Drewno. Pr. Nauk. Donies. Komunik. 2010, vol. 53, nr 184

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WETTABILITY OF WOOD SURFACES TREATED WITH IONIC LIQUIDS

The aim of the research was to measure the wettability of wood surface protected with three ionic liquids differing in terms of cation and anion structure as well as fungicidal properties. Herbicidal ionic liquids with functional anion, nitrate(V) with cation derived from natural coconut oil and ionic liquid with dodecylbenzenesulfonate anion were tested. The investigation was carried out on pine wood Pinus sylvestris L. The presented results indicate that the ionic liquids containing 12-carbon hydrophobic alkyl chain in their structure, i.e. [DDA][ABS] and [ArqC35][NO_3], worsened wood wettability, thus improved the protection of wood against water.

Keywords: wettability, contact angle, ionic liquids, wood

Introduction

Microbiological destruction processes of wood caused not only by fungi, but also by algae, bacteria, insects or marine organisms, can be sufficiently inhibited or eliminated thanks to preservation of wood with chemicals often aided by physical treatment, e.g. high temperature processing. Current wood protection, having no negative consequences for the environment, prefers replacement of classic preservatives with biodegradable components. Heat treatment of wood, leading to elimination of nutrients for fungi, increases wood natural resistance to

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microbiological decomposition and simultaneously decreases its susceptibility to damping [Hakkou et al. 2005; Noskowiak 2007]. The hydrophobization effect together with improved durability can be achieved through modification of wood with organosilicon compounds [Tinggaut et al. 2005; Gosh et al. 2008; Sèbe, Brook 2001], synthetic resins [Bach et al. 2005] and other hydrophobic agents. Fungistatic and fungicidal properties of quaternary ammonium salts and then ionic liquids have opened those compounds the door to application in wood preservation [Pernak et al. 2004, 2005; Zabielska-Matejuk 2005]. The consequence of the amphiphilic character of those compounds is their adsorption on the surface of microorganism cells, which is especially visible in the case of chemotrophic bacteria that are constituents of water biocenosis and soil. It can cause their elimination from the environment.

The possibility of ionic liquid structure modification is one of the most precious features of those organic compounds. They facilitate matching of a biologically active structure to a microorganism species and, in the case of an increase in resistance, exchange of the functional group for a more efficient. The introduction of the hydrophobic alkyl chain (relatively specific anions) into the ionic liquid structure makes it possible to obtain multifunctional compounds that are biocidal and able to protect a lignocellulosic conglomerate, such as wood, against water. This property of ionic liquids makes the process of wood preservation easier, because they lower wettability, hygroscopicity and impregnability of wood, thus inhibiting colonisation of wood by microorganisms and their growth in it. The investigation of changes in wettability of wood surface before and after the treatment with ionic liquids can be a confirmation of the hydrophobic character of protection with those chemicals. The assessment of wood surface wettability can be made on the basis of the measurement of contact angles, calculation of free surface energy, work of adhesion, and critical surface tension of wetting [Gray 1962; Gunnells et al. 1994; Liptakowa, Paprzycki 1984; Lis, Proszyk 2001].

In this study wettability (contact angle) of wood surface protected with three ionic liquids differing in terms of cation and anion structure as well as fungicidal properties was investigated. Herbicidal ionic liquids with functional anion, nitrate(V) with cation derived from natural coconut oil and ionic liquid with dodecylbenzenesulfonate anion were tested.

Materials and methods

The ionic liquids were developed and synthesised in the Institute of Chemical Technology and Engineering of the Poznan University of Technology by M. Kot [Pernak et al. 2009]. Structures of the synthesised compounds were confirmed by the analysis of ^{1}H NMR and ^{13}C NMR spectra (Varian 300 VT type spectroscope). The prepared compounds had the form of wax.

For the research the following compounds were taken into consideration:
- [Ciech][1] – ionic liquid with didecyldimethylammonium cation and herbicidal anion,
- [DDA][ABS] – didecyldimethylammonium dodecylbenzenesulfonate,
- [ArqC35][NO_3] – nitrate(V) with cation derived from natural coconut oil [Zabielska-Matejuk, Pernak 2009].

The investigation was carried out on Scots pine sapwood *Pinus sylvestris* L. of the density of 480–520 kg/m^3. The samples' dimensions were 100 × 50 × 10 mm (the longer edges were parallel to the fibers). The measurements of contact angle were performed on samples conditioned at a temperature of 20±1°C and humidity of 65±2% to a moisture content of 12±1%. The isopropanol solution of [Ciech][1] and [DDA][ABS] and water solution of [ArqC35][NO_3] in the amount of 50 g pure active substance on m^2 of wood were applied using a paint brush on the sanded surfaces (100 × 50 mm) of tangential and radial section of the samples. Then the samples were conditioned for 4 weeks in the dishes over a saturated solution of ammonium nitrate with a moisture content of 12±1%. The average angle measured between the covered surface and the water drop remaining on it, called the contact angle, was determined on the basis of a 10-measurement set (5 measurements on early wood and 5 measurements on late wood). The average contact angle was determined every second for 60, 180 or 240 seconds (depending on the preservative type and section of wood). For the purpose of comparison the contact angle for uncovered wood (control samples) was also measured. For each drop around 5µl of redistilled water of a temperature of 23±1°C was used.

The measurements were taken using a KSV CAM 101 apparatus.

Results and discussion

The highest value of the contact angle was determined for wood with didecyldimethylammonium dodecylbenzenesulfonate. The contact angles of samples protected with [DDA][ABS] remained around the level of 50 deg for over 4 minutes. Wood treated with that ionic liquid demonstrated much better water repellency than in the case of untreated wood and wood treated with other preservatives. Better resistance to water, in comparison with untreated wood, was obtained also for nitrate(V) with cation derived from natural coconut oil treatment. In the case of [Ciech][1] the water drop applied on the wood surface spilt and soaked into it immediately. As it is illustrated in fig. the water drop was absorbed into the protected surface after 2 seconds of measurements.

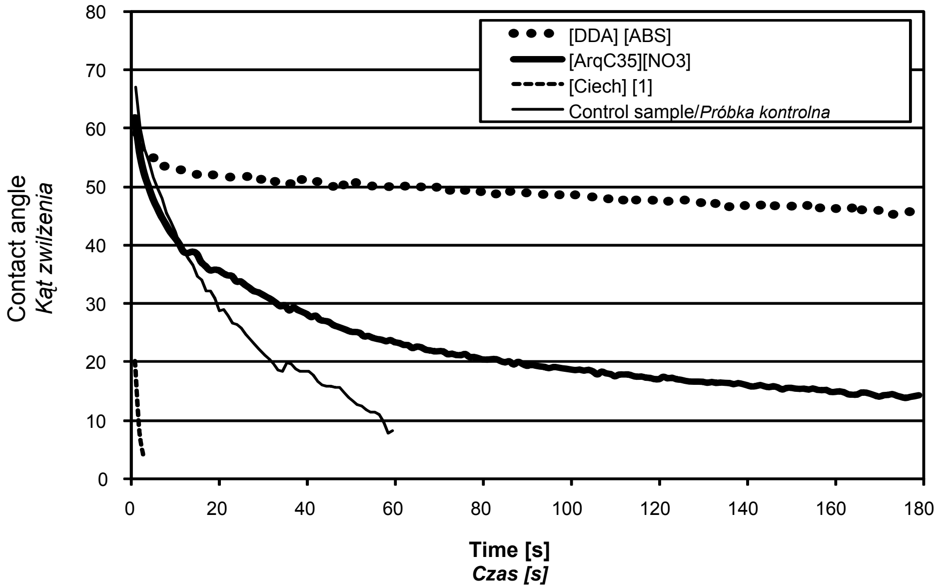

Fig. 1. Contact angles determined on the wood radial section
Rys. 1. Kąty zwilżania wyznaczone na przekroju promieniowym

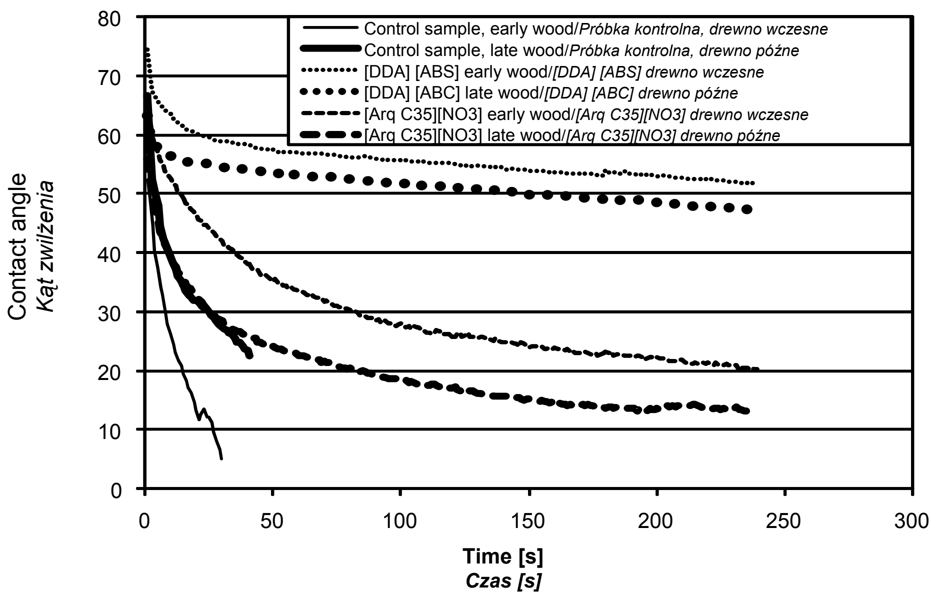

Fig. 2. Contact angles determined on the tangent section of the control samples and the samples treated with [DDA][ABS] and [ArqC35][NO_3]
Rys. 2. Kąty zwilżania wyznaczone na przekroju stycznym dla próbki kontrolnej oraz dla próbek zabezpieczonych [DDA][ABS] i [ArqC35][NO_3]

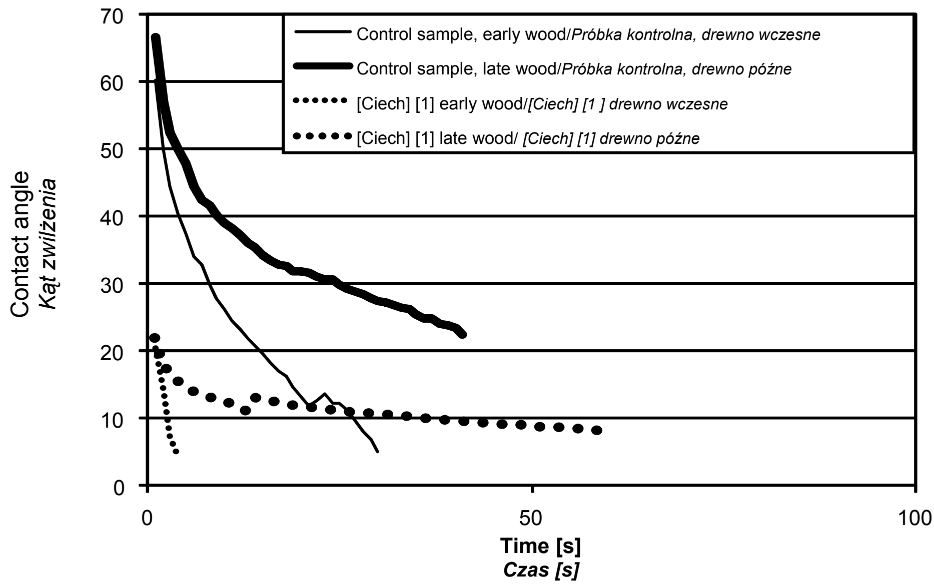

Fig. 3. Contact angles determined on the tangent section of the control samples and the samples treated with [Ciech] [1]
Rys. 3. ***Kąty zwilżania wyznaczone na przekroju stycznym dla próbki kontrolnej oraz dla próbki zabezpieczonej* [*Ciech] [1]***

The tested ionic liquids behaved differently depending on whether early or late wood was concerned. The results presented in fig 4 and fig 5 indicate that early wood treated with [DDA][ABS] and [ArqC35][NO_3] demonstrated better water repellency than late wood.

However, this difference is much bigger in the case of the tangential section of wood treated with nitrate(V) with cation derived from natural coconut oil. Unlike behaviour was observed in the case of unprotected wood, where water repellency of early wood was smaller than that of late wood on the tangential section. According to Herczeg [1965] it is hard to draw unequivocal conclusions whether this phenomenon is a consequence of greater roughness or the differences in chemical composition of early wood and late wood, such as the content of extractives. However, it can be assumed that better penetration of the above-mentioned ionic liquids into early wood can cause its better protection against water.

Even though both ionic liquids [DDA][ABS] and [ArqC35][NO_3] improved water repellency of wood, the application of the latter can be limited. This limitation is caused by the white marks which occurred after water absorption of the wood samples. The explanation of this phenomenon can be that nitrate(V) with cation derived from natural coconut oil is soluble in water.

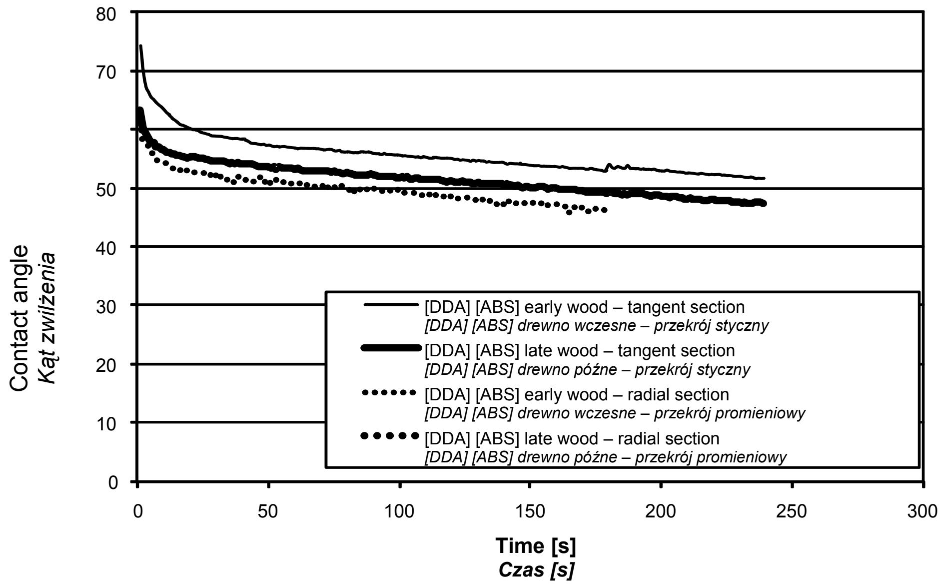

Fig. 4. The contact angles of early wood and late wood protected with [DDA] [ABS] depending on the wood section

Rys. 4. Kąty zwilżania drewna wczesnego i późnego zabezpieczonego [DDA][ABS] w zależności od przekroju

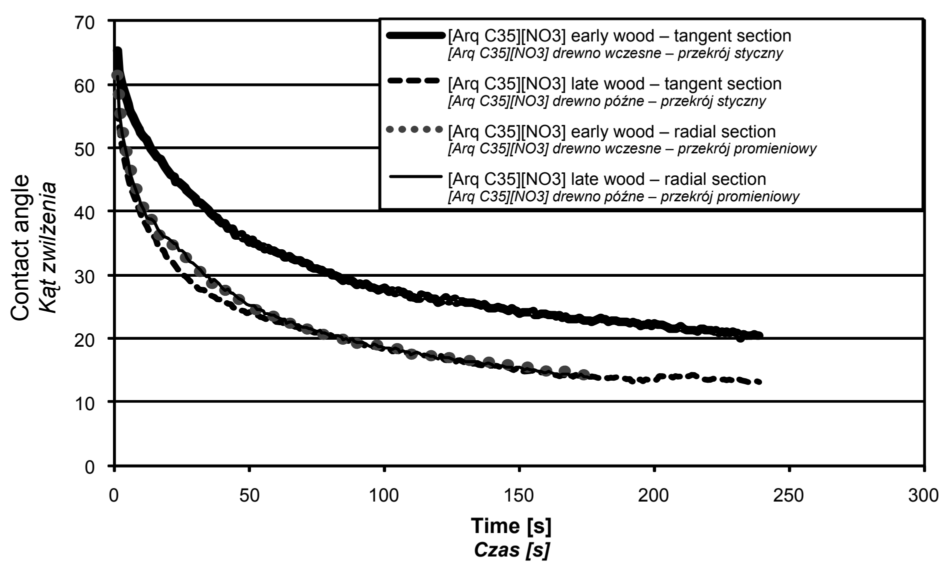

Fig. 4. The contact angles of early wood and late wood protected with [Arq C35] [NO$_3$] depending on the wood section

Rys. 4. Kąty zwilżania drewna wczesnego i późnego zabezpieczonego [Arq C35 [NO$_3$] w zależności od przekroju

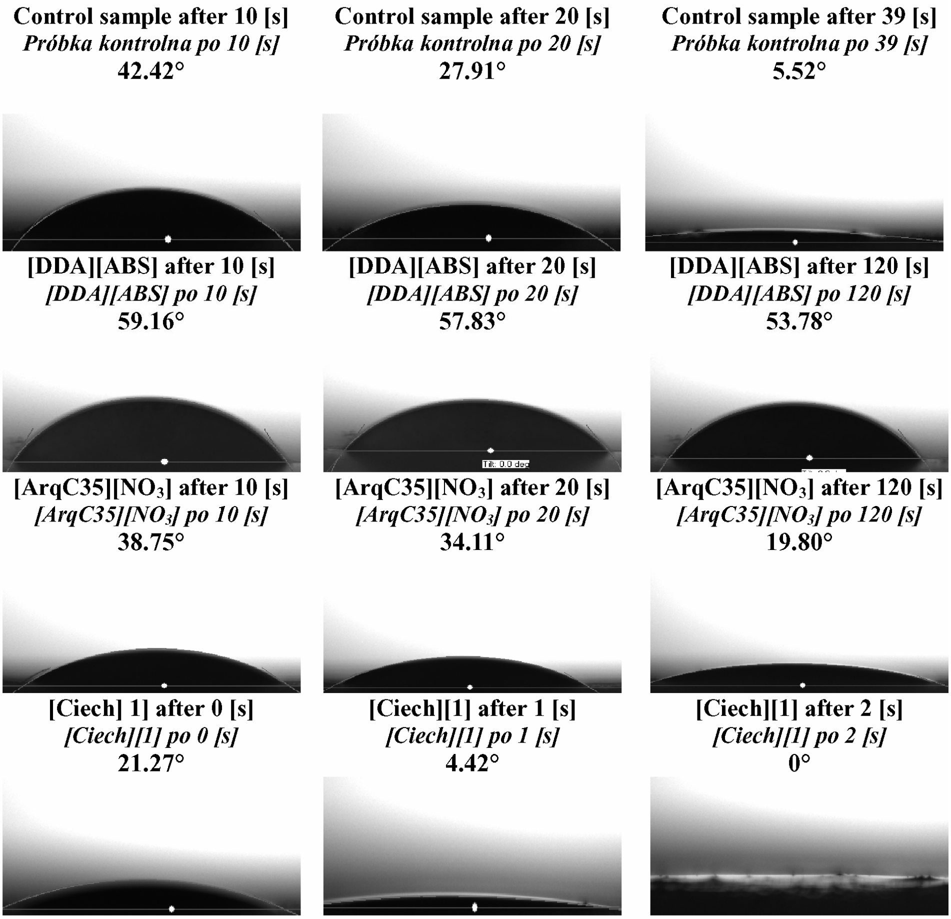

Fig. 5. The average contact angles determined on the radial section
Rys. 5. Średnie kąty zwilżania wyznaczone na przekroju promieniowym

The contact angle, determined by drawing a tangent to the drop at the contact point between the liquid and the solid intersection, is the most direct indicator of wettability. From the practical point of view, this parameter can be very useful for selection of a proper method for finishing of wood or unfinished panels. Chemical treatment of wood by different compounds with reactive groups, especially with polymer, can lead to an increase in the hydrophobic character of wood, both on its surface and inside it [Bach et al. 2005].

This study demonstrates a possibility of quick assessment of the influence of ionic liquids on wood wettability using the contact angle measurement. The presented results indicate the potential of ionic liquids for protection of wood against water, especially of didecyldimethylammonium dodecylbenzenesulfonate which significantly decreases the absorption of water by wood. The contact angle of wood protected with ionic liquids depends on the length of the hydrocarbon chain in their structure. The compounds with a hydrophobic dodecyl alkyl substituent in the anion of [DDA][ABS] were the most effective in terms of decreasing the wetting of the treated Scots pine sapwood. The compound developed from coconut oil [ArqC35][NO_3], containing a mixture of hydrocarbon chain ranging from C_8 to C_{14}, demonstrated lower wood hydrophobization ability. The introduction of herbicidal anion into the structure ionic liquids with didecyldimethylammonium cation caused an increase in the treated wood wettability in comparison with the control wood.

Conclusions

The results presented above lead to the following conclusions:

– the two out of the three tested ionic liquids, i.e. [DDA][ABS] and [ArqC35][NO_3] containing the long hydrocarbon chain, worsened the wettability of wood, thus improved the protection of wood against water,
– the wood treated with [Ciech][1] had higher wettability than the untreated wood,
– in the case of wood treated with [DDA][ABS] and [ArqC35][NO_3] significant differences in terms of early wood and late wood wettability on the tangential section were observed.

Acknowledgements

This study was carried out with the financial support of the European Regional Development Fund within the framework of the Innovative Economy Operational Programme in Poland in the years 2007–2013, project number POIG.01.03.01-30-074/08 “Ionic liquids in innovative technologies connected with processing of lignocellulosic raw materials”.

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BADANIA ZWILŻALNOŚCI DREWNA ZABEZPIECZONEGO POWIERZCHNIOWO CIECZAMI JONOWYMI

Streszczenie

Przedstawiono badania zwilżalności drewna zabezpieczonego powierzchniowo trzema cieczami jonowymi, o zróżnicowanej strukturze zarówno kationu, jak i anionu oraz skuteczności działania grzybobójczego. Zbadano „herbicydowe ciecze jonowe” z funkcyjnym anionem, azotan(V) z kationem pochodzenia naturalnego z oleju kokosowego oraz ciecz jonową z anionem dodecylobenzosulfonowym. Badania wykonano na drewnie sosny *Pinus sylvestris* L. Wykazano, iż ciecze jonowe zawierające w strukturze 12-weglowy, hydrofobowy łańcuch alkilowy [DDA][ABS] oraz [ArqC35][NO_3], wprowadzone do drewna wpływają na pogorszenie jego zwilżalności, a tym samym na zwiększenie jego odporności na działanie wody.

Słowa kluczowe: zwilżalność, kąt zwilżania, ciecze jonowe, drewno