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PRACE NAUKOWE - RESEARCH PAPERS

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PROTIC IONIC LIQUIDS AS A NEW HARDENER-MODIFIER SYSTEM FOR MELAMINE-UREA-FORMALDEHYDE ADHESIVE RESINS

This paper presents the results of investigations on the possibility of using protic ionic liquids as a hardener and modifier of melamine-urea-formaldehyde (MUF) adhesive resins. In research dialkylmethylammonium dodecylbenzenesulfonate base protic ionic liquids with varied amounts of carbon in alkyl group were used. The plywood manufactured using protic ionic liquids and MUF resin was characterized by a complete water resistance of glue lines, thus meeting the requirements of EN-314-02 standard.

Keywords: MUF adhesive resin, protic ionic liquid, modifier-hardener system, plywood

Introduction

For the curing of adhesive amino resins we use ammonium salts of strong inorganic acids, primarily nitrates, sulfates and chlorides (coming out of use for environmental reasons), inorganic acids (phosphoric acid) and organics (formic acid, oxalic acid), as well as acid anhydrides [Pizzi 1994]. In order to increase hydrolytic resistance of adhesive joints, melamine salts are used [Weinstabl et al. 2001; Zanetti, Pizzi 2003, 2004].

Much research on alternative hardeners that cause viscoelastic dissipation of energy of glue lines and an increase in their resistance to external factors has

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been conducted independently [Wang, Pizzi 1997; Proszyk et al. 2002; Pizzi et al. 2002; Zanetti et al. 2002; Kamoun, Pizzi, Zanetti 2003; Zanetti, Pizzi 2004]. In the Wood Technology Institute we have been studying a new generation of "multitasking" hardener of amino resins. Based on preliminary studies, we have found that ionic liquids can meet these expectations.

Ionic liquids are chemical organic compounds composed solely of ions (cation and anion) and having a melting temperature below the boiling point of water [Deetlefs, Seddon 2010; Kichner 2009]. Ionic liquids have been applied in many fields of human activity [Rogers, Seddon 2002; Wasserscheid, Welton 2008]. They have also been broadly used in wood technology, especially in wood preservation [Han et al. 2008; Pernak et al. 2008; Stasiewicz et al. 2008; Pernak et al. 2004, 2005, 2006, 2008; Zabielska-Matejuk et al. 2004; Zabielska-Matejuk 2005]. Ionic liquids are often referred to as "designed compounds", and they owe this description to the fact that they offer a possibility of modelling their properties by selecting cation and anion. This creates the possibility of obtaining compounds that, in addition to cross-linking properties, allow the adhesive bond to obtain the desired physical and mechanical properties.

From this perspective, it can be interesting to apply protic ionic liquids (PILs). They are a special case of ionic liquids that are synthesised by the transfer of a proton derived from the acid to the free electron pair on the nitrogen atom present in the amine [Welton 1999].

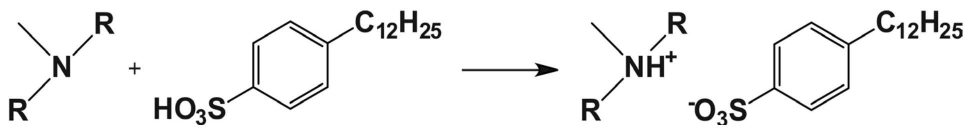
This paper presents the results of conducted research on the usefulness of dialkylmethylammonium dodecylbenzenesulfonate base protic ionic liquids as a hardener-modifier system for melamine-urea-formaldehyde adhesive resin.

Materials and methods

General procedure for synthesis of protic ionic liquids

All reagents were purchased from a commercial source (Sigma-Aldrich) and used as received. 0.05 mol of tertiary amine was dissolved in 100 cm^3 of methanol and then 0.05 mol of dodecylbenzenesulfonic acid (70%) was added. The solution was stirred at cool bath in 20^{o}C for 30 min. Methanol was then removed in vacuum. Next, in order to obtain hydrophobic ionic liquids, water (50 cm^3) was added to the raw product and then the mixture was shaken. The mixture was stirred for an additional 30 min. After the separation of phases, the organic phase was washed with 10 cm^3 of distilled, cold water until free amine was no longer detected. Water was then removed and the residue was dried at 50^{o}C in vacuum.

In this research PILs with alkyl substituent of the following amounts of carbon were used: 4 (butyl – C_4H_9) , 6 (hexyl – C_6H_{13}), 8 (oktyl – C_8H_{17}), 10 (decyl – $C_{10}H_{21}$). PILs were developed and synthesised in the Institute of Chemical Technology and Engineering, Poznan University of Technology.



$R = C_nH_{2n+1}$ where n = 4, 6, 8, 10

Fig 1. Reaction of synthesis of protic ionic liquids
Rys.1. Reakcja syntezy protonowych cieczy jonowych

MUF resin

In our studies we applied MUF resins condensed on a lab scale for the molar ratio of formaldehyde : melamine : urea as follows 3.8 : 1.0 : 1.0. The condensation was a three-stage process performed at a temperature of 82 ± 2°C and 0.2 mole of urea was additionally condensed in the third stage. Condensation was carried out to water tolerance in the range of 100 ÷ 130%. Polycondensate was not distilled. The synthesis details are presented hereinbefore [Jóźwiak, Proszyk, Jabłoński 2003]. The resins were stored at a temperature of 20 ± 2°C.

The basic physicochemical properties of the resin were determined using the following methodologies:

- apparent viscosity using Emil rotational viscometer in accordance with PN-92/C-89402,
- content of dry mass according to DIN EN 827 (weighed sample 2.0 ± 0.1 g was dried in a thermal chamber with natural air circulation, at 120 ± 1°C for 120 ± 1 min),
- pH applying pH-meter with combined electrode, according to PN-ISO 1148,
- gel time at 100°C, according to BN 75/3537-01,
- free formaldehyde content by sulphite method, according to DIN EN 1243.

The MUF resin was characterised by the following basic properties: apparent viscosity of 35 mPa·s, solid content 52.3%, pH value 9.48, gel time at 100°C – 103 s, and free formaldehyde content 0.76 %.

Preparation of glue mixtures

To arrive at the technological conditions that are necessary for the appropriate bonding of adhesives, the viscosity of polycondensate was increased by adding potato starch to the amount of 5% of solid mass of the resin, thus obtaining a viscosity of 2100 ± 100 mPa·s. The gelatinization process was carried out in a water bath at 80 ± 2°C.

Then protic ionic liquids in the amount of 20% of solid mass of the resin were added. For control purposes, the glue mixtures hardened with solid NH_4NO_3 to the amount of 3.2% of solid mass of the resin were prepared.

The gel time at 100°C for the glue mixture (without starch) was determined independently according to the BN 75/3537-01 standard.

Preparation and test of plywood

The glue mixtures were spread in a quantity of 180 g/m^2 on the surfaces of beech veneer. Three-layered plywood in the form of 300 × 300 mm sheets that were 1.8 mm thick (moisture content of veneer 6 ± 1% was glued after 40 min assembly time with the use of a laboratory press in the following conditions: unit pressure 1.8 MPa, temperature 125 ± 2°C and time 10 min. The plywood was prepared for selected variants (PIL-butyl and PIL-decyl) after 1 day and 30 days after application of the glue mixtures. The plywood was produced using the same pressing parameters. All plywood types were conditioned for 7 days in standard atmosphere, i.e. temperature of 23 ± 2°C and relative humidity of 50 ± 5%.

Then samples were cut to determine the shear strength (R_t) of the adhesive glue line of the plywood in accordance with the EN 314-1 standard. Before determining the shear strength of the bonds, the samples were subjected to hydrothermal treatments in accordance with item 5.1.1 (24 h soaking in water at a temperature of 20 ± 3°C) and 5.1.3 (4 h boiling in water as well as 16 h drying in air at a temperature of 60 ± 3°C and 4 h boiling in water and cooling in water to a temperature of 20 ± 3°C) of the EN314-1 standard. All the samples were tested wet in a Schopper testing machine at loads up to 500 daN. Rupture of the samples occurred within 30 ± 10 s. After shear tests, the samples were dried and the percentage share of the bond surface covered with wood fibers, i.e. wood failure (WF), was determined by comparing the pictures of bond damage with those presented in the EN 314-1 standard.

Results

The results of research on the application of protic ionic liquids in plywood manufacturing technology are summarised in tables 1 and 2 and illustrated in fig. 2 and 3.

The gel time at 100°C of the adhesive glue mixtures ranged from 287 s (PIL-butyl group) to 540 s (PIL-decyl). During the test a strong foaming of the adhesive mixtures was observed. A cured adhesive was characterised by relatively high flexibility (low hardness) compared to the control variant. Organoleptic assessment indicated that the adhesive could be modified under the influence of PIL. The gel time of PIL-cured adhesive masses was from 3 to 6 fold higher compared with the control hardener NH_4NO_3 (gel time 96 s) used. For these reasons, the plywood pressing time was set at 10 min.

Table 1. Shear strength and wood failure of three-layer beech plywood with MUF resin hardened with PILs with different amounts of carbon in alkyl group after tests according to EN 314-01 standard

Tabela 1. Wytrzymałość na ścinanie i udział ścięcia próbki w drewnie trzywarstwowych sklejek bukowych po testach według EN 314-01 uzyskanych z żywicy MUF utwardzanej protonowymi cieczami jonowymi z różną liczbą atomów węgla w grupie alkilowej

Shear strength and wood failure of plywood after tests according to EN 314-01 *Wytrzymałość na ścinanie i udział ścięcia próbki w drewnie po testach wg EN 314-01*			Hardener type *Typ utwardzacza*				
			Alkyl group in PILs *Grupa alkilowa w protonowej cieczy jonowej*				Control *Kontrolny*
Type of test *Rodzaj testu*	Basic statistics *Statystyki podstawowe*	Unit *Miano*	C_4H_9	C_6H_{13}	C_8H_{17}	$C_{10}H_{21}$	NH_4NO_3
item 5.1.1. IF-20	$x_{max.}$	MPa	3.62	3.48	3.89	3.91	3.58
	$x_{avg.}$		2.97	3.08	3.14	3.33	3.04
	$x_{min.}$		2.23	2.53	2.40	2.76	2.52
	δ_{n-1}		0.46	0.40	0.55	0.41	0.40
	ν	%	15.3	13.0	17.4	12.4	13.1
	WF		85	95	99	95	95
item 5.1.3. AW-100	$x_{max.}$	MPa	2.73	3.22	3.48	2.88	3.01
	$x_{avg.}$		2.39	2.73	2.65	2.48	2.62
	$x_{min.}$		1.74	1.73	1.81	2.01	1.88
	δ_{n-1}		0.34	0.43	0.65	0.29	0.39
	ν	%	14.1	15.8	24.4	11.5	15.0
	WF		20	60	60	20	50

$x_{max.}$ – maximum, $x_{avg.}$ – average, $x_{min.}$ – minimum, δ_{n-1} – standard deviation, ν – variation coefficient, WF – wood failure

$x_{max.}$ – maksimum, $x_{avg.}$ – średnia, $x_{min.}$ – minimum, δ_{n-1} – odchylenie standardowe, ν – współczynnik zmienności, WF – zniszczenie w drewnie

The effect of the size of the alkyl group in cation in PIL on the reactivity mass of the MUF adhesive resin is presented in fig. 2. It can be observed that with an increase in the number of carbon atoms in alkyl group, the reactivity of the adhesive mass decreased to increase the gel time. The relationship was linear with a high correlation coefficient ($r^2 = 0.972$). This phenomenon can be explained by the increase in the length of the alkyl chain which causes a decrease in proton mobility and greater steric barriers. These factors may influence a decrease in the reactivity of the adhesive mass.

Table 2. The effect of assembly time on shear strength and wood failure of three-layer beech plywood with MUF resin hardened with PILs with different amounts of carbon in alkyl group after tests according to EN 314-01 standard
Tabela 2. Wpływ roboczego czasu klejenia na wytrzymałość na ścinanie i udział ścięcia próbki w drewnie trzywarstwowych sklejek bukowych po testach według EN 314-01 uzyskanych z żywicy MUF utwardzanej protonowymi cieczami jonowymi z różną liczba atomów węgla w grupie alkilowej

Shear strength and wood failure of plywood after tests according to EN 314-01 *Wytrzymałość na ścinanie i udział ścięcia próbki w drewnie po testach wg EN 314-01*			Hardener type *Typ utwardzacza*					
			Alkyl group PILs *Grupa alkilowa w protonowej cieczy jonowej*				Control *Kontrolny*	
			C_4H_9		$C_{10}H_{21}$		NH_4NO_3	
Type of test *Rodzaj testu*	Basic statistics *Statystyki podstawowe*	Unit *Miano*	Assembly time (days) *Roboczy czas klejenia (dni)*					
			1	30	1	30	0[1]	1[2]
p. 5.1.3. AW-100	$x_{max.}$	MPa	3.14	2.05	2.88	2.31	3.01	2.27
	$x_{avg.}$	MPa	2.32	1.73	2.48	2.01	2.62	1.77
	$x_{min.}$	MPa	1.75	1.38	2.01	1.63	1.88	1.39
	δ_{n-1}	MPa	0.46	0.23	0.28	0.22	0.39	0.33
	ν	%	19.9	13.4	11.5	11.2	15.0	18.5
	WF	%	48	10	18	20	53	43

$x_{max.}$ – maximum, $x_{avg.}$ – average, $x_{min.}$ – minimum, δ_{n-1} – standard deviation, ν – variation coefficient, WF – wood failure
$x_{max.}$ – maksimum, $x_{avg.}$ – średnia, $x_{min.}$ – minimum, δ_{n-1} – odchylenie standardowe, ν – współczynnik zmienności, WF – zniszczenie w drewnie
[1] 40 min
[2] after 30 days waterproof plywood was not achieved
po 30 dniach nie uzyskano sklejki wodoodpornej

The properties of beech plywood are presented in tables 2, 3 and illustrated in fig. 3. The plywood types were characterised by very high quality waterproof glue lines. No effect of the size of the alkyl group on waterproof glue lines was observed. Rt values were similar and ranged from 2.39 MPa (PIL-butyl) to 2.73 MPa (PIL-hexyl). Slightly higher values of WF were obtained for hexyl and octyl substituents. The results were similar to those obtained using NH_4NO_3 as a hardener (control plywood).

The plywood fulfilled the requirements of the EN-314-02 standard in terms of strength and water resistance of glue lines, regardless of PILs used.

The effects of assembly time on the quality of beech plywood are given in table 2. We managed to obtain waterproof plywood for variants seasoned for 1 day and 30 days, produced using glue with PIL modifiers. However, in the case of control plywood we did not achieve waterproof glue lines after 30 days.

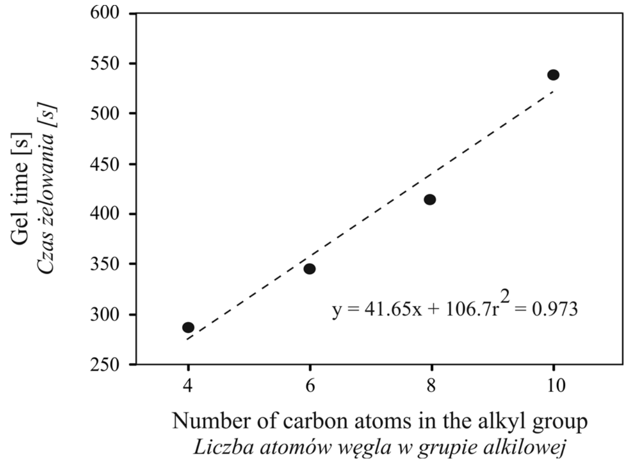


Fig. 2. Gel time at 100°C for MUF resins cured with PILs with different amounts of carbon atoms in alkyl group
Rys. 2. Czas żelowania w 100°C żywic MUF utwardzanych protonowymi cieczami jonowymi z różną liczbą atomów węgla w grupie alkilowej

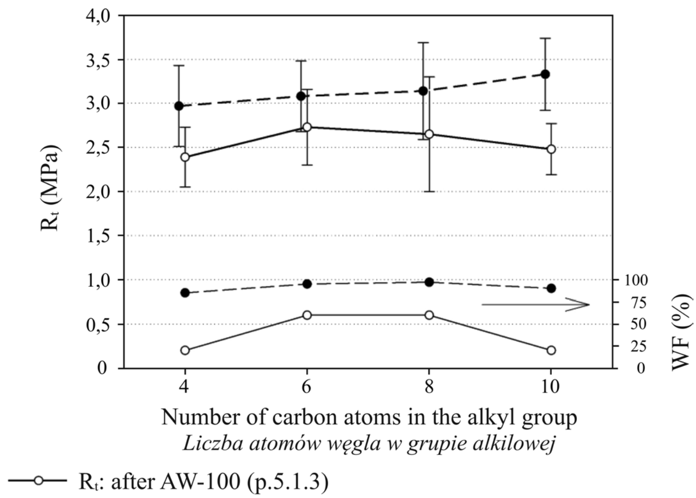


Fig.3. Shear strength (Rt) and wood failure (WF) of three-layer beech plywood with MUF resin hardened with PILs type with different amounts of carbon in alkyl group after tests on an IF-20 and AW-100 item 5.1.1 and 5.1.3. according to EN 314-01 standard
Rys.3. Wytrzymałość na ścinanie (Rt) i udział ścięcia próbki w drewnie (WF) trzywarstwowych sklejek bukowych po testach IF-20 and AW-100 p.5.1.1 and 5.1.3 według EN 314-01 uzyskanych z żywicy MUF utwardzanej protonowymi cieczami jonowymi z różną liczbą atomów węgla w grupie alkilowej

To sum up, based on the results of the tests it can be concluded that PILs are fully useful in plywood manufacturing technologies using MUF resins. They are interesting compounds, fulfilling the function of modifier and/or hardener of MUF resin: a phenomenon which has as yet not been described in literature. The relatively low reactivity of studied PILs may be increased by the use of a combined hardener, i.e. ionic liquid/Lewis acid. Gluing plywood for up to 30 days indicates a strong possibility of modelling the process and the technology of bonding. Studies have proved that there is great potential in the application of protic ionic liquid as hardeners-modifiers. It seems purposeful to conduct further research on the use of PILs in wood material technology. The method of synthesis of protic ionic liquids and their use as a modifier of adhesive amine resins has been submitted for patent protection.

Summary

Based on the research conducted, it was found that dialkylmethylammonium dodecylbenzenesulfonate base protic ionic liquids made a whole hardener of MUF resins that could simultaneously perform the function of a modifier, plasticizing the adhesive glue line. The plywood types obtained were characterised by very high water resistance and quality of adhesive bonding. They met the requirements of EN-314-02 standard, for class 3 of gluing quality. The application of protic ionic liquids as amino resin glue hardeners would expand technological capabilities in plywood manufacturing.

Acknowledgements

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PROTONOWE CIECZE JONOWE JAKO NOWE UTWARDZACZE - MODYFIKATORY KLEJOWYCH ŻYWIC MELAMINOWO-MOCZNIKOWO-FOMALDEHYDOWYCH

Streszczenie

Do utwardzania klejowych żywic aminowych stosowane są sole amonowe silnych kwasów nieorganicznych (głównie azotany), siarczany, chlorki (wychodzące z użycia ze względów ekologicznych), kwasy nieorganiczne oraz organiczne, a także bezwodniki kwasowe. W celu zwiększenia odporności hydrolitycznej spoin klejowych stosuje się sole melaminy. W wielu ośrodkach naukowych prowadzone są badania nad uzyskaniem alternatywnych utwardzaczy, powodujących uplastycznienie i zwiększających odporność spoiny na działanie czynników zewnętrznych.

W Instytucie Technologii Drewna w Poznaniu, w ramach Projektu nr POIG.01.03.01-30/074/08 „Ciecze jonowe w innowacyjnych technologiach związanych z przetwarzaniem surowców lignocelulozowych”, prowadzone są badania nad zastosowaniem cieczy jonowych do utwardzania – modyfikacji klejowych żywic melaminowo-mocznikowo-formaldehydowych.

Celem badań było sprawdzenie przydatności protonowych cieczy jonowych jako utwardzaczy –modyfikatorów klejowych żywic MUF. Do badan wytypowano protonowe dodecylbenzosulfoniany dialkilometylamoniowe, zaliczane do protonowych cieczy jonowych. Poszczególne ciecze różniły się liczbą węgli w grupie alkilowej. Wytworzono trzywarstwowe sklejki bukowe utwardzane zastosowanymi protonowymi cieczami jonowymi.

Na podstawie przeprowadzonych badań stwierdzono, że zastosowane protonowe ciecze jonowe stanowią pełnowartościowe utwardzacze żywic MUF, mogące wypełniać równocześnie funkcję modyfikatora - plastyfikatora spoiny klejowej. Zastosowanie protonowych cieczy jonowych jako utwardzaczy klejowych żywic aminowych poszerza możliwości technologiczne w zakresie wytwarzania sklejki. Uzyskane sklejki charakteryzowały się bardzo wysoką wodoodpornością spoin klejowych i spełniały wymagania EN-314-02.

Słowa kluczowe: żywica klejowa MUF, protonowa ciecz jonowa, system modyfikator-utwardzacz, sklejka