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APPLICATION OF AMMONIUM IONIC LIQUIDS IN PARTICLEBOARD TECHNOLOGY

Within the framework of Project no. POIG.01.03.01-30/074/08 "Ionic liquids in innovative technologies connected with processing of lignocellulosic raw materials" the Wood Based Panels and Glues Department of the Wood Technology Institute in Poznan carried out research aiming at application of ionic liquids in particleboard technology. The objective of the research was application of [DDA][NO₃] and [BA][NO₃] ionic liquids in preservation technology of panels resistant to biotic factors. The method for application of ionic liquids to particleboards, the type and amount of chosen ionic liquids, as well as their influence on standard parameters of the panels were investigated. In the tests the amine resin available on the domestic market and particles obtained from debarked Scots pine chips were used. The results of the research demonstrated that ionic liquids worsened parameters of the panels, but improved their resistance to decay fungi.

Keywords: particleboard, ionic liquids, decay fungi, mould fungi

Introduction

The term "ionic liquids" refers to salts composed entirely of ions. The most characteristic features of those salts are: melting point below 100°C, low vapour pressure, and chemical and thermal stability. Depending on the end use the

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properties of ionic liquids can be adjusted accordingly by altering their anions and cations.

Recently the interest in application of ionic liquids in wood related industries has been growing. Ionic liquids are considered to be new generation of solvents which emit no volatile organic compounds. Extensive research on wood dissolution in ionic liquids and extraction of cellulose from wood waste using ionic liquids has been carried out [Libert, Heinze 2008]. Kilpelainen et al. [2007] investigated the details of dissolution of wood-based lignocellulosic materials with ionic liquids. Xie et al. [2007] described effective homogenous chemical modification of wood in ionic liquids. Another interesting application of ionic liquids can be wood preservation [Pernak et al. 2004, 2005; Zabielska-Matejuk 2005, 2008; Han et al. 2009]. According to Zabielska-Matejuk [2008] some ionic liquids demonstrated good penetration into wood and effective wood protection against decay, stain or mould fungi. The possibility of modification of the structure of ionic liquids facilitates design of compounds with specific properties such as for example biocidal activity and the ability to protect wood [Zabielska-Matejuk, Pernak 2009].

Recent developments in the above-mentioned field show great potential of ionic liquids and might lead to improvement of performance of both wood and wood composites. Particleboards in common with wood intended mostly for building industry must be protected from biotic and degradation factors to ensure their long-term performance. Currently used wood preservatives might be environmentally unfriendly and harmful to human health. Introduction of ionic liquids into wood-based panels technology is aimed at improvement of biological durability of those materials. The important issue is finding such preservatives which have not only good fungicidal parameters but also insignificant influence on glue curing time and board parameters.

The aim of the research was to study the influence of the type, amount and the method of application of ionic liquids on standard parameters of panels. The produced panels were also tested for their resistance to *Coniophora puteana* fungus after 16 weeks of incubation and to mould fungi. The study involved the use of [DDA][NO₃] and [BA][NO₃] ionic liquids.

Materials and methods

During the research two types of ionic liquids were selected:

- [DDA][NO₃] – didecyldimethylammonium nitrate(V),
- [BA][NO₃] – benzalkonium nitrate(V).

The ionic liquids were developed and synthesized in the Institute of Chemical Technology and Engineering of the Poznan University of Technology.

Two methods for application of ionic liquids to particleboards were proposed. The first method consisted in dissolution of ionic liquid in water and

pouring of that solution into the particleboard laboratory blender before gluing of chips. The second method consisted in dissolution of ionic liquid directly in glue.

One-layer particleboards of the dimensions of 700×500×16 mm were produced from particles made of peeled, pine chips in laboratory conditions. The nominal density of the panels was 680 kg/m³. As a binding agent urea-formaldehyde resin (molar ratio of formaldehyde to urea 1.10) was used.

All the produced panels were tested for bending strength [PN-EN 310] and internal bond strength perpendicular to the plane of the board [PN-EN 319].

Table 1. Research variant

Tabela 1. Wariant badań

Sample <i>Próbka</i>	Type of ionic liquid added <i>Rodzaj dodanej cieczy jonowej</i>	Amount of ionic liquid added [kg/m ³] <i>Ilość dodanej cieczy jonowej [kg/m³]</i>	Method of ionic liquid addition to particleboard <i>Metoda dodania cieczy jonowej do płyty wiórowej</i>
0	–	–	–
A1.1	[DDA][NO ₃]	4.5	in water solution <i>w roztworze wodnym</i>
A1.2	[DDA][NO ₃]	4.5	in glue <i>w kleju</i>
A2.1	[DDA][NO ₃]	4.5	in water solution <i>w roztworze wodnym</i>
A2.2	[DDA][NO ₃]	9.0	in glue <i>w kleju</i>
B1.1	[BA][NO ₃]	4.5	in water solution <i>w roztworze wodnym</i>
B1.2	[BA][NO ₃]	4.5	in glue <i>w kleju</i>
B2.1	[BA][NO ₃]	9.0	in water solution <i>w roztworze wodnym</i>
B2.2	[BA][NO ₃]	9.0	in glue <i>w kleju</i>

The resistance to mould fungi was tested using a method based on Building Research Institute Instruction No. 355/98 [1998]. The tested specimens of particleboards protected with the ionic liquids were of the dimensions of 50 × 50 thickness mm. On reaching the moisture content of 12±1% the samples were exposed to the action of a mixture of pure cultures of the following fungi: *Aspergillus niger* v. Tieghem, *Penicillium funiculosum* Thom, *Pecilomyces varioti* Bainer, *Trichoderma viride* Persoon ex Fries, *Alternaria tenuis* Link ex Fries (mixture), or to the action of a pure culture of *Chaetomium globosum* Kunze for

fungus for 4 weeks. The growth of mycelium on the surface of samples was measured after 4 weeks of incubation at the temperature of $27\pm 1^\circ\text{C}$ and 90% relative humidity using the following scale in accordance with the above-mentioned instruction:

0 – no visible under the microscope growth of fungi on the sample,

1 – trace growth of fungi on the sample hardly visible to the naked eye but well visible under the microscope or visible to the naked eye growth limited to the edge of the sample,

2 – visible to the naked eye growth of the fungi on the sample, but less than 15% of the surface is covered with fungus,

3 – over 15% of the surface is covered with fungi visible to the naked eye.

To compare the degree of mould coverage, control boards and the samples of Scots pine sapwood were tested.

The resistance of tested materials to wood-decaying fungi was defined by determination of mass loss of the tested samples due to brown rot fungi action, according to methods based on PN-EN 113 and PN –ENV 12 083 (*Basidiomycotina*). The particleboard samples of the dimensions of 50×30 thickness mm protected with ionic liquids were sterilised with steam in an autoclave. Then the samples were exposed to the action of a pure culture of *Coniophora puteana* (Schum. ex Fr.) Karst fungus for 16 weeks and mass loss of specimens was determined. It was compared with the mass loss of Scots pine sapwood to calculate the DSI (Decay Susceptibility Index) expressed as:

$$\text{DSI} = T \times 100/S \quad (1)$$

where: T – mean loss in board mass [%],

S – mean loss in the mass of the appropriate set of specimens of Scots pine sapwood [%].

The DSI values of 100 indicate the same decay resistance as that of pine wood, lower DSI values for particleboards protected with the ionic liquids meant they proved more resistant to the attack of the fungus.

Results and discussion

The results of the internal bond and bending strength measurements done for the particleboard with the additives of [DDA][NO₃] and [BA][NO₃] ionic liquids are presented in fig. 1. Both mentioned ionic liquids worsened the parameters of particleboards. The bending strength dropped about 44 in relation to the control board marked “0” when 4.5 kg/m^3 of [DDA][NO₃] ionic liquid in water solution was added. Double amount of that ionic liquid also applied in water solution did not cause further fall in the bending strength. When the same ionic liquid was added in the amounts of 4.5 and 9 kg/m^3 directly to the glue, a smaller but still

significant fall in the bending strength was observed. A similar situation was observed for $[\text{BA}][\text{NO}_3]$, but in that case the ionic liquid decreased the bending strength by about 30% independently of the application method and the additive amount. However, the method for $[\text{DDA}][\text{NO}_3]$ application influenced the internal bond of the panels. In that case addition of the ionic liquid directly to glue was a more preferable method. The way of application of the second ionic liquid, i.e. $[\text{BA}][\text{NO}_3]$, did not cause as much differences between the values of the internal bond of the panels. During particleboard production different preservatives can be added to glue, but chips can be treated before gluing as well. From the practical point of view, according to Drouet [1992], application of preservatives separately is more beneficial, because it facilitates fast shifting of production. However, Basturk [2008] draws attention to the fact that the method of applying chemical solution directly to the dried particles before or after glue application also has its limitations. The researcher suggests that, due to the moisture content of adhesive, only 5 to 7% of chemical solution should be used for treatment, otherwise an excessive increase in the moisture content can cause blisters and delamination during pressing.

The results of mechanical tests presented in fig. 1 and fig. 2 demonstrate clear influence of ionic liquids selected for this research on the particleboards' parameters. However, it can be pointed out that, in comparison with didecylmethylammonium nitrate (V), benzalkonium nitrate (V) affected mechanical properties of the panels to a smaller extent.

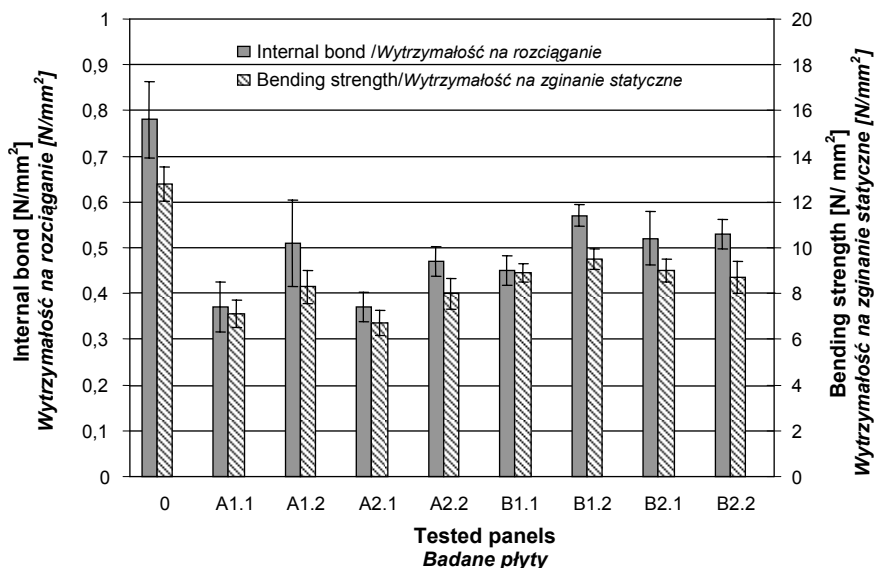


Fig. 1. Bending strength and internal bond of the tested particleboards

Rys. 1. Wytrzymałość na zginanie oraz rozciąganie badanych płyt wiórowych

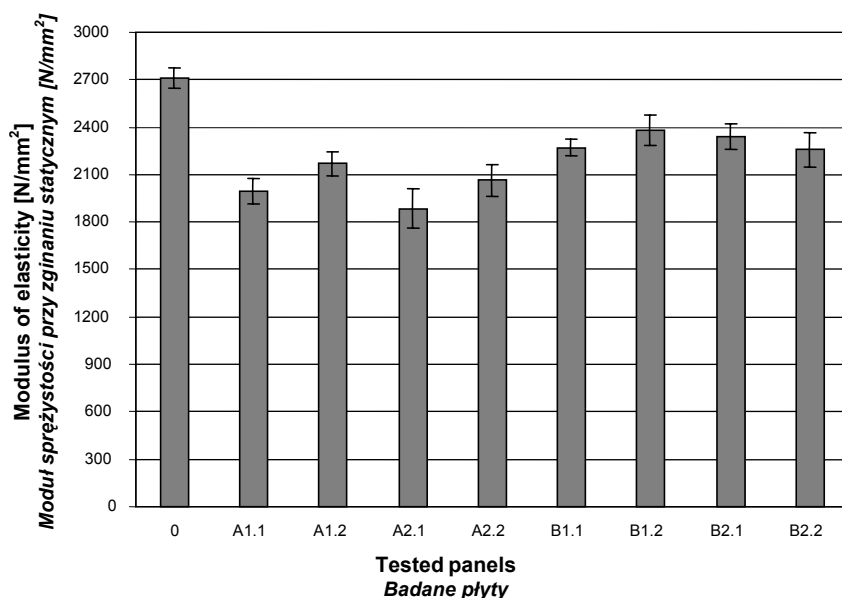


Fig. 2. Modulus of elasticity of the tested particleboards

Rys. 2. Moduł sprężystości badanych płyt wiórowych

Table 2 presents the resistance of the tested materials to wood-decaying fungi and the mixture of moulds. Independently of the application method (in water or in glue), the particleboards protected with [DDA][NO₃] ionic liquids in the amount of 9 kg of dry mass per m³ of the panel demonstrated the highest resistance to brown rot *Coniophora puteana*. The decay susceptibility index (DSI) was 45.6 and 51.8. In the case of application of the same amount of benzalkonium nitrate(V), i.e. [BA][NO₃], the worst protection effect was obtained. The mass loss caused by the test fungi ranged from 28.3 to 31.5%. (DSI was from 91.6 to 101.9). After applying a smaller amount of the ionic liquids to the glue (4.5 kg/m³) the protection against destruction by micro-organisms was not achieved. The control samples degradation during the test was about 40.7%.

The degree of mould coverage of the surface indicates various resistances of the particleboards with the ionic liquid to the mixture of mould fungi and to *Chaetomium globosum*. The method of application and the amount of ionic liquids introduced into the particleboards did not result in complete protection of their surface against the growth of mould fungi.

Table 2. Resistance of particleboards protected with the ionic liquids to *Coniophora puteana* after 16 weeks of incubation and to mould fungi
Tabela 2. Odporność płyt wiórowych zabezpieczonych cieczami jonowymi na działanie *Coniophora puteana* po 16 tygodniach inkubacji oraz na działanie grzybów pleśniowych

Tested sample <i>Badana próbka</i>	Ionic liquid type <i>Rodzaj cieczy jonowej</i>	Amount of ionic liquid added <i>Ilość dodanej cieczy jonowej</i>	Moisture content in wood after exposure to <i>C. puteana</i> <i>Wilgotność drewna po narazeniu na działanie <i>C. puteana</i></i>		Mass loss of wood after exposure to <i>C. puteana</i> <i>Utrata masy drewna po narazeniu na działanie <i>C. puteana</i></i>		DSI*	Degree of the mould growth on the surface <i>Stopień zaplesnienia powierzchni</i>	
			min	max	min	max		<i>Chaetium globosum</i>	<i>Mixture Mieszanina</i>
0 Control particleboard <i>Płyta wiórowa kontrolna</i>	–	–	103.3	128.8	38.7	45.8	131.73	3	3
A2.1	[DDA][NO ₃]	9 in water solution <i>w roztworze wodnym</i>	51.4	58.3	13.7	14.2	45.63	–	–
A2.2	[DDA][NO ₃]	9 in glue <i>w kleju</i>	59.5	64.2	15.3	16.5	51.78	1.2	3
B1.2	[BA][NO ₃]	4.5 in glue <i>w kleju</i>	84.4	108.3	34.1	36.3	114.56	2.4	3
B2.1	[BA][NO ₃]	9 in water solution <i>w roztworze wodnym</i>	69.5	77.8	27.7	28.7	91.59	3	0.8
B2.2	[BA][NO ₃]	9 in glue/w kleju	78.8	95.4	29.7	32.3	101.94	1.4	1.6
Pine wood <i>Drewno sosny</i>	–	–	51.8	59.2	25.7	36.9	–	3	3

Conclusions

On the basis of the obtained results the following conclusions can be drawn:

- Both ionic liquids applied significantly lowered mechanical properties of the panels. However, in comparison with didecyldimethylammonium nitrate(V), benzalkonium nitrate(V) affected the panels' mechanical properties to a smaller extent.
- The method of application of [DDA][NO₃] ionic liquids had essential influence on the internal bond. In that case, a more preferable method was addition of the ionic liquid directly to glue. The method of [BA][NO₃] application did not cause as much difference between the values of the internal bond of the panels as it did in the above-mentioned case.
- There were no significance differences in mechanical properties of the panels depending on the amount of the ionic liquids applied. A greater amount of the ionic liquids in particleboards can lead to better protection against fungi without causing further fall in the internal bond and bending strength of the panels.
- Independently of the application method (in water or in glue), [DDA][NO₃] ionic liquids in the amount of 9 kg of dry mass per m³ of the panel demonstrated the highest resistance to brown rot fungi.

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List of standards

PN-EN 312 Particleboards– Specifications

PN-EN 310 Wood – based panels – Determination of modulus of elasticity in bending and of bending strength

PN-EN 319 Particleboards and fiberboards – Determination of tensile strength perpendicular to the plane of the board

ZASTOSOWANIE CIECZY JONOWYCH W TECHNOLOGII PŁYT WIÓROWYCH

Streszczenie

W Zakładzie Materiałów Drewnopochodnych i Klejów w ramach Projektu nr POIG.01.03.01-30/074/08 „Ciecze jonowe w innowacyjnych technologiach związanych z przetwarzaniem surowców lignocelulozowych” realizowane są badania zmierzające do zastosowania cieczy jonowych w technologii płyt wiórowych. Celem badań jest wykorzystanie cieczy jonowych w technologiach zabezpieczania płyt na działanie czynników biotycznych. Dotychczasowe badania obejmowały opracowanie sposobu wprowadzania cieczy do wiórów przeznaczonych do wytwarzania płyt, poznanie wpływu rodzaju i ilości wybranych cieczy jonowych – [DDA][NO₃], [BA][NO₃] – na standardowe właściwości. Stosowano klejową żywicę aminową dostępną na rynku krajowym i wióry pozyskane z korowanych zrębków sosnowych. Badania wykazały, że zastosowane ciecze jonowe obniżają właściwości mechaniczne płyt, poprawiają natomiast ich odporność na grzyby rozkładu brunatnego.

Słowa kluczowe: płyta wiórowa, ciecze jonowe, grzyby rozkładu brunatnego, grzyby pleśniowe

