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Effect of molar ratio of melamine-urea-formaldehyde adhesive resins condensed no-waste method's on the selected properties of the polycondensates during storage time
I. Basic physicochemical properties

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Abstract
The subject of research was defining of the effect of molar ratio on the selected physicochemical properties of adhesive MUF during storage at a temperature of 20 ± 2°C. The studied resins were characterized a very high stability during a period of 5-18 months storage time in normal conditions.

Keywords: MUF , resin, condensation, adhesive, viscosity, formaldehyde, waste

INTRODUCTION

Adhesive amino resins occupy a leading position among the bonding agents used in the various fields of wood industry. Participation of amino resins in the general range of adhesives produced for the wood industry stands at 85%. Common use of amino resins due to their many advantageous properties such as water solubility, high reactivity, colorless glue line and high resistance to biotic, and for MUF and MF resins high hydrolytic resistance of adhesive glue line [Pizzi 200].

In the Wood Technology Institute research on the synthesis of amino resins, polycondensation, especially MUF resin [Jóźwiak et al. 2003, Jóźwiak and Jabłoński, 2007] has been conducted for many years. New MUF resin synthesized non-waste way has been recently developed [Jóźwiak 2011]. The idea of new MUF resins, enrolls in global ecological trends and policy which is friendly for people and their environment. However, an important impulse was the desire for a simplified condensation, which would be available even for the low-tech device manufacturers of plywood.

This paper presents research on effect of molar ratio of MUF adhesive resins condensed no-waste way on the selected physicochemical properties in function of storage time.

MATERIALS AND METHODS

The research object consisted of MUF resins synthetized in laboratory scale according to the developed conception by a three-step method excluding the operation of concentration with the application of formalin with a high methanol content and variable molar ratio formaldehyde (F) : melamine (M): urea (U) like as (4.6÷2.8):1.0:1.0. The condensation was a tree-stage process performed at temperature of 80± 2°C. Condensation was carried out to water tolerance in the range of 100÷150%. Polycondensate was not distillated. Details concerning the synthesis were presented earlier [Jóźwiak 2011]. For each variant was obtained about 1 kg of resin. Resins were stored at a temperature of 20 ± 2°C.

The basic properties of the resin was determined using the following methodologies:

- apparent viscosity using Emil rotational viscometer in compliance with PN-92/C-89402

- gel time at 100°C according to BN 75/3537-01
- free formaldehyde content by sulphite method according to DIN EN 1243
- pH applying pH-meter with combined electrode according to PN-ISO 1148

RESULTS

The course of change of apparent viscosity of MUF resins as a function of the storage time and molar ratio of the resins was shown in Fig. 1. Examined relationship was approximated by an exponential function.. Resins with higher molar ratios were characterized by a significantly lower growth rate viscosity (lower exponent of exponential equation) and greater stability.

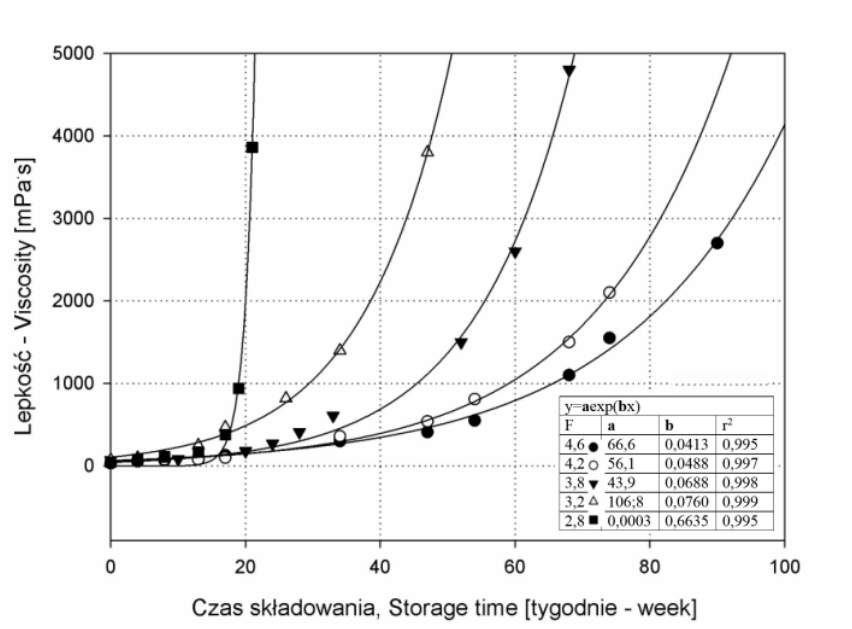


Fig. 1. Apparent viscosity changes of MUF resins during storage (in the table - data after exponential approximation)

The course of change of the content of formaldehyde and the reactivity of the resins as a function of storage time and the molar ratio of polycondensates was shown in Figs. 2 and 3. It was stated that increasing formaldehyde content and the reactivity of the resins with increasing molar ratio. The gel time at 100°C fluctuated in a range of from 133 - 94 s. The relatively high content of formaldehyde (0.49 – 1.18%) was resulted from the presence of volatile compounds such as: polymeric glycols methylene semiformal and methanol. The formaldehyde content during storage decreased in a linear function. The process was characterized by similar dynamics, regardless of the molar ratio (a slight difference of the slopes of linear equations). Decreasing of formaldehyde content not accompanied a significant decrease of resin pH (baseline 9.4±0.2; and a final 9.0±0.2),well characteristic of the processes occurring during storage polycondensates amine [Mattheij et al. 2005]. It can be concluded that the primary cause lowering of the formaldehyde content was his reaction with oligomers or monomers of resin. It can be stated that there were a limited extent

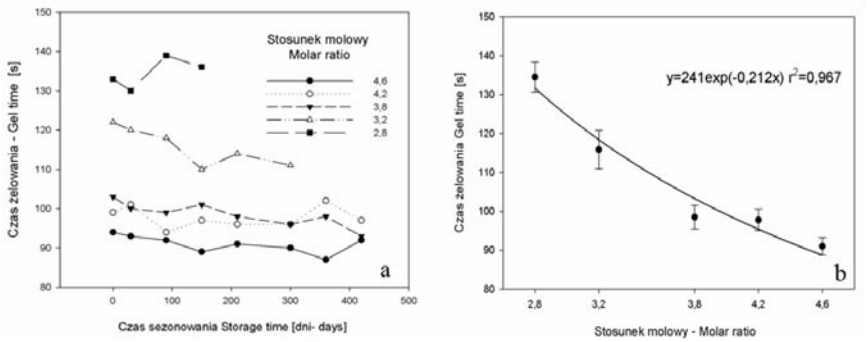
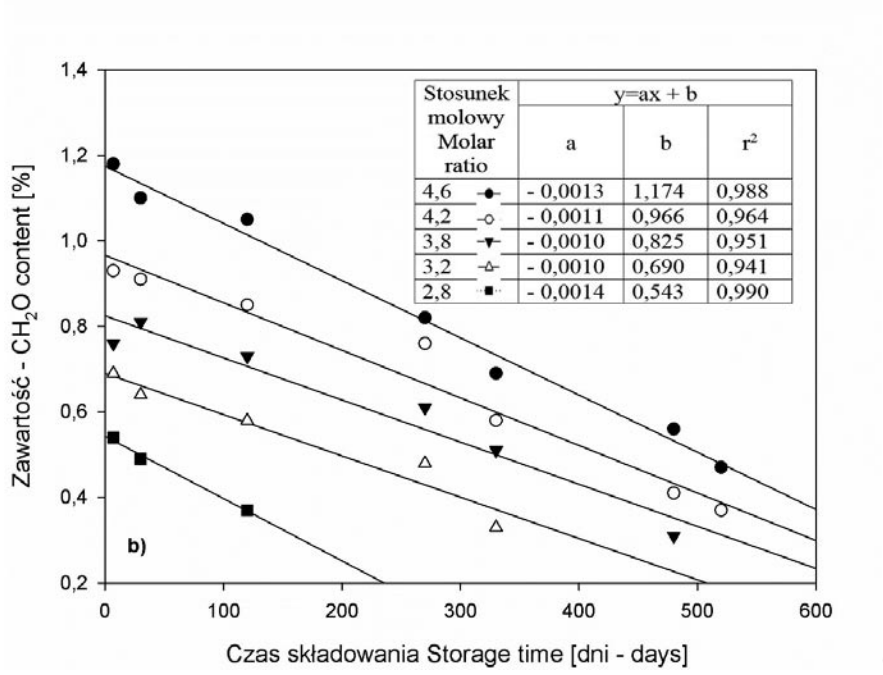


Fig. 2. Effect of storage time (a) and molar ratio (b) on gel time in temperature 100°C MUF resin condensed no-waste method's

The increase of substrate molar ratio caused a higher formaldehyde content in MUF resin.



Stosunek molowy Molar ratio	y=ax + b		
	a	b	r^2
4,6	- 0,0013	1,174	0,988
4,2	- 0,0011	0,966	0,964
3,8	- 0,0010	0,825	0,951
3,2	- 0,0010	0,690	0,941
2,8	- 0,0014	0,543	0,990

0,

Fig. 3. Effect of storage time and molar ratio on the formaldehyde content in MUF resin condensed no-waste method's (in the table - data after linear approximation)

known from the literature disproportionation Canizzaro reactions and the oxidation of formaldehyde to formic acid.

CONCLUSIONS

The studied resins were characterized by a very high stability during a period of 18 months storage time in normal conditions. At the same time, the increase of substrates molar ratio caused an increase of resin stability. During the aging of resins, there followed an increase of their viscosity , with a slight increase of reactivity and a decrease of formaldehyde content. There were no significant changes in the pH value. The relationship were substantially

characteristic of the adhesives MUF polycondensates adhesive MUF [Tohmura et al. 2001], as well as UF resins [Myers 1984, Dunky 2004]. So far, the suitability of liquid adhesive MUF resins for use during 10 to 18 months has not been reported in the available literature.

REFERENCES

DUNKY M. (2004): Adhesives based on formaldehyde condensation resins. Macromolecular Symposia(217),1:417-430.
MYERS G. E. (1984): How mole ratio of UF resin effects formaldehyde emission and other properties particleboard : a literature critique. For. Prod. J. (34), 5: 35-41
JÓŹWIAK M. (2011): Badania fizykochemicznych procesów zachodzących w czasie starzenia się klejowych żywic MUF . Wydawnictwo UP w Poznaniu.
JÓŹWIAK M., JABŁOŃSKI W. (2007): Z badań nad wybranymi technologiami wytwarzania sklejki przy zastosowaniu klejowych żywic polikondensacyjnych. Technologia Drewna Wczoraj, Dziś, Jutro" Studia i szkice na jubileusz Profesora Ryszarda Babickiego. Poznań 2007: 183-193
JÓŹWIAK M., PROSZYK S., JABŁOŃSKI W. (2003): Adhesive melamine-urea-formaldehyde resins modified with natural alkyloresorcinols. Drewno-Wood (46):18-30.
MATTHEIJ J., EVERS L. LITVINOVV. (2005): The Phenomena of Instability of MUF Resins: Improve your Amino Resin Performance:9th European Panel Products Symposium. 5-7 October 2005.187-199.
PIZZI A. (2000): Tannery row - The story of some natural and synthetic wood adhesives. Wood Sci. and Technol. 34 (4): 277-316.
TOHMURA S., INOUE A. SAHARI S.H. (2001): Influence of the melamine content in melamine-urea-formaldehyde resins on formaldehyde emission and cured resin structure J.of Wood Sci., (47), 6

Streszczenie: *Wpływ stosunku molowego żywic melaminowo-mocznikiwo-formaldehydowych (MUF) kondensowanych sposobem bezodpadowym na wybrane właściwości polikondensatów w czasie ich składowania II. Podstawowe właściwości fizyko-chemiczne*

W pracy przedstawiono badania nad wpływem czasu składowania i stosunku molowego żywic melaminowo-mocznikiwo-formaldehydowych (MUF) na wybrane właściwości fizyko-chemiczne. W badaniach zastosowano żywicę MUF o stosunku molowym M:U:F w zakresie (4,6÷2,8):1.0:1.0 kondensowane sposobem bezodpadowym. Na podstawie rezultatów przeprowadzonych badań stwierdzono że klejowe żywice MUF syntetyzowane w warunkach laboratoryjnych, według opracowanej koncepcji, sposobem trójstopniowym, z pominięciem operacji zagęszczania, przy zmiennych stosunkach molowych F:M:U w zakresie (4,6÷2,8):1,0:1,0 charakteryzowały się bardzo wysoką stabilnością (od 4 do 16 miesięcy) w czasie składowania w warunkach normalnych. Wzrost stosunku molowego substratów powodował podwyższenie stabilności żywic. W czasie starzenia się żywic następował wzrost ich lepkości, przy niewielkim podwyższeniu reaktywności, zaś obniżeniu ulegała zawartość formaldehydu.

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