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UF-pMDI Hybrid Resin for Waterproof Particleboards Manufactured at a Shortened Pressing Time

Hibridno ljepilo UF-pMDI za vodootporne ploče iverice proizvedene uz skraćeno vrijeme prešanja

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ABSTRACT • *The aim of the study was to determine properties and potential shortening of pressing time of particleboards resinated with urea-formaldehyde (UF) resin thanks to its modification with pMDI (polymeric 4,4' - methylene diphenyl isocyanate), introduced to the resin at 2.5 – 10 %. Tests showed that strength properties and water resistance of manufactured boards were improved with the increase of the pMDI amount introduced to UF resin. Furthermore, particleboards manufactured at a shortened pressing time were characterized by better mechanical and physical properties than those of reference boards manufactured under identical conditions, resinated with pure UF resin.*
It should be emphasized that boards, manufactured with a 10 % share of pMDI in the glue mixture, irrespective of their pressing time, were characterized by water resistance measured by the V100 test at the level required by the standard for exterior boards not bearing loads (type P3).

Keywords: *particleboard, UF resin, pMDI, water resistance, mechanical properties*

SAŽETAK • *Cilj provedene studije bio je odrediti svojstva i mogućnosti skraćenja vremena prešanja ploča iverica lijepljenih urea-formaldehidnim (UF) ljepilom modificiranim pMDI-jem (polimerni 4,4' – metilen difenil izocijanat) u količini 2,5 do 10 %. Testiranje je pokazalo da se s povećanjem količine pMDI-ja u UF ljepilu poboljšava čvrstoća i vodootpornost ploča. Nadalje, ploče iverice proizvedene uz kraće vrijeme prešanja imale su bolja mehanička i fizikalna svojstva od referentnih ploča proizvedenih uz jednake uvjete i lijepljene čistim UF ljepilom. Treba naglasiti da su ploče proizvedene s ljepilom koje ima udjel pMDI-ja 10 %, neovisno o vremenu prešanja, imale vodootpornost mjerenu testom V100 na razini koju zahtijeva norma za ploče u vanjskoj uporabi bez opterećenja (tip P3).*

Ključne riječi: *ploče iverice, UF ljepilo, pMDI, vodootpornost, mehanička svojstva*

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1 INTRODUCTION
1. UVOD

UF resins are some of the most common adhesives used in the wood-based material industry. Their low price and good strength properties of glue lines under dry conditions result in their being widely applied despite their low water resistance. In order to increase water resistance of UF resins, they are commonly modified with melamine. Melamine-urea-formaldehyde (MUF) resins may be produced by adding melamine or its salts to UF resin, mixing melamine-formaldehyde (MF) resin directly with UF resin or in the process of reagent cocondensation (Mercer and Pizzi, 1994; Prestifilippo *et al.*, 1996; Cremonini *et al.*, 1997; Cremonini and Pizzi, 1999; Zhao and Pizzi, 2000; Weinstabl *et al.*, 2001). Despite such an increase in water resistance of glue lines, this method has some drawbacks, e.g. slight melamine solubility and the necessity to prepare adequately condensed UF resin. Resins thus modified also undergo accelerated aging processes. However, the introduction of appropriate modifiers to MUF resins facilitates the enhancement of their pot life and further improvement of water resistance. Phenolic resins are most commonly used as modifiers of MUF resins and thus produced melamine-urea-phenol-formaldehyde (MUPF) resins have been successfully applied for many years in the manufacture of both wood-based boards and exterior plywood (Cremonini *et al.*, 1996a; Cremonini *et al.*, 1996b; Cremonini *et al.*, 1996c; Prestifilippo and Pizzi, 1996). Thanks to them it is possible to manufacture plywood with light glue lines characterized with good water resistance. Unfortunately, with resins of this type it is not possible to reduce relatively long pressing times of this material.

In literature on the subject, attention has been focused on isocyanate adhesives and methods for using their properties in UF resin modification. Investigations conducted in this respect showed that the application of isocyanates as curing agents in urea–formaldehyde resins improves the glue line strength to a considerable degree and increases their water resistance. Pizzi and Walton (1992) showed that a 1–2 % addition of polymeric MDI to UF resin effectively reduces its susceptibility to hydrolysis and accelerates cross-linking, which may result in potential shortening of pressing time for boards manufactured with the use of such modified UF resin. Furthermore, studies conducted by Mansouri et al. (2006) showed that an addition of pMDI to UF resin at 15% significantly improved resistance of glue line to the action of hot water. These authors showed that plywood manufactured under such conditions was characterized by sufficient water resistance after 27-minute boiling. Furthermore, Hong Lei et al. (2006) showed that already a 5 % addition of pMDI to MUPF resin makes it possible to manufacture particleboards with a 130 % higher water resistance, measured by internal bond after the boiling test in comparison to that of board resinated with pure MUPF resin.

In view of the above mentioned reports, the aim of this study was to investigate the potential shortening pressing time of particleboards resinated with UF resin modified with pMDI, with the simultaneous improvement of their water resistance and maintenance of good mechanical properties.

2 MATERIALS AND METHODS
2. MATERIJAL I METODE

UF resin modified with pMDI at 0, 2.5, 5 and 10 % in relation to UF resin weight was used to resinate particles. A 2 % addition of ammonium nitrate (NH_4NO_3) in relation to dry weight of resin was used as a curing agent for UF resin.

The analyzed single-layer particleboards with the density of 700 kg/m^3 and thickness of 12 mm were manufactured from pine chips, using the following pressing parameters: pressing time of 22, 19 and 16 s/mm board thickness, pressure of 2.5 MPa, resination rate of 12 % and temperature of 200 ºC.

The following properties of particleboards were examined according to the relevant European Standards (EN):

- modulus of rupture (MOR) and modulus of elasticity (MOE) - EN 310
- internal bond (IB) - EN 319
- internal bond after the boiling test (V100) - EN 1087-1
- swelling in thickness after immersion in water (TS) - EN 317
- formaldehyde content (CH_2O) - EN 120

For each combination (pressing time and amount of pMDI introduced to UF resin) 3 particleboards were manufactured. A total of 12 samples were cut from each board, to be used in testing of mechanical and physical properties. The results of analyses of individual properties were thus a mean of 36 measurements. The results of these determinations were subjected to statistical analysis.

3 RESULTS AND DISCUSSION
3. REZULTATI I DISKUSIJA

The results of studies of the effect of the amount of pMDI introduced to UF resin on properties of particleboards manufactured with such modified UF resin, pressed at 22 s/mm thickness, are presented in Table 1. It results from the studies conducted in this respect that the higher the amount of pMDI introduced to resin, the better the improvement in the strength properties of boards. Thus already with the addition of 2.5 % of pMDI, a 7 % and 24 % increase was observed in bending strength and internal bond, respectively, while in case of the maximum amount of modifier (10 %), these properties are improved on average by as much as 32 %. The applied method of UF resin modification also had a significant effect on the improvement of water resistance of manufactured boards. It was observed that with increasing the addition of pMDI to UF resin, a considerable decrease in their hydrophilic character was found. Measurements of water resistance showed that the substitution of UF resin with pMDI makes it possible to manufacture boards with increased water

Table 1 Properties of particleboards depending on the amount of pMDI introduced to UF resin
Tablica 1. Svojstva ploča iverica ovisno o količini pMDI-ja u UF ljepilu

Pressing time *Vrijeme prešanja*	**Amount of pMDI** *Količina pMDI-ja*	**CH_2O[1]**	**MOR**	**MOE**	**IB**	**TS**	**V100**				
s/mm	%	mg/100g d.m.b[2]	$N \cdot mm^{-2}$			%	$N \cdot mm^{-2}$				
							15’	30’	60’	90’	120’
22	0	3.60	15.0	2570	1.00	32.3	-	-	-	-	-
	standard deviation		2.3	390	0.10	3.6	-	-	-	-	-
	2.5	3.83	16.1	2620	1.24	29.0	0.06	-	-	-	-
	standard deviation		1.3	70	0.09	2.1	0.01	-	-	-	-
	5	2.95	18.4	2780	1.32	26.7	0.13	0.08	-	-	-
	standard deviation		2.5	290	0.09	1.3	0.05	0.02	-	-	-
	10	2.52	19.6	2960	1.32	25.1	0.30	0.25	0.14	0.10	0.09
	standard deviation		1.7	180	0.10	1.6	0.04	0.04	0.03	0.01	0.02

[1]CH_2O –formaldehyde content / *sadržaj formaldehida*; MOR – modulus of rupture / *modul loma*; MOE – modulus of elasticity / *modul elastičnosti*; IB – internal bond / *čvrstoća raslojavanja*; V100 – internal bond after the boiling test / *čvrstoća raslojavanja nakon testa kuhanja*; TS – swelling in thickness after immersion in water / *debljinsko bubrenje nakon uranjanja u vodu*.
[2]d.m.b.- dry matter of board / *suha tvar ploče*

resistance by 10 to 22 %, measured by board thickness swelling under the influence of soaking in water. Although absolute values of swelling are higher than those specified by the standard, it needs to be taken into account that they were single-layer boards devoid of face layers with a higher resination rate, considerably hindering penetration of water into the boards, and that no additional hydrophobic agents were applied in their manufacture. Tests also showed that boards manufactured with a 10% proportion of pMDI in the glue mixture were characterized by water resistance, measured by internal bond after the boiling test, being generally of the value specified in the standard for type 3 boards ($0.09\ N \cdot mm^{-2}$ according to PN-EN 312) (Table 1).

As it could have been expected, the introduction of pMDI to UF resin resulted in an improvement of hygienic standard of manufactured boards. Tests conducted in this respect showed that the introduction of pMDI to UF resin at 10 % resulted in a reduction of formaldehyde content in the board by as much as 30 % (Table 1), which is of particular importance in view of the current need to adapt the emission of formaldehyde from wood-based materials to meet the requirements of the California Air Resources Board – CARB, more strict than European standards.

Results of investigations conducted on the potential to reduce pressing time of boards, depending on the amount of pMDI introduced to urea resin, are presented in Table 2. Investigations conducted in this respect showed that particleboards manufactured at each pressing time, irrespective of the amount of pMDI applied as a modifier of UF resin, were characterized by better properties than those of reference boards manufactured under identical conditions, resinated with pure UF resin. Thus, the mean increase in bending strength and internal bond in boards, irrespective of their pressing time, was 16 % and 28 %, respectively, for minimum (2.5 %) and maximum (10 %) amounts of pMDI introduced to urea resin. Moreover, it should be particularly stressed that boards manufactured with a 10 % proportion of pMDI in the glue mixture, irrespective of their pressing time, were characterized by water resistance measured by the V100 test generally consistent with the value required by the standard for type P3 boards ($0.09\ N \cdot mm^{-2}$) (Table 2).

As it could have been expected, with a reduction of pressing time of boards their formaldehyde content increases. As shown by data presented in Table 2, in boards resinated with UF resin with a 10 % addition of pMDI, the content of CH_2O increases from 2.52 to 4.04 mg/100g d.m.b. Still with respect to the control board pressed for the shortest time and resinated with pure UF resin it was found to be by 17 % lower.

In turn, assuming particleboard resinated with pure UF resin and pressed at 22 s/mm thickness as the reference board, it was found that the introduction of pMDI already at 2.5 % makes it possible to manufacture boards with better properties at pressing time reduced by as much as 38 % (16 s/mm). Analyses showed that boards manufactured under such conditions had strength properties higher by 8 and 13 % for bending strength and internal bond, respectively, compared to the reference board (Fig. 1). Moreover, it should be

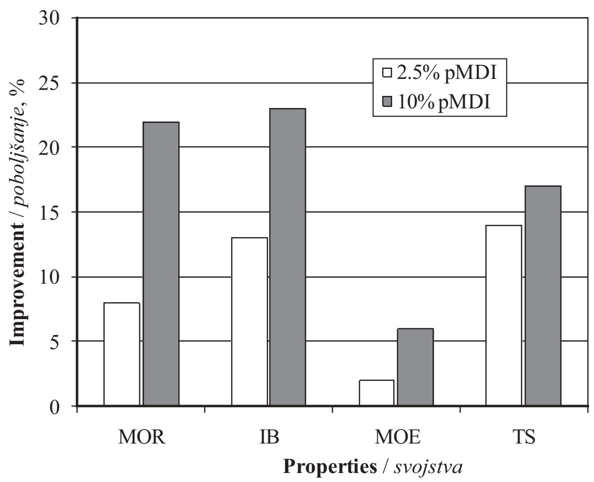

Figure 1 Improvement of board properties manufactured at pressing time reduced to 16 s/mm in relation to properties of the reference board glued with pure UF resin and pressed at 22 s/mm thickness
Slika 1. Poboljšanje svojstava ploča proizvedenih uz smanjeno vrijeme prešanja 16 s/mm u odnosu prema svojstvima referentne ploče lijepljene UF ljepilom i prešane pri 22 s/mm

Table 2 Properties of particleboards depending on pressing time and the amount of pMDI introduced to UF resin
Tablica 2. Svojstva ploča iverica ovisno o vremenu prešanja i količini pMDI-a u UF ljepilu

Pressing time *Vrijeme prešanja*	**Amount of pMDI** *Količina pMDI-ja*	CH_2O[1]	MOR	MOE	IB	TS	V100				
s/mm	%	mg/100g d.m.b[2]	N·mm^{-2}			%	N·mm^{-2}				
							15’	30’	60’	90’	120’
19	0	-	13.9	2450	0.97	31.7	-	-	-	-	-
	standard deviation		1.5	130	0.12	2.3	-	-	-	-	-
	2.5	-	16.1	2540	1.16	30.5	0.04	-	-	-	-
	standard deviation		2.5	310	0.14	2.3	0.01	-	-	-	-
	5	-	18.2	2630	1.26	27.7	0.12	0.08	-	-	-
	standard deviation		2.1	720	0.10	2.3	0.01	0.02	-	-	-
	10	-	18.4	2990	1.25	26.1	0.29	0.24	0.14	0.10	0.10
	standard deviation		1.7	140	0.12	1.3	0.02	0.03	0.02	0.02	0.02
16	0	4.87	13.9	2400	1.00	32.5	-	-	-	-	-
	standard deviation		1.7	370	0.11	2.5	-	-	-	-	-
	2.5	4.73	16.2	2510	1.13	27.8	0.03	-	-	-	-
	standard deviation		1.6	250	0.13	2.1	0.01	-	-	-	-
	5	4.01	17.4	2620	1.12	28.1	0.11	0.08	-	-	-
	standard deviation		1.2	200	0.11	1.7	0.01	0.02	-	-	-
	10	4.04	18.3	2730	1.23	26.7	0.27	0.20	0.11	0.10	0.09
	standard deviation		3.8	510	0.13	1.6	0.06	0.05	0.01	0.04	0.02

[1]CH_2O –formaldehyde content / *sadržaj formaldehida*; MOR – modulus of rupture / *modul loma*; MOE – modulus of elasticity / *modul elastičnosti*; IB – internal bond / *čvrstoća raslojavanja*; V100 – internal bond after the boiling test / *čvrstoća raslojavanja nakon testa kuhanja*; TS – swelling in thickness after immersion in water / *debljinsko bubrenje nakon uranjanja u vodu.*
[2]d.m.b.- dry matter of board / *suha tvar ploče*

emphasized that these boards met the requirements of the standard EN 312 for boards bearing loads and used under dry conditions (MOR 16 N·mm^{-2}, MOE 2300 N·mm^{-2} and IB 0.4 N·mm^{-2} for type P4 boards). Such fluctuations of testing results for properties of particleboards manufactured at a reduced pressing time probably result from the fact that pMDI applied as a modifier of UF resin increases the reactivity of resin to such a degree that it facilitates an appropriate course of its cross-linking process, resulting in the manufacture of boards with good mechanical properties and elevated water resistance even at pressing time reduced by almost 40 %.

4 CONCLUSION
4. ZAKLJUČAK

Based on the conducted analyses, it should be stated that the higher the amount of pMDI introduced to UF resin, the bigger the improvement of strength properties and water resistance of manufactured boards. In turn, boards manufactured at a shorter pressing time were characterized by better mechanical and physical properties than reference boards manufactured under identical conditions, resinated with pure UF resin. It should be underlined that boards manufactured with a 10 % proportion of pMDI in the glue mixture, irrespective of their pressing time, were characterized by water resistance measured by the V100 test at the level required by the standard for exterior boards not bearing loads (type P3). Moreover, the introduction of pMDI to urea resin already at 2.5 % made it possible, at pressing time reduced to 16 s/mm, to manufacture boards with better bending strength and internal bond compared to the reference board, pressed at 22 s/mm. As it could have been expected, the introduction of pMDI to UF resin resulted in an improvement of hygienic standard of manufactured boards.

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