Oxidative Activation of Bagasse Fibers Surfaces in Medium Density Fiberboard Manufacturing

Oksidativna aktivacija površine vlakanaca u proizvodnji MDF ploča

ABSTRACT • This study presents the investigation of the effects of oxidant type (nitric acid and potassium dichromate), oxidant content (three different levels as 2, 4, and 6 percent) and urea-formaldehyde (UF) resin percentage (two levels as 5 and 7 percent) on mechanical and physical properties of interior grade medium density fiberboard made from bagasse fibers. Some panel properties were studied, such as modulus of rupture (MOR) and modulus of elasticity (MOE) in bending, compression-shear strength (C.S sth.), water absorption (WA) and thickness swelling (TS) after 2- and 24-hour immersion in cold water. In addition, the results indicated the best values for WA and TS after 2- and 24-hour immersion, and C.S. sth. was discerned at 7 percent UF resin content, together with 6 percent nitric acid. Furthermore, the greatest values for MOR and MOE were related to 7 percent UF resin content together with 4 percent nitric acid.

Keywords: medium density fiberboard, bagasse, oxidative activation, nitric acid, potassium dichromate

SAŽETAK • U studiji je istražen utjecaj vrste oksidansa (dušične kiseline i kalijeva dikromata), sadržaja oksidansa (2, 4 i 6 %) i postotnog udjela urea-formaldehidne smole (UF) (5 i 7 %) na mehanička i fizička svojstva ploča vlaknatica srednje gustoće, proizvedenih od bagasse vlakana. Analizirana su ova svojstva ploča: modal loma (MOR) i modul elastičnosti (MOE) pri savijanju, tlačno-smicajna čvrstoća (C.S sth.) te upijanje vode (WA) i debljinsko bubrenje (TS) nakon 2 i 24 sata potapanja u hladnoj vodi. Rezultati su pokazali najbolje vrijednosti za WA i TS nakon 2 i 24 sata potapanja, te za C.S sth. pri 7 %-tnom sadržaju UF smole i pri 6 % dušične kiseline. Nadalje, najveće vrijednosti za MOR i MOE zabilježene su pri 7 %-tnom sadržaju UF smole i pri 4 % dušične kiseline.

Ključne riječi: ploče vlaknatice srednje gustoće, bagasse, oksidativna aktivacija, dušična kiselina, kalijev dikromat

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1 INTRODUCTION

1. UVOD

Faced with an increasing worldwide wood fiber shortage, environmental considerations, and in order to meet the future demand, the use of non-wood lignocellulosic fiber resources has been increased, and wood composites industry is showing a renewed interest in the production of panel products from agricultural residues (Chow, 1975; Odozi et al., 1986; Sampatharajan et al., 1992). Unfortunately, in Iran, similar to many developing Asian countries, deforestation and over harvesting have raised environmental awareness, which focused on the studies for using non-wood renewable resources in composite panel production. Non-wood based resources are getting more important as a raw material in the manufacture of composite panels. For countries like Iran, agricultural residues show excellent potential in composite manufacturing industries. Among them, sugarcane residue is one of the best raw materials for that purpose. Bagasse is abundant, unused, and can be obtained at a very low cost. Its lignin content is low and its open structure will facilitate liquid penetration (Zare-Hosseinabadi et al., 2008).

Composite panels, such as medium density fiberboard (MDF), are widely used in the construction and furniture industries (Maloney, 1996; Sellers, 2001; Reddy and Yang, 2005). A large amount of increasingly more expensive petroleum-derived adhesives are needed for their manufacture. For example, the production of medium density fiberboard requires a large volume of adhesive, which accounts for up to 20% of the production costs (Pierre-Louis et al., 2008). In addition, during production and end-use of MDF, particleboards, and other adhesively bonded products glued with formaldehyde-containing adhesives, such as urea-formaldehyde, formaldehyde emissions are a concern for the manufacturers and consumers (Maloney, 1996; Sellers, 2001). The stringent environmental and human health safety regulations have prompted research into reducing the amount of harmful and/or expensive adhesive components and replacing synthetic adhesives with more environmentally-friendly and safer alternatives (Widsten and Kandelbauer, 2008). One of the considerable potential techniques is the use of oxidizing chemicals to bond wood components (Johns and Woo, 1978). As early as 1939, Tischer (1939) reported on the use of oxidizing agents, such as potassium or sodium dichromate or nitric acid. He concluded that the use of an oxidant may be interpreted as leading to inter-fiber bonding (Tischer, 1939). Surface activation is today a common industrial process for many materials, e.g. in the paper, plastic, metal, wood and wood composites (Nussbaum, 1993). With an activated surface, a higher surface energy is obtained. This gives better bonding qualities in a subsequent operation. Hydrogen bonding and covalent bonding are thereby facilitated, resulting in much stronger bonding than the Van der Waals forces possible between low energy surfaces (Nussbaum, 1993). A number of techniques are today available for achieving activated bonding (Nussbaum, 1993). Nimz (1974) reported on the use of hydrogen peroxide, a strong oxidizing agent, in mixtures with potassium ferricyanide and pulping residues to bond medium density particleboards. Stofko and Zavarin (1977) reported on the use of a wide variety of oxidants including chromates, nitrates, nitrites, peroxides, perchlorates, permanganates, ferric compounds, and persulfates. Excellent bonding is reported when such materials are dispersed throughout the mat of a high-density fiberboard furnish and hot pressed.

The objective of this study was to evaluate the effects of oxidative activation of bagasse fiber by nitric acid and potassium dichromate on resin consumption, as well as investigate some mechanical and physical properties of dry formed bagasse MDF boards.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

2.1 Raw material

2.1. Sirovina

Moist depithed bagasse was collected from the MDF moist depithing plant at one of the Agro-Industrial Sites in Southwest of I. R. Iran. Industrial urea-formaldehyde resin (solid content 60 %, PH 6.8-7.1, viscosity 30-45 sec., density 1.28 g·cm⁻³, gel time 50-65 sec., free formaldehyde max 2 %, pot life 5 hours, water tolerance 6 parts, storage life 4 weeks) was prepared from Tiran Shimi resin factory, I. R. Iran. The chemicals including HNO₃ (100456 nitric acid 65 %), K₂Cr₂O₇ (1048625 potassium dichromate), C₂H₈N₂ (800947 ethylene diamine) and NH₄Cl (1011430 ammonium chloride) were supplied by MERCK-schuchardt, Germany.

2.2 Bagasse steaming and defibering

2.2. Razvlaknjivanje bagasse

The bagasse was delivered to the Pulp and Paper Laboratory, Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, I. R. Iran. A laboratory batch steaming system was used for cooking the bagasse. A sufficient quantity of bagasse was transferred into the steaming vessel and saturated steam was then injected. After a short presteaming time to equalize the steam pressure and temperature inside the steaming vessel, the exhaust valve was closed and steam pressure and temperature were raised up to the start point of steaming condition. The steaming time was started after reaching the target steaming temperature and continued for 5 minutes. One steaming temperature of 175 °C (p = 6 bar) was used. The cooked bagasse was discharged and defibered using a 25 cm laboratory atmospheric single disc refiner. The refined fibers were air dried to reach equilibrium moisture content under laboratory conditions and then fluffed using a hand mixer. Final drying to 1.5 % moisture content was achieved by drying at 110 °C in a laboratory tray dryer. Finally, dried fibers were stored in sealed plastic bags until used.
2.3 Experimental layout

The fibers were then treated by oxidants and resinated by urea-formaldehyde resin according to full factorial experimental design with three factors and $2^3 \times 2$ levels shown in Table 1.

### Table 1 Full factorial experimental design with three factors and $2^3 \times 2$ levels

<table>
<thead>
<tr>
<th>Type of oxidant</th>
<th>UF resin level, %</th>
<th>Oxidant level, %</th>
<th>Treatment No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric acid</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Potassium</td>
<td>2</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>dichromate</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
<td>10</td>
</tr>
</tbody>
</table>

A three-factorial experiment with a completely randomized design was used for the analysis of variance (ANOVA) of the data, and Duncan’s Multiple Range Test (DMRT) was used for differentiation and classification of the average values.

2.4 Chemical treatment

Oxidative activation of bagasse fibers were carried out before gluing. For this purpose, each of the two different types of oxidant were used at three levels of 2, 4 and 6 percent (based on fiber dry basis). Nitric acid and potassium dichromate were added to dry bagasse fibers by spraying in a laboratory rotary drum blender and then stored in sealed plastic bags for 2 hours, after homogenous mixing.

2.5 Panel manufacturing

The panel characteristics and constant parameters for making MDF panels have been presented in Table 2.

Two different levels of 5 and 7 percent of urea-formaldehyde (UF) resin (based on the dry fiber content) were used. An amount of solid ammonium chloride, ethylene diamine (as a cross linking agent), and distilled water were mixed into the liquid UF resin to dilute the resin and achieve the target mat moisture content. Neither paraffin nor other water repellent additives were used. The diluted glue was sprayed onto treated fibers with consistent parameters using a laboratory rotary drum blender consisting of an internal spray nozzle. Then, the resinated fibers were manually formed into mats using a wooden frame. All the fiber mats were hot-pressed under the same hot-pressing parameters (Table 2).

According to Table 1, 12 combinations, and three panels per each combination were made, which resulted in a total of 36 treated bagasse MDF panels.

2.6 Panel testing

After cold stacking, to reach equilibrium moisture content, all treated MDF panels were kept in a conditioning chamber at 20±3 °C and 65±1 % MC for 2 weeks, in accordance with ASTM standard method (ASTM D 1037-99, 2005). The properties of density, compression-shear strength ($C.S.s.th.$), modulus of rupture (MOR) in bending and modulus of elasticity (MOE) in bending dry condition, thickness swelling (TS) and water absorption ($W_d$) after 2 and 24-hour immersion in cold water were measured in accordance with EN standard methods (EN 310: 1993; EN 319: 1993; EN-317: 1993).

3 RESULTS AND DISCUSSION

The average properties of bagasse medium density fiberboard panels have been presented in Table 3. The results of ANOVA test on the effect of different variables, including the resin percentage, oxidant type, and oxidant content on physical and mechanical properties of test panels, have been summarized in Table 4.
The analyses showed that nitric acid was superior to potassium dichromate. Furthermore, the physical and mechanical properties of test panels improved with increasing of resin percentage and oxidant content (Table 3 and 4). Resin percentage showed a strong effect on both physical and mechanical properties of MDF boards. The effect of resin percentage on MDF properties was significant at 99% confidence level. In general, the properties of wood-based particleboards and medium density fiberboards are strongly dependant on the average density and to some extent on the amount of UF resin (Suzuki and Kato, 1999; Halvarsson et al., 1996; Gomez-Bueso et al., 2000; Shi et al., 2000; Halvarsson et al. 2008).

In general, the properties of wood-based particleboards and medium density fiberboards are strongly dependant on the average density and to some extent on the amount of UF resin (Suzuki and Kato, 1999; Halvarsson et al., 1996; Gomez-Bueso et al., 2000; Shi et al., 2000). This might be ascribed to increase fiber surface wettability, fiber surface resin coverage and fiber-fiber contact point, that create cross links (interbonds) between resinated fibers, which leads to the increased forces holding the fibers followed by the increase of resin percentage and consequently also the increase of furnish moisture content (Gomez-Bueso et al., 2000; Halvarsson et al., 2008).

### Table 3

**Average values of the properties of bagasse MDF boards**

<table>
<thead>
<tr>
<th>Treat. No.</th>
<th>MC %</th>
<th>Density (g/cm³)</th>
<th>MOR (MPa)</th>
<th>MOE (MPa)</th>
<th>C.S. sth. (MPa)</th>
<th>WA, %</th>
<th>TS, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.1</td>
<td>0.70</td>
<td>9.7</td>
<td>1579</td>
<td>0.65</td>
<td>160</td>
<td>177</td>
</tr>
<tr>
<td>2</td>
<td>8.3</td>
<td>0.714</td>
<td>9.97</td>
<td>1513</td>
<td>0.73</td>
<td>125</td>
<td>137</td>
</tr>
<tr>
<td>3</td>
<td>8.3</td>
<td>0.712</td>
<td>9.87</td>
<td>1798</td>
<td>0.74</td>
<td>101</td>
<td>110</td>
</tr>
<tr>
<td>4</td>
<td>8.2</td>
<td>0.72</td>
<td>12.3</td>
<td>2013</td>
<td>0.89</td>
<td>94</td>
<td>104</td>
</tr>
<tr>
<td>5</td>
<td>8.1</td>
<td>0.709</td>
<td>12.7</td>
<td>1988</td>
<td>0.92</td>
<td>86</td>
<td>95</td>
</tr>
<tr>
<td>6</td>
<td>8.3</td>
<td>0.72</td>
<td>11.6</td>
<td>1896</td>
<td>0.93</td>
<td>79</td>
<td>86</td>
</tr>
<tr>
<td>7</td>
<td>8.4</td>
<td>0.70</td>
<td>10</td>
<td>1611</td>
<td>0.67</td>
<td>143</td>
<td>157</td>
</tr>
<tr>
<td>8</td>
<td>8.4</td>
<td>0.716</td>
<td>9.1</td>
<td>1465</td>
<td>0.67</td>
<td>149</td>
<td>163</td>
</tr>
<tr>
<td>9</td>
<td>8.2</td>
<td>0.70</td>
<td>8.2</td>
<td>1373</td>
<td>0.63</td>
<td>150</td>
<td>166</td>
</tr>
<tr>
<td>10</td>
<td>8.4</td>
<td>0.71</td>
<td>10.7</td>
<td>1604</td>
<td>0.78</td>
<td>123</td>
<td>137</td>
</tr>
<tr>
<td>11</td>
<td>8.1</td>
<td>0.71</td>
<td>12.3</td>
<td>1884</td>
<td>0.83</td>
<td>117</td>
<td>131</td>
</tr>
<tr>
<td>12</td>
<td>8.3</td>
<td>0.7</td>
<td>12.3</td>
<td>1884</td>
<td>0.82</td>
<td>114</td>
<td>131</td>
</tr>
</tbody>
</table>

### Table 4

**The results of ANOVA test on the effect of variables on MDF properties**

<table>
<thead>
<tr>
<th>Independent variable</th>
<th>Dependent variable/ Zavisna varijabla</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MC, D, MOR, MOE, C.S. sth., WA, TS</td>
</tr>
<tr>
<td>B</td>
<td>A, B</td>
</tr>
<tr>
<td>A&gt;B</td>
<td></td>
</tr>
<tr>
<td>A&gt;C</td>
<td></td>
</tr>
<tr>
<td>A&gt;B+C</td>
<td></td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>2.14</td>
</tr>
</tbody>
</table>

**A – oxidant type / vrsta oksidansa; B – resin percentage / udjel smole; C – oxidant level / razina oksidansa; **S** – significant at 5 percent level / značajno na razini 5%; **S** – significant at 1 percent level / značajno na razini 1%; NS – non-significant / nije značajno; C.V. – coefficient of variance (standard deviation/mean) / koeficijent varijacije (standardna devijacija/srednja vrijednost); MC – moisture content / sadržaj vode; D – density / gustoća; MOR – modulus of rupture / modul loma; MOE – modulus of elasticity / modul elastičnosti; C.S. sth. – compression-shear strength / tlačno-smicajna čvrstoća; WA – water absorption / upijanje vode; TS – thickness swelling / debljinsko bubrenje.**
Water absorption and thickness swelling decreased with increasing oxidant content from 2 to 6 percent. This is in agreement with the results of Shen (1974) and Back (1991). Moreover, the highest effect was observed on thickness swelling, as for 6 % oxidant content it was up to 20 % less than that of 2 % (Fig. 3). Rowell (1986; 1987) pointed out that modifying the cell wall polymers to make them more hydrophobic or bulking them with bonded chemicals would reduce the tendency of wood to swell and shrink by change in moisture content. This may be the reason why WA and TS were generally reduced by an increasing in oxidant content. Another reason for this may be attributed to high wettability of the oxidized fibers due to functional groups increasing, consequently good penetration of water-soluble urea-formaldehyde resin and its better performance. Also, the use of an oxidant may be interpreted as leading to inter-fiber bonding (Johns and Woo, 1978).

Finally, the results showed that the effects of interaction of oxidant type, oxidant content and resin percentage on MOR, MOE and WA were significant at 99 % confidence interval ($\alpha \leq 0.01$) (Table 4). In addition, the highest values for MOR and MOE were related to the combination of 2 and 4 percent nitric acid along with 7 percent UF resin content (12.7 MPa and 2013 MPa, respectively) (Tables 3 and 4). The best value for C.S. strength was attributed to the combination of 6 percent nitric acid along with 7 percent UF resin content (0.93 MPa). The lowest values of WA and TS were also achieved for the combination of 6 percent nitric acid along with 7 percent UF resin content. The values of 79 %, 86 %, 27 % and 30 % were measured, respectively, for WA and TS after 2 and 24-hour immersion in cold water (Tables 3 and 4). Oxidative attack on lignin and especially on hemicelluloses or cellulose can also lead to some chain scission. While this process produces adequate wet strength and water swelling resistance, dry strength can be reduced (Allan and Neogi, 1971; Stenberg, 1978). One of the reasons for very high water absorption and thickness swelling might be ascribed to the fact that no water repellent additive was used. On the other hand, the natural mixture of cellu-

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**Figure 1** Effect of oxidant type on modulus of rupture (MOR), modulus of elasticity (MOE) and C.S. strength

**Figure 2** Effect of oxidant type on water absorption and thickness swelling after 2 and 24-hour immersion in cold water

**Figure 3** The influence of oxidant percentage on water absorption and thickness swelling after 2 and 24-hour immersion
lose, lignin and hemicelluloses in wood material possesses a better resistance to water and water absorption than expected for annual plant materials (Halvarsson et al., 2009). Consequently, the fiberboard produced of annual plant materials might have even worse water-resistant properties than fiberboards made of wood material (Sauter, 1996; Markessini et al., 1997; Han, 2001; Mantanis and Berns, 2001; Wasylciw, 2001; Ye et al., 2007). The ability of water absorption into the oxidized lignocellulosic materials will also increase and contribute to a higher water sensitivity of low resin fiberboards (Halvarsson et al., 2009).

Even though the addition of nitric acid and potassium dichromate improved the fiberboard properties, none of the manufactured bagasse fiberboards met the European wood-based MDF standard (EN 622-5: 2006). The water swelling properties were adversely affected, so TS and WA were several times higher than specified by the MDF standard.

4 CONCLUSIONS

4. ZAKLJUČAK

According to the results, mechanical and physical properties of chemically treated bagasse MDF boards were strongly dependent on resin percentage. The higher resin contents, the better mechanical and physical properties. Nitric acid showed better results than potassium dichromate, especially for thickness swelling. Furthermore, the properties of bagasse MDF boards improved with increasing oxidant content. Mechanical and physical properties of medium density fiberboards made from low resin oxidized bagasse fibers were not acceptable according to the requirements of the EN standards for MDF. Further studies should focus on methods for improving physical properties and mechanical strength of medium density fiberboards.

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