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APPLICATION OF NIR SPECTROSCOPY FOR ANALYSIS OF AMINO ADHESIVE RESINS APPLIED IN WOOD BASED MATERIALS

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Transmission-reflection NIR spectroscopy was applied for qualitative and quantitative investigations of liquid amino (UF and MUF) adhesive resins. NIR spectra of resins were characterized with the used PLSR (partial last square regression) and MLR (multiple linear regression) methods.

Keywords: NIR spectroscopy, wood adhesive, MUF, UF, melamine content

INTRODUCTION

In the past few year we were observing rapid development of NIR spectroscopy techniques (Workman 1993). This technique is evaluated as extremely economic, fast, non-invasive and integrated method of multiple-component qualitative and quantitative analysis mainly used for organic products. NIR spectroscopy has established itself as a primary method of analysis for agriculture products and could be more widely applied in application in industrial processes (Stark 1986).

This technique has been applied in wood research (Mroczyk, Kasprzyk and Gawęcki 1992, Olsson et al. 1995, Brunner et al. 1996) as well as for control in technology of wood based materials production (Kniest 1992, Niemz et al. 1992).

This method has been applied in polymers analysis (Alam, Stanton and Hebner1995, Siesler 1995).

In this paper, as attempt has been undertaken for the use of NIR technique for analysis of liquid UF and MUF resins, used for gluing of wood based materials.

It is commonly know, that UF resins are characterized by low durability of glue line upon action of variable atmospheric conditions (Dinwoodie 1983). This disadvantage is not present with MF resins, but due to economic reasons, they did not found wide use as the adhesive in wood working industry.

Similar properties have MUF resins, which are relatively cheaper. They are obtained by copolycondensation of melamine, urea and formaldehyde, or by mixing UF with MF resins (Pizzi 1993). Water resistance of obtained glue lines from MUF resins is determined by the conditions of synthesis, and by the quantity of used melamine in the condensation process. Information on probable course of synthesis can be obtained on the base of NMR ^{13}C spectra (Mercer and Pizzi 1994). However quantitative share of melamine in liquid polycondensates can be determined as well with the use of classic methods (Widmer 1956), as with the use of UV spectroscopy (Marutzky, Ranta and Schriever 1978). Having in mind that the classic methods are characterized by the long time studies, and that UV analysis has low suitability in industry practice.

The aim of this study was to use NIR spectroscopy for qualitative and quantitative analysis of liquid MUF resins, particularly for the determination of melamine content.

MATERIALS AND METHODS

The study was carried out on the industrial scale UF and MUF resins. UF resins differed with condensation conditions and molar ratio of U:F, which was in the range of 1.16-1.24 MUF

Table 1

Tabela 1

Properties of adhesive resins

Właściwości żywic klejowych

Resin Żywica	Molar ratio Stosunek molowy	Properties, Właściwości				Manner of condensation Sposób kondensacji	Main application Główne zastosowanie
		Viscosity mPa·s Lepkość mPa·s	Solid contents % Zawartość suchej masy %	Free CH_2O % Wolny CH_2O %	Gel time in 100° s Czas żelowania w 100°C s		
UF_1	1.16:1	520	66.3	0.06	78	pressure, continue ciśnieniowo-ciągły	particleboard płyty wiórowe
UF_2	1.20:1	1800	65.0	0.12	70	non pressure bezciśnieniowy	interior plywood sklejka suchotrwała
UF_3	1.26:1	1700	66.1	0.16	64		
MUF	3.9:1:1	1000	62.0	0.19	86		exterior plywood sklejka wodoodporna

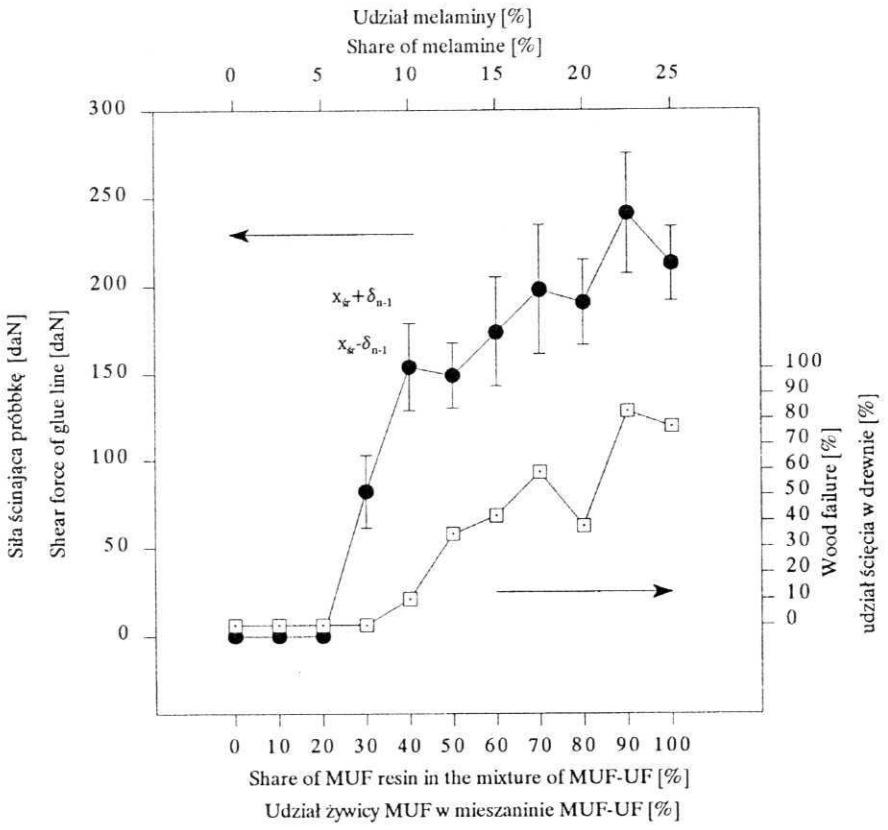

Fig.1. Effect of melamine content in system of MUF-UF on water resistance of glue line after the test acc. p.5.1.3. EN-314-1 standard
Rys.1. Wpływ udziału melaminy w masach klejowych żywic MUF-UF na wodoodporność spoin klejowych po teście p.5.1.3. EN-314-1

resin with high melamine contents was condensed in laboratory with molar ratio of F:M:U suitable 3.9:1.0:1.0. The selected properties of the resins are presented in Table 1. Content of the of free formaldehyde was determined with sulphite method in temperature 5°C accordingly to EN-1243:1993 standard. From resin MUF and UF were made mixtures by weight with different melamine content in the range of 0-25% in calculation upon the mass content in 62% liquid resin. On Fig.1 presented is example course of water resistance changes of glue lines obtained from applied in studies MUF and UF (F:U 1.2:1.0) and their mixtures. After 60 min from the moment of mixing of the resins the transmission-reflection, spectra NIR were recorded with the use of spectrophotometer NIR Systems 6500 in the range 1100-2400 nm every 2 nm measuring log 1/R with use of quartz cuvette. Quantitative analysis of data was made for 22 tests measuring twice their absorption. Treatment of data was made using program SEZAM. In this work was used the MLR-algorithm (Multiple Linear Regression) and PLSR (Partial Last Square Regression). There was calculated: standard error of estimation (SEE), standard error of prediction (SEP), correlation coefficient R and value of function F.

RESULTS

Raw NIR spectra of amino resins are presented on Fig.2. The greatest changes were observed in range 1900–2500 nm. The UF spectra are characterized by the same courses. Other conditions of their condensation as well as their different molar ratios (F:U) are not visible on NIR spectra. Interpretation of spectrum in basic way is hindered by the water presence, which absorbs at following lengths of waves: 1150, 1350, 1440, 1790 and 1930 nm. Therefore, bands characteristic for resin, will be more suitable to analyse the spectra of second derivative. These spectra are illustrated on Fig.3.

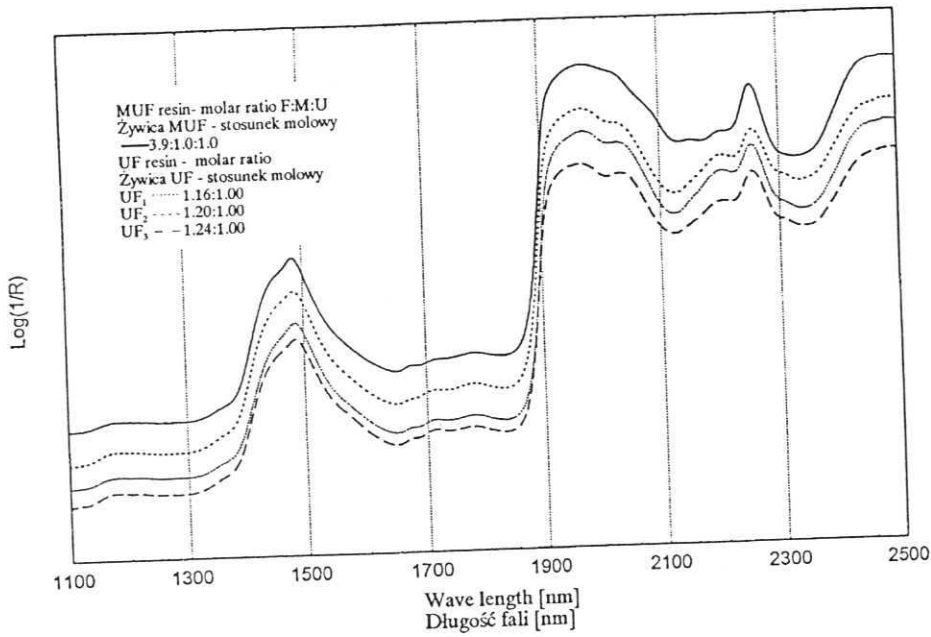

Fig.2. Raw NIR spectra of MUF and UF resins
Rys.2. Wyjściowe widma NIR żywic MUF i UF

On the spectrum of UF resins is observed characteristic triplet of overtones of basic vibrations NH and their complex vibrations at 1420 nm (1st overtone $2\nu NH_{as.}$), 1444 mn (combo $\nu NH_{as.} + \nu NH_{sym}$) and 1488 nm (1st overtone $2\nu NH_{sym.}$). In the long range bands of composite vibrations occur, derived from amino and amide groups at waves length: 1978 nm ($\nu NH_{as.} + \delta NH$ amide II) , 1988 nm ($\nu NH_{as.} + \nu CO$ amide I), 2034 nm ($\nu NH_{as.} + \nu CN$ amide III) and 2050 nm ($\nu NH_{sym.} + \nu CN$ amide III). Above that two bands composed of NH: 2154 nm ($\nu NH_{as.} + \delta NH_{roc.}$) 2198 nm ($\nu NH_{sym.} + \delta NH_{roc.}$). For the composite vibrations of amino and amide groups in the range 2030-2060 nm are overlapped of vibrations of OH hydroxyl groups of methylolol, characteristic for UF

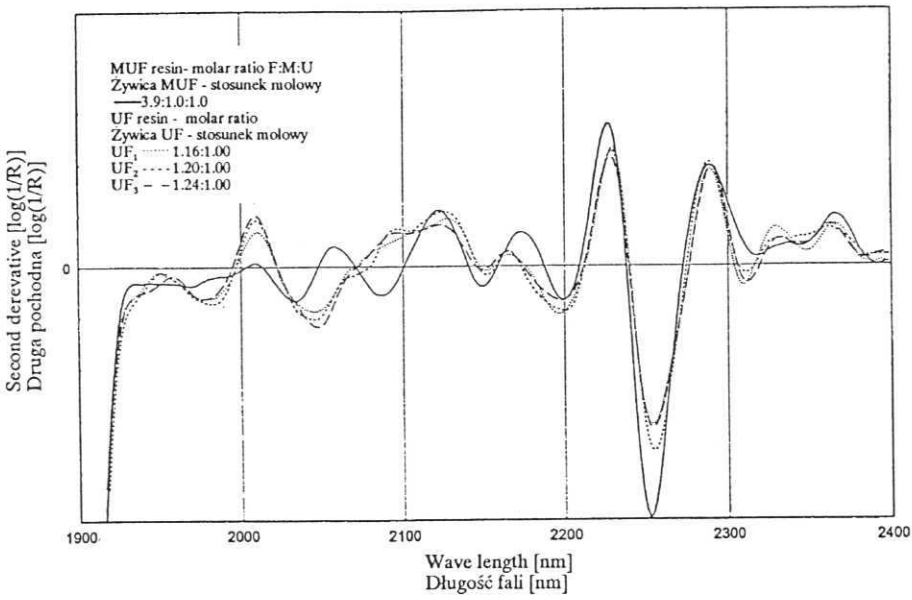

Fig.3. Expanded second derivative spectra of MUF and UF resins
Rys.3. Fragment widma drugiej pochodnej żywic MUF i UF

resins, while vibrations of methylene groups are occurring at 1674, 1714 nm which are complex vibrations, properly 1st overtone $2\nu CH_{2,as.}$. Moreover 1st overtone $2\nu CH_{2,sym.}$ and at 2254 nm overlap composed from two combinations vibrations ($\nu CH_{2,as.} + \delta CH$) and at ($\nu CH_{2,sym} + \delta CH$). Spectrum of MUF resin has close course to the spectra of UF resins. Basic differences are occurring in the range 1930-2150 nm. That is connected with presence of s-triazine ring of melamine. The new band at length of wave 2088 nm of MUF resin connected with combination vibrations ($\nu NH_{sym.} + \delta NH$). Special attention is to be paid for distinct separation on NIR spectra MUF and UF resins of the valence bands of symmetrical and asymmetrical bands as of groups NH and as of CH, which in Mid-IR occur in form of wide overlaps. This property could be used for structural investigations of amino resins. Observed qualitative differences between studied resins, were used for analysis of melamine contents in adhesive polycondesates. On the Fig.4 are presented spectra of mixtures of UF-MUF resins with known melamine contents. Differences in the course of spectra in univocal way are connected with diversified quantitative contents of melamine. Calibration has been made using MLR and PLSR methods. The best calibration was won at three length of wave, but determinations made at two wave lengths are sufficient for proper quantitative analysis of melamine in amino resins (Table 2), what results from great specified of NIR spectra of tested systems. Determination at one length of wave was improper because of very low of value function F and about 7-8 time highest value SEE and SEP. That is verified

Table 2
Tabela 2

Statistical analysis of melamine contents in MUF and UF resin mixtures
Analiza statystyczna zawartości melaminy w mieszaninach żywic MUF i UF

Mixtures Mieszaniny	Wave length [nm] Długość fali [nm]	Statistical method Metoda statystyczna							
		MLR				PLSR			
		r	F	SEE	SEP	f	r	SEE	SEP
MUF – UF_1	2100	0.9550	293	10.020	9.681				
	2144, 2182	0.9987	5490	1.711	1.623	8	0.9997	0.876	0.750
	1992, 2260, 2272	0.9990	7378	1.432	1.333				
MUF - UF_2	1876	0.9658	389	8.212	7.934				
	2156, 2170	0.9975	2666	2.290	2.173	7	0.9994	1.193	1.045
	2064, 2212, 2284	0.9994	7600	1.110	1.033				
MUF - UF_3	2092	0.9560	212	10.181	9.707				
	2140, 2316	0.9989	4204	1.691	1.572	8	0.9999	0.355	0.283
	2140, 2184, 2264	0.9998	12635	0.797	0.721				

r - multiple correlations coefficient
współczynnik korelacji wielokrotnej
F - function F
funkcja F
SEP - standard error of prediction
standardowy błąd predykcji
f - number of factors
liczba czynników

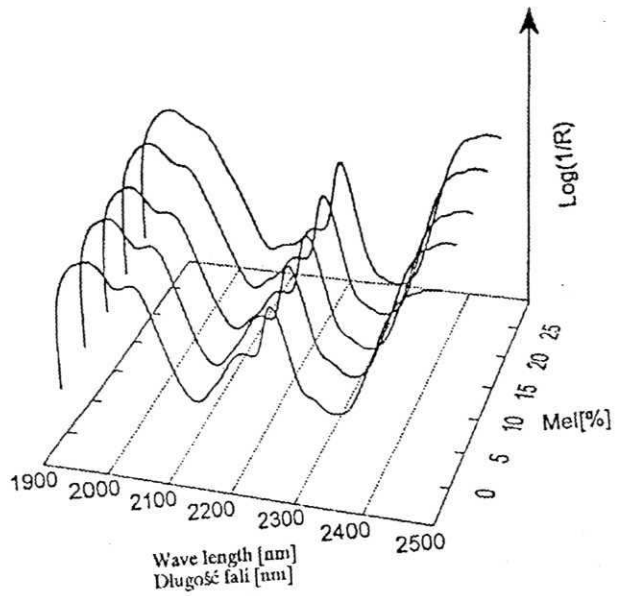

Fig.4. NIR spectra of mixture MUF-UF_3 resins
Rys.4. Widma NIR dla mieszaniny żywic MUF-UF_3

from carried out qualitative analysis. The PLSR method was giving slightly better correlation, what agrees with results (Thomas and Haaland 1990) , that for unlined spectra this method is better recommended. The both methods give small standard calibration error and lower validation error. There were received very high correlation (R=0.997-0.999) of determinations of melamine content in all tested mixtures MUF-UF. Proposed method can be applied in quantitative method analysis of liquid MUF resins.

RECAPITULATION

Carried out investigation of transmission-reflection NIR spectra of liquid amino UF, MUF resins indicate, that this method could be used for qualitative analysis of such type of polycondensates. This method allows distinguishing valence vibration bands of NH and CH groups symmetrical and asymmetrical, which can not be seen on the Mid-IR spectra. NIR spectra of tested systems are high accuracy and can be used for melamine content determination in amino resin containing this compound. It was obtained high correlation of determination of melamine contents in MUF resins. Besides that, it was stated, that analysis with PLSR method gives much better correlation then with use of MLR determination method.

This technique can potentially be used in laboratory investigations and for industrial practice too.

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ZASTOSOWANIE SPEKTROSKOPII NIR DO ANALIZY ŻYWIC AMINOWYCH UŻYWANYCH W PRODUKCJI TWORZYW DRZEWNYCH

Streszczenie

Przedstawiono wyniki analizy jakościowej i ilościowej ciekłych żywic aminowych (UF i MUF) przy zastosowaniu spektroskopii transmisyjno-refleksyjnej NIR. Opracowano metodę oznaczania zawartości melaminy w mieszaninach żywic UF i MUF z wykorzystaniem algorytmu MLR i PLSR.