developed treatment procedures against wrinkling. They introduced pre-condensates of synthetic resins (Urea-formaldehyde - UF and Melamine-formaldehyde - MF), which after impregnation, drying and condensation crosslink, resulting in formation of thermocondensation resins inside the fibres. By this procedure, resistance against wrinkling is improved and their ability to swell diminished. Further development launched the application of cyclic urea derivatives. These compounds link cellulose molecules by formation of bridges, again resulting in decreased swelling ability and better resistance against wrinkling. The first type of such compounds was dimethylolethyleneurea which, however, is prone to hydrolysis. Although less reactive, DMDHEU (dimethyloldihydroxyethylenurea) is a better alternative due to its high stability in acid media (Katović and Soljačić 1994). With magnesium chloride as the acid catalyst to initiate a reaction, it forms cross links in the amorphous regions of fibres. Even today, modified DMDHEU is the main crosslinking agent for cotton in the textile industry, thus improving the quality of textiles (Militz 1993, Voncina et al. 2002). The wrinkle free finish (also known as "Easy Care", "Durable Press", "Wrinkle-Resistant", "Wash and Wear", "No-Iron" etc) give cotton some elastic and resilient properties. Such crosslinked cotton can recover from deformation stresses.

As already mentioned, DMDHEU found its application also as a reagent for chemical modification of wood.

Table 1 *Some physical and chemical properties of DMDHEU (Zydex 2002)*
Tablica 1. *Neka fizikalna i kemijska svojstva DMDHEU-a (Zydex 2002)*

Physical and chemical properties *Fizikalna i kemijska svojstva*	
Form – *stanje*	Pourable liquid – *tekućina*
Colour – *boja*	Clear translucent – *providna*
Odour – *miris*	Pungent smell – *prodoran miris*
Flash point – *točka zapaljenja*	> 70 °C
Explosion hazard – *mogućnost eksplozije*	No explosion hazard – *nije eksplozivna*
Solubility in water – *topljivost u vodi*	Soluble – *topiva*
pH value – *pH vrijednost* (at 50 g/l 30 °C)	5

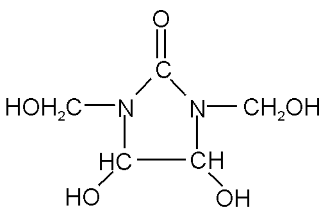

Figure 1 *Chemical structure of dimethyloldihydroxyethylene-urea (DMDHEU) (Voncina et al., 2002)*
Slika 1. *Kemijska struktura dimetiloldihidroksietilenuree (DMDHEU) (Voncina i sur., 2002)*

2 PROPERTIES OF DMDHEU
2 SVOJSTVA DMDHEU-a

DMDHEU can be diluted with cold water in different proportions and, based on its viscosity, it has the ability to penetrate well into the cell walls in wood. Table 1 gives some physical and chemical properties of DMDHEU (Figure 1).

DMDHEU can react with the two hydroxyl groups adjacent to the double bonded oxygen (Figure 1). In the main reaction, these hydroxyl groups react with other reactive hydroxyl groups and form ether bonds, while water splits off (Krause et al. 2003) (Figure 2). The reaction of DMDHEU with cellulose is presented in the first line of Figure 2. It has to be stressed, that crosslinking with cellulose may occur with the N-methylol groups and with hydroxyl groups on the positions 4 and 5. Even mild heating (70 to 80 °C) results in self crosslinking of DMDHEU and in a few hours the compound becomes insoluble in water (Ashaari et al. 1990). Formation of the formaldehyde may take place during use of the DMDHEU treated cellulose, because of aging of unreacted DMDHEU molecules. It is also possible that this free formaldehyde forms crosslinks with cellulose, resulting in the methylene-ether bridge formation. Self crosslinking of unreacted DMDHEU in the treated cellulose is another possible reaction (Soljačić and Katović, 1992).

From the descriptions above it is obvious that free formaldehyde may be present in the treatment formulation as well as in the treated material. Formaldehyde formation during and after the treatment procedure is dependent on various factors, especially the following ones:
- initial quantity of free formaldehyde
- chemical structure of cross-linking agent
- quantity and the type of catalysator or a mixture of catalysators
- time and temperature of condensation
- resistance of a cross-linking agent against hydrolysis
- storage conditions (Soljačić and Katović, 1992).

Formaldehyde may exhibit toxic, allergenic, mutagenic and cancerogenic effects. Therefore, it is very important to diminish the problem of free formaldehyde formation (Katović and Soljačić, 1983) and in the textile sector extensive investigations are underway, in order to find cross-linking agents with a low amount of free formaldehyde or even without it (Katović and Soljačić, 1994).

3 PROCESS PARAMETERS FOR MODIFICATION OF WOOD WITH DMDHEU
3 PARAMETRI MODIFIKACIJE DRVA DMDHEU-om

The wood modification parameters that strongly influence degree of modification and the improvement of material properties are wood species, applied reactant and catalyst, temperature and time.

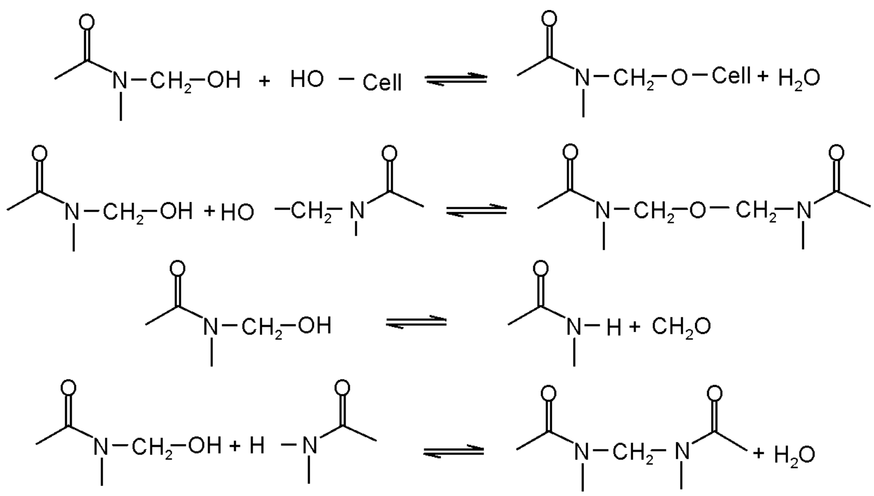

Figure 2
Equilibrium reactions of N-methylol compounds with hydroxyl groups of cellulose and with themselves, formaldehyde release and the reaction with NH groups (Voncina et al. 2002; Petersen, 1985)
Slika 2.
Ravnotežne reakcije N-metilol spojeva s hidroksilnim skupinama celuloze i samih sa sobom, oslobađanje formaldehida i reakcija s NH skupinama (Voncina et al. 2002; Petersen, 1985)

3.1 Catalyst
3.1 Katalizator

The catalysts which have been combined with DMDHEU are aluminium chloride, citric acid and tartaric acid. Treatments were carried out with 10 - 95 % aqueous solutions of DMDHEU at temperatures between 80 and 175 °C (Militz, 1993, Van der Zee et al. 1996). SO_2 is an excellent catalyst for acetalisation with DMDHEU (Yasuda and Minato 1994, Yusuf et al. 1994). Krause et al. (2003) stated that $MgCl_2x6H_2O$ proved to be the most effective catalyst, concerning the antishrink efficiency (ASE). However, $MgCl_2x6H_2O$ is hydrophilic and therefore, the treated wood has higher equilibrium moisture contents (EMC) when $MgCl_2$ x $6H_2O$ is added in higher concentrations. Various measurements showed that citric acid is less effective as a catalyst than $MgCl_2$ x $6H_2O$.

3.2 Temperature
3.2 Temperatura

DMDHEU reacts faster with hydroxyl groups of wood at elevated temperatures. Usually the temperature ranges between 80 and 175 °C (Militz, 1993; Van der Zee et al. 1998). According to reference literature, the optimum modification temperature lies between 100 °C and 125 °C (Yasuda and Minato, 1994, Van der Zee et al. 1996, Krause et al. 2003). However, Ashaari et al. (1990) performed crosslinking of hyroxyl groups in wood with DMDHEU at 55 °C.

3.3 Time
3.3 Vrijeme

Usually, the curing times for modification with DMDHEU are between 16 and 24 hours (Militz, 1993, Van der Zee et al. 1998; Krause et al. 2003). But Ashaari et al. (1990) carried out the modification only in 4 hours.

3.4 Wood species
3.4 Vrsta drva

It has been reported that the following wood species have been successfully modified with DMDHEU:

- Scots pine (*Pinus sylvestris* L.) (Videlov 1989, Van der Zee et al. 1998, Krause et al. 2003),
- Sweetgum tree wood (*Liquidambar styriciflua* L.) (Ashaari et al. 1990),
- Southern pinewood (*Pinus spp.*). (Ashaari et al. 1990),
- Beech wood (*Fagus sylvatica* L.) (Militz 1993),
- Sitka spruce (*Picea sitchensis* Carr.) (Yasuda and Minato, 1994; Yasuda et al. 1994, 1995),
- Japanese cedar (*Cryptomerica japonica* D. Don) (Yusuf et al. 1994, Yalinkilic 1999),
- Japanese beech (*Fagus crenata* Blume) (Yusuf et al. 1994),
- Radiata pine (*Pinus radiata* D. Don) (Yusuf et al. 1995).

3.5 Treatment
3.5 Proces modifikacije

Several different modification procedures were reported.

The most widely used process in textile industry has been directly transferred to the field of wood modification (Pandey 1982, cited by Krause et al. 2003; Yalinkilic, 1999). Before introducing the treatment solution into an evacuated chamber, a 30 minute pre-vacuum period was applied. Specimens were left then in the solution for one week, so that the diffusion could occur, until they sank to the bottom. Then they were air-dried for 1 week. Afterwards, the samples were preheated in a vessel (20 min at 120° C), and dried in vacuum. A gaseous SO_2 was added to the vessel and maintained at the same temperature for 12 h.

Ko et al. (1983), cited by Krause et al. (2003) suggested that after vacuum pressure impregnation, as in the original process described above, the wood samples should be reacted without pre-drying. So, they stored the wood samples into a closed plastic box, filled with a water solution of DMDHEU, so that the wood blocks lay directly on the water surface. In this reaction environment, the samples were heated for 24 hours at 90 °C. After the impregnation stage, the samples were dried at 103 °C for 24 hours. The third part of this process should be the application of steam, but Krause et al. (2003) demonstrated that this operation could not be applied effectively at DMDHEU treated wood.

However, the most frequently used modification procedures are the following ones:

Yasuda and Minato (1994) and Yalinkilic et al. (1999) firstly kept the samples for a certain period under vacuum. Afterwards, the specimens were soaked in an adequate aqueous solution of DMDHEU, until they sank to the bottom. The next step was drying at normal conditions for one week. Then, the samples were put into a chamber, heated to 120 °C and vacuumed, followed by introduction of SO_2. The reaction at 120 °C has to be performed for 24 h.

The other common modification process, reported by Van der Zee et al. (1998) and Krause et al. (2003) consists of vacuum impregnation with a 30 % DMDHEU water solution, containing a catalyst ($MgCl_2x6H_2O$). The following steps are drying at normal conditions and curing for a certain period at 120 °C.

4 PROPERTIES OF THE DMDHEU MODIFIED WOOD
4 SVOJSTVA DRVA MODIFICIRANOG DMDHEU-om

The properties of DMDHEU modified wood like dimensional stability, mechanical characteristics, sorption and especially resistance to wood pests have been studied extensively (Ashaari et al., 1990; Videlov, 1989; Militz, 1993; Yasuda and Minato, 1994; Yasuda et al., 1994; Yusuf et al., 1994; Yasuda et al., 1995; Yalinkilic et al., 1999).

4.1 Dimensional stability
4.1 Dimenzionalna stabilnost

Videlov (1989) reported the possibility of achieving dimensional stability with DMDHEU. Yusuf and co-workers (1994) reported similar results for Japanese cedar (*Cryptomerica japonica* D. Don) and Japanese beech (*Fagus crenata* Blume). DMDHEU diffused into cell walls and reacted with the hydroxyl groups of cellulose upon heating. The degree of dimensional stability increased with the curing temperature (Ashaari et al. 1990). 23.3 %, and 21.9 % ASE (Anti Shrink/Swelling Efficiency) were achieved by DMDHEU modification of sweetgum (*Liquidambar styraciflua*) and pine - (*Pinus spp.*). Absorption of water decreased by 11.3 % and 10.5 %, respectively (Ashaari et al. 1990).

Yasuda and Minato (1994) reported the increase of ASE of DMDHEU treated wood from 25 % up to 55 %, while Yusuf and co-workers (1995) achieved the ASE value as high as 60 %. ASE, higher than 50 % was reported also by Van der Zee (1998) and co-workers as well as by Krause (2003).

4.2 Mechanical properties
4.2 Mehanička svojstva

Mechanical properties depend on wood species, applied chemicals, reactant and catalysts and parameters of modification process (time, temperature).There are only few reports on mechanical properties of wood, modified with DMDHEU. Yasuda and Minato (1994) stated that the modulus of elasticity of the DMDHEU modified wood changed only slightly in the longitudinal direction, while in the radial one, it was increased by 20 - 40 %.

4.3 Acoustic properties
4.3 Akustična svojstva

Because of increased dimensional stability of modified wood, the influence of relative humidity on acoustical properties is reduced. DMDHEU cross-linking reactions improve the vibrational properties of wood as a result of dimensional stability and reduction of internal friction (Akitsu et al. 1993; Yasuda and Minato, 1994).

4.4 Resistance to weathering
4.4 Otpornost prema atmosferilijama

Wood, treated with DMDHEU does not exhibit improved resistance to weathering in comparison with untreated wood, during natural aging as well as during artificial accelerated weathering (Yusuf et al. 1995). SEM observations visualized the formation of large surface checks along the fiber lenghts in the untreated specimens, but only small sized checks were dispersed over the surfaces of DMDHEU modified wood. It has been also proposed, that the wood, modified with DMDHEU shows resistance to photodegradation.

4.5 Resistance to wood decay
4.5 Trajnost

Videlov (1989) obtained a complete protection of pine wood from attack by *Coniophora puteana* with a 15 % weight gain of DMDHEU. However, the results with a modified beech wood (Militz, 1993) did not coincide with the Videlov's ones. Yusuf and co-workers (1994) treated wood of Japanese cedar (*Cryptomerica japonica* D.Don) with DMDHEU and exposed it to brown rot (*Tyromyces palustris*) white rot fungi (*Coriolus versicolor*). They verified the resistance of the modified wood to wood decay fungi. Literature data confirmed these results (Yalinkilic et al., 1999). Yusuf and co-workers (1995) exposed the DMDHEU modified radiata pine wood (*Pinus radiata* D. Don) to natural and artificial accelerated weathering. Afterwards, wood decay tests with brown and white rot fungi (*Tyromyces palustris* and *Coriolus versicolor*) were carried out. The specimens retained their resistance against wood decay. Resistance of modified wood to termites was tested as well and it turned out that the DMDHEU treated wood was susceptible to termites attack (*Coptotermes formosanus*). Increased susceptibility was recorded upon heating modified wood for a certain period at temperatures over 100 °C. Additional experiments to elucidate susceptibility to termite attack are needed.

4.6 Coatings on DMDHEU modified wood
4.6 Prevlake na DMDHEU-om modificiranom drvu

Reviewing the reference literature we could not find any data about the properties of surface coatings on wood, modified with DMDHEU. In general, our preliminary results (Tomažič et al. 2004) showed that the systems (DMDHEU modified wood - surface coatings) gave better performances during natural aging, when compared to the systems with non-modified wood. The reason is very likely in the substrate. It is presumed that the key factor for durability improvement is a high dimensional stability of wood, modified with DMDHEU. However, no direct proof for this assumption has been obtained up to now. Another question that should be investigated is whether the commercial coatings should be adapted for applications on DMDHEU modified wood or not.

5 CONCLUSION
5 ZAKLJUČAK

Wood, modified with 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone, commonly known as dimethyloldihydroxyethylenurea (DMDHEU) is a relatively new material. Up to now, investigations of this matter have been focused on sorption and dimensional properties. Resistance to wood decay fungi and wood boring insects is investigated intensively, and so far improved performance has been shown. Wood, modified with DMDHEU is also partially resistant to UV degradation.

This fact, together with other improved properties of DMDHEU modified wood, makes possible the application of a wide assortment of exterior decorative surface finishes and not only the protective ones.

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Corresponding address:

MIRO TOMAŽIČ, BSc
Biotechnical Faculty
Department of Wood Science and Technology
Rožna dolina, Cesta VIII/34
SI-1001 Ljubljana
SLOVENIA
E-mail: miro.tomazic@bf.uni-lj.si