

QUANTITATIVE ANALYSIS WITH THE AID OF NIR SPECTROSCOPY OF SOME COMPONENTS USED FOR PRODUCTION OF PVAC WOOD ADHESIVES

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SYNOPSIS. Compositions of adhesive commercial components prepared in model versions on the base of PVAC dispersion with trade mark Winacet DP-50, polyacryl copolymer MT-117 and butyraldehyde (in the following systems: DP-50 + MT-117, DP-50 + butyraldehyde and MT-117 + chalk as filler) have been analysed by near infrared spectroscopy (NIR). Near-IR spectra of the glue mixtures were measured in the 1100-2500 nm region, using a NIRSystems 6500 spectrophotometer. The analytical data from NIR spectra were correlated in quantitative aspects of the components of glue mixtures by Partial Least Squares Regression (PLSR) and Multiple Linear Regression (MLR).

KEY WORDS: polyvinylacetate dispersion, polyacrylate copolymer, butyraldehyde, filler, adhesive composition, NIR spectroscopy, quantitative analysis

INTRODUCTION

PVAC adhesives are commonly used in many wood processing industries such as furniture, building woodworking, as well as postforming technologies. The properties of these adhesives were widely presented in many papers. Many research centers carry studies on eliminating some of the disadvantages of conventional PVAC adhesives. Much effort has been devoted to improving some properties, especially the strength and water-, thermal-, solvents- and creep resistance of glue lines and experience influenced of selected factors of gluing processes (SELLARS 1984, JAFFE et AL. 1990, LUČIČ et AL. 1992, CORNYN 1997, PROSZYK et AL. 1997, 1999, 2002, KOVÁČIK and SEDLIAČIK 2001, KRYSZTOFIK and PROSZYK 2000, 2001, QIAO and EASTEAL 2001).

Modifications of PVAC adhesives can be broadly classified as follows:

– copolymerization vinyl acetate with more hydrophobic monomers such as e.g. ethylene, butyl acrylate, methyl methacrylate and 2-ethylhexyl acrylate, or with functional monomers (such as the crosslinkable monomers for example: hydroxy ethyl acrylate, N-methylol acrylamide and N-isobutoxy methyl acrylamide) to increase curing degree of adhesive layers (SEDLIAČIK and SELDIAČIK 1999).

– blendified PVAC dispersion with other adhesive resins or hardeners, e.g. MUF resins, latex, glyoxal, Lewis acids and polyisocyanates (PROSZYK et AL. 1986, GOS and LEWANDOWSKI 1993, KRYSOPIAK et AL. 2003).

Therefore it is very important to have quick analytical methods in production and quality estimation of the conventional and modified PVAC adhesives.

In recent years the industry needs rapid, reliable, non-invasive and cost effective analytical methods for control processes. Spectroscopic techniques can meet these demands. Vibrational spectroscopy is ideally suited to qualitative analysis of starting materials and end products and to quantification of polymer mixtures (FURUKAWA et AL. 2001).

Recent developments of modern fiber-optic-based spectrometers, especially for the near infrared spectroscopy (NIR), opened up new perspectives for process analysis in the adhesive polymers. The use of probes connected to spectrometer via optical fibers allows direct measurements (on-line and in-line) in the product stream without interference in the production process (WORKMANN 1993, ALAM et AL. 1995, SIESLER 1995, STCHUR et AL. 2002).

In the NIR spectral range (700-2500 nm) molecules absorbed light by overtone or combination vibrations. Registration of spectra of samples which are of practical interest in polymer processes is possible. C-H, O-H, N-H and C-O bands observed in NIR spectra are characteristic of polymers and enable identification of most commonly used materials (KASPRZYK et AL. 1997, 2001, LACHENAL 1998).

More often, the mixture of different chemical compounds gives complex spectra with overlapping bands and the changes in intensities are not always related to the content change of only one compound. For these cases it is necessary to use chemometric methods to extract the qualitative or quantitative information from the spectra (KATSUMOTO et AL. 2001).

The quantitative chemometric method used is Principal Component Analysis (PCA), Partial Least Squares Regression (PLSR) and Multiple Linear Regression (MLR).

The implementation of a process control system for quantitative analysis is not an easy process. It is necessary to provide the calibration and the validation methods (KATSUMOTO et AL. 2001).

The aim of this paper are studies of possibility of quantitative analysis with the aid of NIR spectroscopy of selected modifications contents in PVAC wood adhesive dispersions.

MATERIALS AND METHODS

The studies were carried out with the use of the following commercial components of PVAC glue mixtures:

- polyvinylacetate dispersion with trade mark Winacet DP-50 (producer: Firma Chemiczna „Dwory” S.A.) with following characteristics: solid content 50.34%, viscosity (25°C) 1400 mPa·s and pH 5.1,
- polyacryl copolymer with trade mark MT-117 (producer: Ośrodek Badawczo-Rozwojowy Kauczuków i Tworzyw Winylowych w Oświęcimiu) with following properties: solid content 44.02%, dynamic viscosity (25°C) 820 mPa·s and pH 4.9,
- butyraldehyde (pure-chemical reagent, Fluka),
- standard chalk (99% CaCO₃).

Three adhesive systems were made by weight with different modifying agents content:

- Winacet DP-50 (2-24% s.c.) + MT-117 (2-14% s.c.),
- Winacet DP-50 (24-30% s.c.) + butyraldehyde (0.5-4.0% s.c.),
- MT-117 (14% s.c.) + standard chalk (2-24% s.c.).

Thus, the concentration of particular modifiers in prepared glue mixtures was expressed upon the solid content (s.c.). Each of twenty two adhesive systems were prepared. Using mechanical mixer has ensured uniformity of mixtures. After 30 min from the moment of mixing of the adhesives the transmission-reflection, NIR spectra were measured. The transmission-reflection spectra were recorded at ambient temperature in the wavelength range 1100-2500 nm at 2 nm intervals, using a NIRSystems 6500 spectrophotometer (NIRSystems Inc., Maryland, USA) measuring $\log(1/R)$ with use of quartz cuvette. Duplicate spectra, including a sample re-pack, were recorded for each sample with a mean spectrum being stored for statistical analysis. Spectral was performed using SESAM program. The spectra were correlated with concentrations using 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 AND DISCUSSION

For example Figure 1a illustrates that $\log(1/R)$ spectra (raw NIR spectra) of polyvinylacetate (DP-50)-polyacryl copolymer (MT-117) mixtures and pure components DP-50 and MT-117. The NIR spectra of pure adhesives components and their mixture showed wide overlapping and monotonous character. This band is composed of multiple absorption bands. The second derivative spectra show separate peaks (Fig. 1b).

The two dominant peaks in the spectra (Fig. 1a and 1b) are apparent at 1434 and 1928 nm, represent the O-H stretch first overtone and the O-H combination band in water, respectively. On the band O-H water overlapping the C=O stretch second overtone ($3\nu_{C=O}$) in PVCA dispersion (DP50) or acryl copolymer (MT-117).

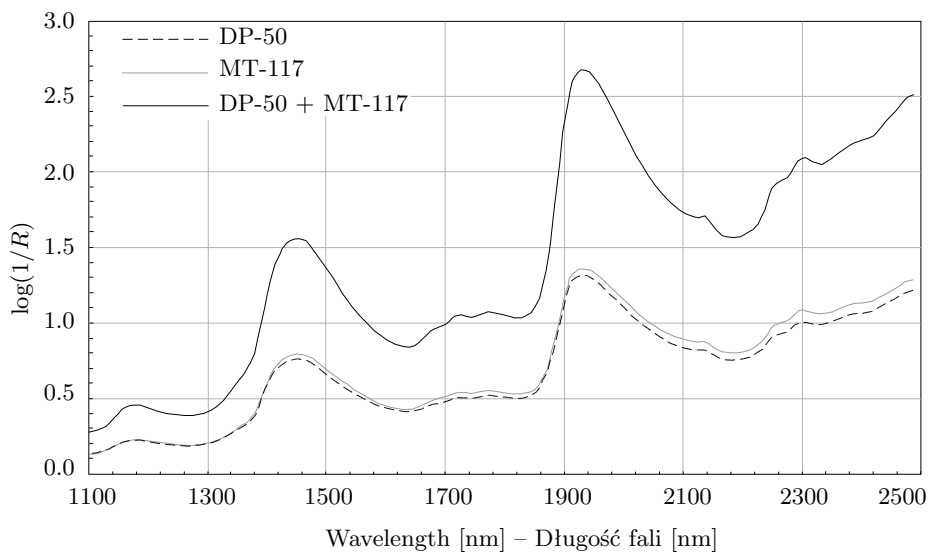


Fig. 1a. NIR spectra of polyvinylacetate (DP-50) and polyacryl (MT-117) dispersions and DP-50 + MT-117 mixture
 Rys. 1a. Widma NIR dyspersji poliocctanowinylowej (DP-50) i poliakrylowej (MT-117) oraz mieszaniny DP-50 + MT-117

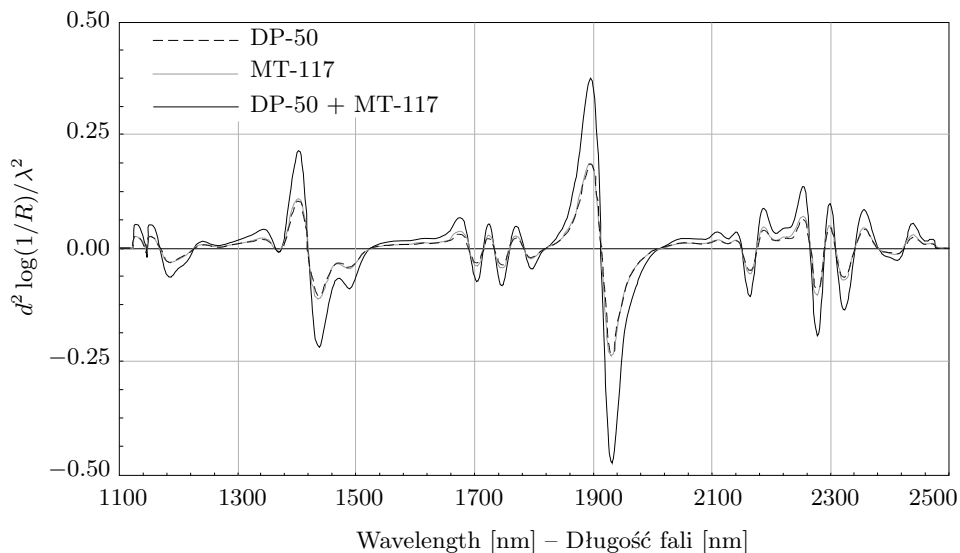


Fig. 1b. Second derivative NIR spectra of polyvinylacetate (DP-50) and polyacryl (MT-117) dispersions and DP-50 + MT-117 mixture
 Rys. 1b. Widma NIR drugiej pochodnej dyspersji poliocctanowinylowej (DP-50) i poliakrylowej (MT-117) oraz mieszaniny DP-50 + MT-117

The absorption at 1702 and 1745 nm are (due respectively) to the first overtones of C-H stretching vibrations ($2\nu\text{CH}$) of CH_3 and CH_2 groups respectively, whilst those at 2274 and 2322 nm are the C-H combination bands ($\nu\text{CH} + \delta\text{CH}$) (MURRAY 1987). The bands at range 2123-2161 nm are the combination bands ($\nu\text{C}=\text{O} + \nu\text{CH}$), then the band about 2412 nm is the combination bands ($\nu\text{C}-\text{O} + \nu\text{CH}$) both of polyvinylacetate and polyacryl dispersion. Generally the NIR spectrum of DP50 dispersion was not very different from the spectrum of MT-117 (Fig. 1a, b).

The NIR spectra of second adhesives systems (DP-50 + butyraldehyde) and their pure component show Figure 2a (raw spectra) and Figure 2b second derivative spectra. Near peaks of water and DP50 characterized above is the strong combination band ($\nu\text{CH} + \nu\text{C}=\text{O}$) at 2223 nm in-CHO of butyraldehyde. Other peaks of butyraldehyde were generally associated with C-H absorptions, e.g. 1720 nm is characteristic of C-H first overtone ($2\nu\text{CH}$) whereas 2413 and 2469 nm are combination bands ($\nu\text{CH} + \nu\text{C}-\text{O}$).

Figure 3a and 3b show the raw and second derivative spectra the third adhesive systems: acryl copolymer M-117 with chalk. The NIR of chalk spectra are only large peak at 2367 nm ($3\nu(\text{CO}_3)^{-2}$). The presence of water in the MT-117 dispersion is obvious from the large peaks at 1930 nm.

The selection of wavelengths for quantitative analysis of study in this paper adhesives is very difficult, due to the NIR spectra data overlapping peaks. By using multivariate methods to evaluate spectroscopic data, it is possible to select useful data to interpret and model highly complex spectra with overlapping peaks. In this paper the calibration multivariate techniques model MLR and PLSR was used.

Table 1 shows results of the statistical analysis at chosen wavelengths with the aid MLR and PLSR. Quantitative analysis of MT-117 in Winacet DP-50 dispersion is a good correlation between NIR predicted and actual values ($r = 0.9510$) only at three selected wavelengths: 2108, 2118 and 2204 nm. Also value SEE and SEP are about 4 times lower than at one wavelength.

Calibrations generally become better, using an increased number of wavelengths; methods using single wavelength calibrations are more sensitive to interference from other compounds present in the sample. However, multiple regression (MR), which is frequently used, assumes orthogonality, or almost so, between the independent variables (X-variables). Since data from digitized curves, e.g. a spectral curve, are strongly co-linear, MR is inappropriate for this purpose (WOLD et AL. 1984).

Quantitative analysis the butyraldehyde content in DP-50 dispersion is possible just at two wavelengths: 2248 and 2288 nm – correlation coefficient was ($r = 0.9792$). The best correlation ($r = 0.9956$) was achieved by using three wavelengths (2246, 2328 and 2380 nm). Similar for quantitative analysis of chalk in MT-117 acryl copolymer for two wavelengths: 2166 and 2168 nm we obtained good multiple coefficient of correlation ($r = 0.9298$) and the best correlation ($r = 0.9939$) at three wavelengths: 2212, 2232 and 2244 nm.

For a linear regression of spectral data between 1100 and 2500 nm against the proband modifiers concentration values the partial least-squares multivariate

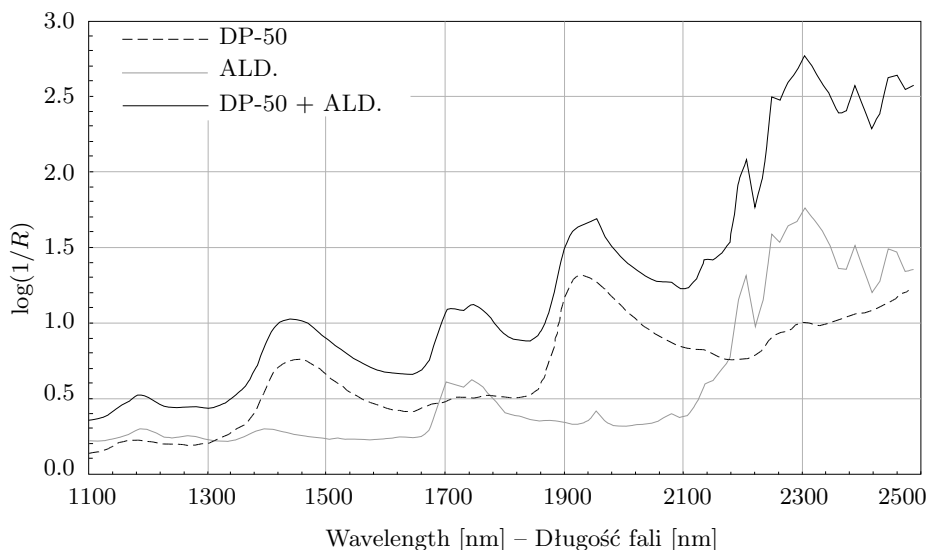


Fig. 2a. NIR spectra of polyvinylacetate (DP-50) dispersion and butyraldehyde (ALD.) and DP-50 + ALD mixture

Rys. 2a. Widma NIR dyspersji poliocctanowinylowej (DP-50) i aldehydu masłowego (ALD.) oraz mieszaniny DP-50 + ALD.

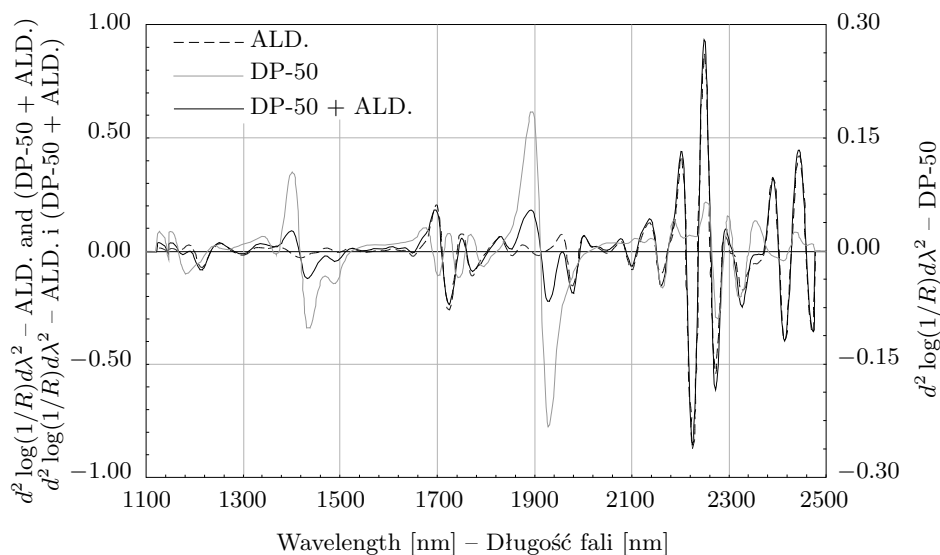


Fig. 2b. Second derivative NIR spectra of polyvinylacetate (DP-50) dispersion and butyraldehyde (ALD.) and DP-50 + ALD. mixture

Rys. 2b. Widma NIR drugiej pochodnej dyspersji poliocctanowinylowej (DP-50) i aldehydu masłowego (ALD.) oraz mieszaniny DP-50 + ALD.

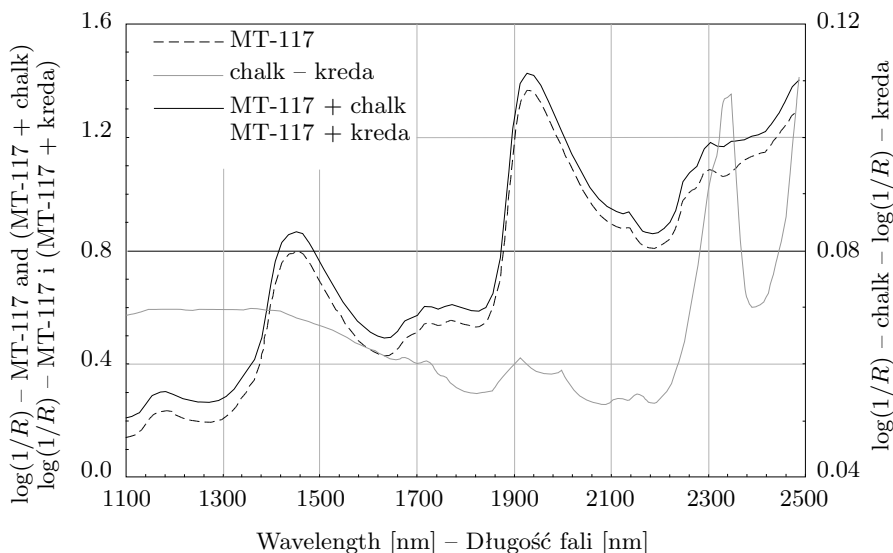


Fig. 3a. NIR spectra of polyacryl (MT-117) dispersion and chalk and MT-117 + chalk mixture

Rys. 3a. Widma NIR dyspersji poliakrylowej (MT-117) i kredy oraz mieszaniny MT-117 + kreda

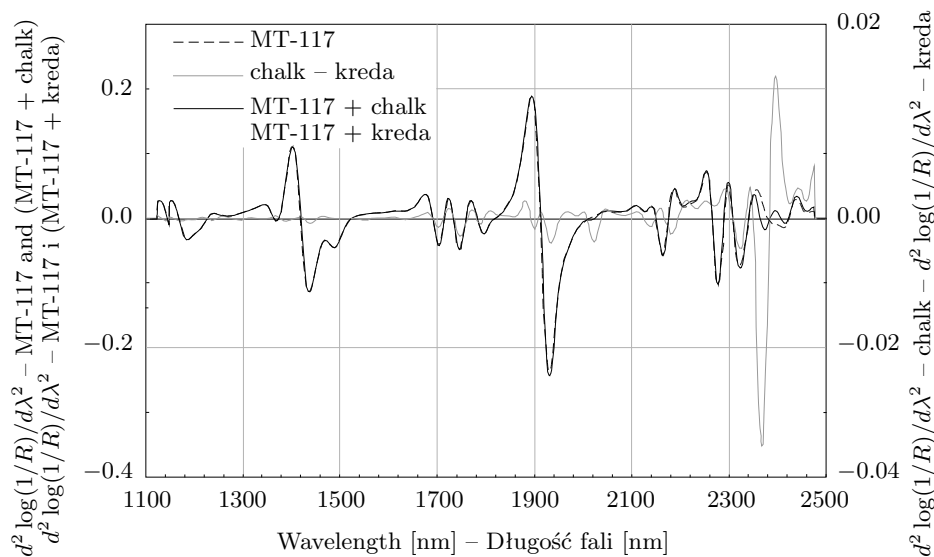


Fig. 3b. Second derivative NIR spectra of polyacryl (MT-117) dispersion and chalk and MT-117 + chalk mixture

Rys. 3b. Widma NIR drugiej pochodnej dyspersji poliakrylowej (MT-117) i kredy oraz mieszaniny MT-117 + kreda

Table 1. Statistical analysis (MLR and PLSR) of polyacrylate dispersion MT-117, butyraldehyde (ALD.) and chalk contents in polyvinylacetate Winacet DP-50 glue mixtures
 Tabela 1. Analiza statystyczna (MLR i PLSR) zawartości kopolimeru poliakrylowego MT-117, aldehydu masłowego (ALD.) i kredy w masach klejowych sporządzonych na bazie dyspersji poliocctanowinyłowej Winacet DP-50

Glue mixtures Masy klejowe	Statistical method Metoda statystyczna								
	MLR					PLSR			
	λ [nm]	R	F	SEE	SEP	f	r	SEE	SEP
DP-50	2300	0.3291	3	4.758	4.568	10	0.9679	0.984	1.147
+	2336, 2352	0.8490	30	2.720	2.663				
MT-117	2108, 2118, 2204	0.9510	122	1.258	1.237				
DP-50	1700	0.8788	207	0.329	0.309	7	0.9895	0.175	0.188
+	2248, 2288	0.9792	388	0.198	0.203				
ALD.	2248, 2328, 2380	0.9956	604	0.116	0.114				
MT-117	1340	0.7832	521	1.382	1.301	4	0.9632	1.031	1.334
+	2166, 2168	0.9298	409	1.111	1.020				
Chalk	2212, 2232, 2244	0.9939	433	0.885	0.840				

λ – wave length, r – multiple correlations coefficient, F – statistical function, SEE – standard error of estimation, SEP – standard error of prediction, f – number of factors.
 λ – długość fali, r – współczynnik korelacji wielokrotnej, F – funkcja F, SEE – standardowy błąd estymacji, SEP – standardowy błąd predykcji, f – liczba czynników.

calibration algorithm was applied also. As can be seen, the PLSR method was giving slightly better correlation quantitative analysis of acryl copolymer modifier (MT-117) in PVAC than MLR algorithm. In this case the SEE and SEP are lower than obtained by MLR algorithm. Similar result used algorithm PLSR obtained for analysis of amino adhesives resins modified with melamine (KASPRZYK et AL. 2001). This is agree with results of studies by THOMAS and HAALAND 1990 – a multivariate calibration method such as Partial Least Squares Regression (PLSR) is more suitable for calibrating spectral data, since it handles covariation between variables as well as moderate non-linear. But for analysis of butyraldehyde in DP-50 and chalk in MT-117 were obtained good correlations using both MLR (from two wavelengths calibration) and PLSR algorithm.

RECAPITULATION

The results of this investigation demonstrate that the contents of polyvinylacetate dispersion with trade mark Winacet DP-50, polyacryl copolymer MT-117, butyraldehyde and chalk as filler in three adhesive systems: DP-50 + MT-117, DP-50 + butyraldehyde and MT-117 + chalk can be determined in quantitative

aspects with the aid of NIR spectroscopy in the 1100-2500 nm region using for analysis both MLR and PLSR algorithm. All the compositions are determined simply by measuring a set of NIR spectra of the glue mixtures. Furthermore, remote sensing can be performed with the use of fibre optics. This technique can be potentially used in laboratory investigations and for industrial process control.

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ANALIZA ILOŚCIOWA ZA POMOCĄ SPEKTROSKOPII NIR WYBRANYCH SKŁADNIKÓW STOSOWANYCH W PRODUKCJI KLEJÓW PVAC DO DREWNA

Streszczenie

Przedstawiono rezultaty badań eksperymentalnych w zakresie możliwości analizy ilościowej komponentów zawartych w dyspersyjnych klejach PVAC do drewna z wykorzystaniem transmisyjno-refleksyjnej spektroskopii NIR. W ujęciu modelowym na bazie dyspersji polioctanowinylowej Winacet DP-50, kopolimeru akrylowego MT-117, aldehydu

masłowego oraz kredy jako wypełniacza spreparowano 22 masy klejowe, które poddano analizie w zakresie długości fali 1100-2500 nm, stosując aparat NIRSystems 6500 (NIR-Systems Inc., Maryland, USA). Opracowano procedurę badań, wyznaczając preferowane długości fal w zakresie oznaczania zawartości wybranych składników w klejach PVAC z wykorzystaniem analizy statystycznej w ujęciu algorytmu MLR i PLSR. Zaproponowany sposób umożliwi bardzo szybkie i precyzyjne prowadzenie odnośnych analiz ilościowych.

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