

STUDIES UPON THE RHEOLOGICAL PROPERTIES OF WATERBORNE SILANE ADHESION PROMOTERS APPLIED IN GLUING PROCESSES IN FURNITURE INDUSTRY

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SYNOPSIS. The rheological properties of selected adhesion promoter have been studied. For experiment two-component waterborne adhesion promoter with the isocyanate catalyst was used. The rheological properties were determined with the use of rotary rheoviscometer equipped with system of axial cylinders. Tests were carried out in the range of shearing rate from 1.5 up to 1312.0 s⁻¹, and measurement temperature 15-30°C.

KEY WORDS: adhesion promoter, hardener, temperature, rheological property, Ostwald de Waele's model, viscous flow

INTRODUCTION

Foils and edges based on the various thermoplastic polymers are commonly used in furniture industry in various technologies of the finishing of the surfaces of board elements. The analysis of the methods of preparation of surfaces of those synthetic materials for gluing, shows that interesting possibilities in the scope of enhancement of its gluability are created when using adhesion promoters, especially based on organic silanes. These agents became more widely offered to industrial practise not long ago and only by some specialised producers. They are produced as waterborne and solvent-borne systems that most often base on silicon acid derivatives in form of organic silanes. They can be applied in any way as very thin layers on practically all glued surfaces without any limitations (MARCINIEC et AL. 1990, 1993, MARCINIEC and GULIŃSKI 1992, MARCINIEC and FOLTYNOWICZ 1995, GULIŃSKI and MACIEJEWSKI 1998, MACIEJEWSKI et AL. 1998 a, b). After application of such an agent in the form of a single layer it is subjected to drying until complete solidification. In case of solvent-borne systems that show high

volatility the drying process is conducted in natural environment, while for waterborne systems a heat source is used. Waterborne adhesion promoters hardened with isocyanate catalyst have a different properties in various temperatures.

In this paper results of investigations of amount of hardener in waterborne adhesion promoter upon the course of rheological properties in function of changes of temperatures are presented.

EXPERIMENTAL

For experiments commercial waterborne, silane adhesion promoter, and isocyanate hardener were used. Selected properties of the adhesion promoter are given in Table 1. The mixtures of adhesion promoter without hardener, or with addition of 2.5 and 5.0% of hardener were prepared.

Table 1. Properties of adhesion promoter used in experiments
Tabela 1. Właściwości promotora adhezji użytego do doświadczeń

Properties – Właściwości	Values – Wartości
Colour – Barwa	transparent – przezroczysty
Density [g/cm ³] – Gęstość [g/cm ³]	1.0 ± 0.05
Dynamic viscosity [mPa·s] – Lepkość dynamiczna [mPa·s]	600 ± 200
Solid content [%] – Zawartość suchej substancji [%]	25 ± 2
pH value – Odczyn chemiczny, pH	7.5 ± 0.5

The investigations of rheological properties were carried out with using a rotational rheoviscmeter Rheotest-2 equipped with system of coaxial cylinders, in the range of temperatures 15-30°C with a step at every 5°C according to procedures described in PN-79/C-89404 and PN-86/C-81555 standards, while shearing rate ($\dot{\gamma}$) was within values 1.5 – 1312.0 s⁻¹.

RESULTS AND DISCUSSION

The analysis of the experimental data performed on the basis of evaluation criteria provided in literature (KEMBŁOWSKI 1973, WHORLOW 1980, WIŚNIEWSKI 1988) showed, that the adhesion promoter, both with and without hardener, in the tested scope of $\dot{\gamma}$ value, followed the dependence in the form of $\eta = \tau/\dot{\gamma} \neq \text{constants}$ (where: η – apparent viscosity, τ – shearing stress). Therefore the above mentioned systems can be classified as non-newtonian liquids. It was observed, that as the $\dot{\gamma}$ value had been increasing the apparent viscosity of these systems had been being lowered. It could be also stated, that considered systems showed rheological stability at a given $\dot{\gamma}$ value and constant temperature; because irrespective of the shearing time a specified dependence in relation $\dot{\gamma} - \tau$ was set.

The above observations and the results of the preliminary analysis of flow curves determined in a graphical way, allowed for the classification of the tested adhe-

sive promoters to non-newtonian rheostable liquids thinned by shearing. Figure 1 presents the influence of the amount of hardener added to the adhesion promoter on the flow curves in various temperature in function $\tau = f(\gamma)$, and the course of apparent viscosity $\eta = f(\gamma)$.

Basing on the analysis of results presented in papers (PROSZYK 1993, JÓŹWIAK and PROSZYK 1997, 2000, PROSZYK et AL. 1999) on rheological properties of different bonding agents applied in woodworking industry and on described analytical procedures, it was decided to prepare a mathematical description of flow curves $\tau = f(\gamma)$. The experimental data was to be considered following the universal Schulman formula:

$$\tau^{1/n} = \tau_y^{1/n} + (\eta_p \cdot \gamma)^{1/m}$$

where: τ_y – flow limit, η_p – viscosity, n and m – rheological parameters.

This formula allows for the classification of the tested liquid to specified rheological models.

For the approximation of the experimental data to an appropriate rheological model and for the determination of its parameters a computer program was used. The computations were performed after a thorough test recommended in literature. The computer application analysed models preselected in the preliminary experimental data evaluation, made required mathematical transformations to encoded linear forms and solved them using the method of the least squares. Then a decoding took place and the searched values of rheological parameters of each model were determined (KADZIŃSKI et AL. 1990). The basic measure that characterized the accuracy of regression relation was a correlation coefficient (r). The analysis of the experimental data following Schulman model showed that the tested adhesive promoter represents rheostable liquids, that do not show flow limit. No significant influence of hardener share in an adhesive promoter on its rheological properties was observed. The determined values of the τ_y parameter for that systems were near zero or were very small so they could be left out of the account, because of their being within the error rate.

Performing the analyses it was proved that for the approximation of the experimental data of examined systems in the scope of flow curves the Ostwald de Waele model is of best usability. The model has the following form:

$$\tau = k \cdot (\gamma)^{n_1}$$

where: k – coefficient of consistence, n_1 – exponent.

Table 2 shows the values of rheological parameters of mentioned model as well as correlation coefficients. Values R^2 obtained in the calculations, indicate the accuracy of rheological model selection. For all considered cases the exponent $n_1 < 1$, which, according to the literature, proves that η of these systems lowers together with the γ increase. Therefore mentioned systems represents the category of rheostable liquids, that do not show flow limit and that are thinned by shearing. In Polish literature these liquids are called as pseudoplastic ones, while in foreign publications, especially in English ones they are referred to as liquids of structural viscosity.

The analysis of the data in Table 2 shows that the most sensitive rheological parameter in the Ostwald de Waele model that is subjected to significant

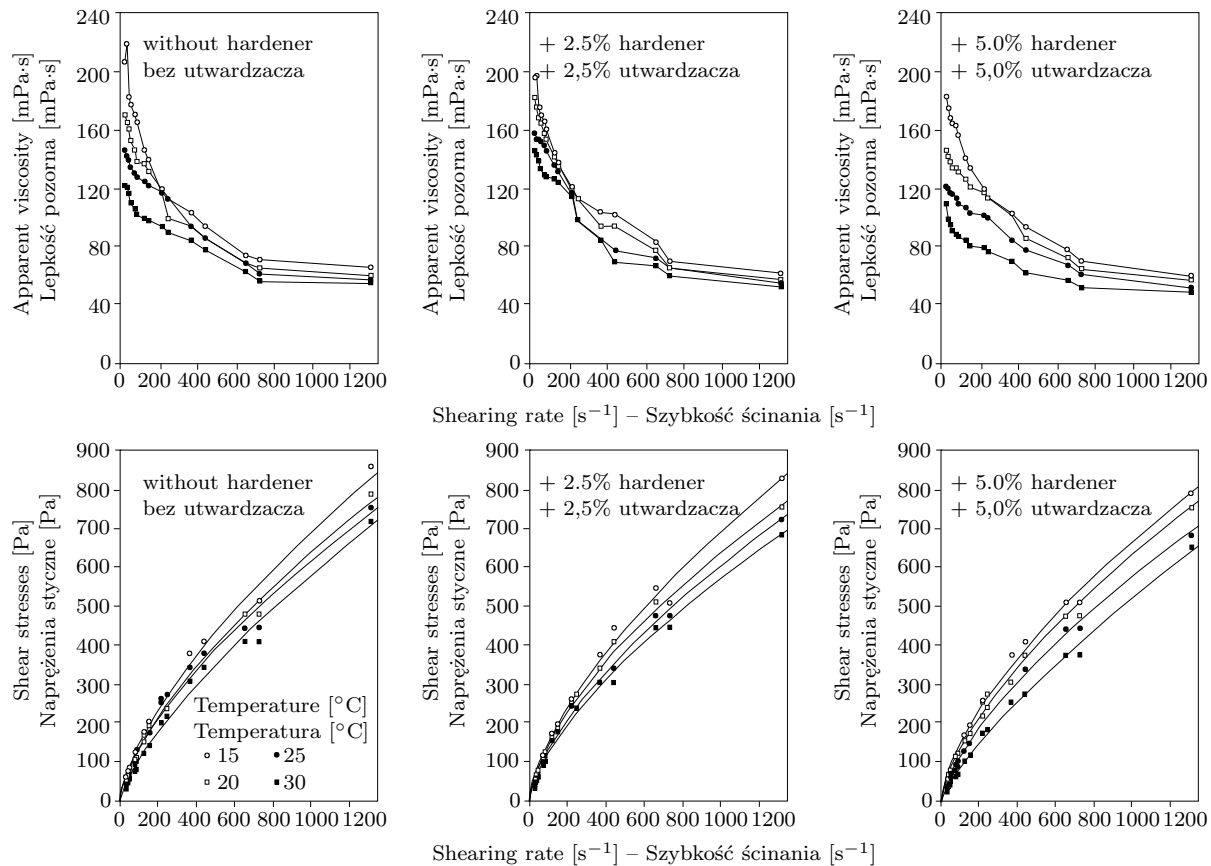


Fig. 1. Effect of hardener share in adhesion promoter on shear stress and viscosity in various temperatures
 Rys. 1. Wpływ ilości utwardzacza w promotorze adhezji na naprężenia styczne oraz lepkość w różnych temperaturach

Table 2. Influence of hardener share in adhesion promoter on the course of rheological parameters in function of the temperature in Ostwald de Waele model

Tabela. 2. Wpływ udziału utwardzacza w promotorze adhezji na kształtowanie się w funkcji temperatury parametrów reologicznych w modelu Ostwalda de Waele

Amount of hardener Ilość utwardzacza [%]	Temperature Temperatura [°C]	Model's parameter Parametry modelu		Coefficient of correlation Współczynnik korelacji R^2
		k [Pa·s]	n_1 [-]	
–	15	6.826	0.668	0.987
	20	6.081	0.674	0.987
	25	6.303	0.664	0.978
	30	3.738	0.730	0.985
2.5	15	7.868	0.648	0.988
	20	8.326	0.628	0.987
	25	6.963	0.647	0.992
	30	6.445	0.650	0.986
5.0	15	7.910	0.620	0.991
	20	6.804	0.656	0.982
	25	5.142	0.684	0.990
	30	2.540	0.771	0.994

changes in the scope of considered factors is coefficient of consistence k_1 . Values of that coefficient are within the range of 2.540-8.326. The general analysis of obtained data indicates that together with the increase of hardener a tendency of the increase of k_1 coefficient takes place. It can be also stated that the significant decrease of that coefficient takes place together with the temperature increase. Consequently, the n_1 exponent that is the measure of the deviation of an analysed liquid from a newtonian one, is subjected to smaller changes and is within a range of 0.6-0.7. It should be pointed out here the more n_1 values are far from 1 the more clear non-newtonian liquid properties are.

The analysis of the rheological models that describe the $\eta = f(\tau)$ dependency for rheostable liquids allowed for the statement that in the analysed scope of γ the experimental data could be properly approximated using 3-parameter Ellis model in the form:

$$\eta' = \frac{\eta_0}{1} + \left(\frac{\tau}{\tau_{1/2}} \right)^{\alpha_1 - 1}$$

Parameters of that model are η_0 (Pa·s), $\tau_{1/2}$ (Pa) and α_1 .

The values of rheological parameters of Ellis model for each systems are presented in Table 3.

Evaluating the course of changes of rheological parameters of Ellis model determined for each system some rules of the behavior of apparent viscosity η_0 and shear stress $\tau_{1/2}$ at various measurement temperatures were observed. Values of parameters were within a range of 0.69-1.02 and were lowered together with the increase of temperature and hardener share in adhesion promoter.

According to KEMBŁOWSKI (1973) relations in the scope of η_0 and $\tau_{1/2}$ values for the tested systems could be expressed as a factor that is a quotient of these parameters' values called, a characteristic time of liquid. Table 3 presents the calculated values of that factor. The analysis of the data contained in the table proves that the increase of the hardener's share in adhesion promoter causes the increase of α_1 parameter value.

Table 3. Effect of hardener share in adhesion promoter on the course of rheological parameters in function of the temperature in Ellis model

Tabela 3. Wpływ udziału utwardzacza w promotorze adhezji na kształtowanie się parametrów reologicznych w funkcji temperatury w modelu Ellisa

Amount of hardener Ilość utwardzacza [%]	Temperature Temperatura [°C]	Model's parameter Parametry modelu			Characteristic time of liquid Charakterystyczny czas płynu $\eta_0/\tau_{1/2}$ [-]
		η_0 [Pa·s]	$\tau_{1/2}$ [Pa]	α_1 [-]	
–	15	0.17	0.21	1.02	0.81
	20	0.14	0.20	0.87	0.70
	25	0.12	0.20	0.83	0.60
	30	0.10	0.19	0.77	0.53
2.5	15	0.15	0.22	0.91	0.68
	20	0.14	0.21	0.87	0.67
	25	0.12	0.20	0.83	0.60
	30	0.11	0.20	0.80	0.55
5.0	15	0.14	0.22	0.87	0.64
	20	0.12	0.20	0.84	0.60
	25	0.10	0.19	0.77	0.53
	30	0.08	0.17	0.69	0.47

Moreover a graphical method was used for the determination of apparent activation energy of viscous flow (E_η) of adhesion promoter with a various level of hardener. The obtained results for some example shearing rates are presented in Figure 2. The analysis of the data contained in the figure indicates that E_η values are within a wide range of 8.3-28.0 kJ/mole, depending on shearing rate and hardener share. Together with the increase of shearing rate, the values of activation energy of the viscous flow of adhesion promoter are significantly lowered. Moreover the presence of the hardener causes the increase of activation energy of viscous flow.

CONCLUSIONS

1. Waterborne silane adhesion promoter represents a category of rheostable non-newtonian liquids thinned by shearing without flow limit (pseudoplastic liquid). No influence of hardener share on rheological properties of the evaluated product was observed.

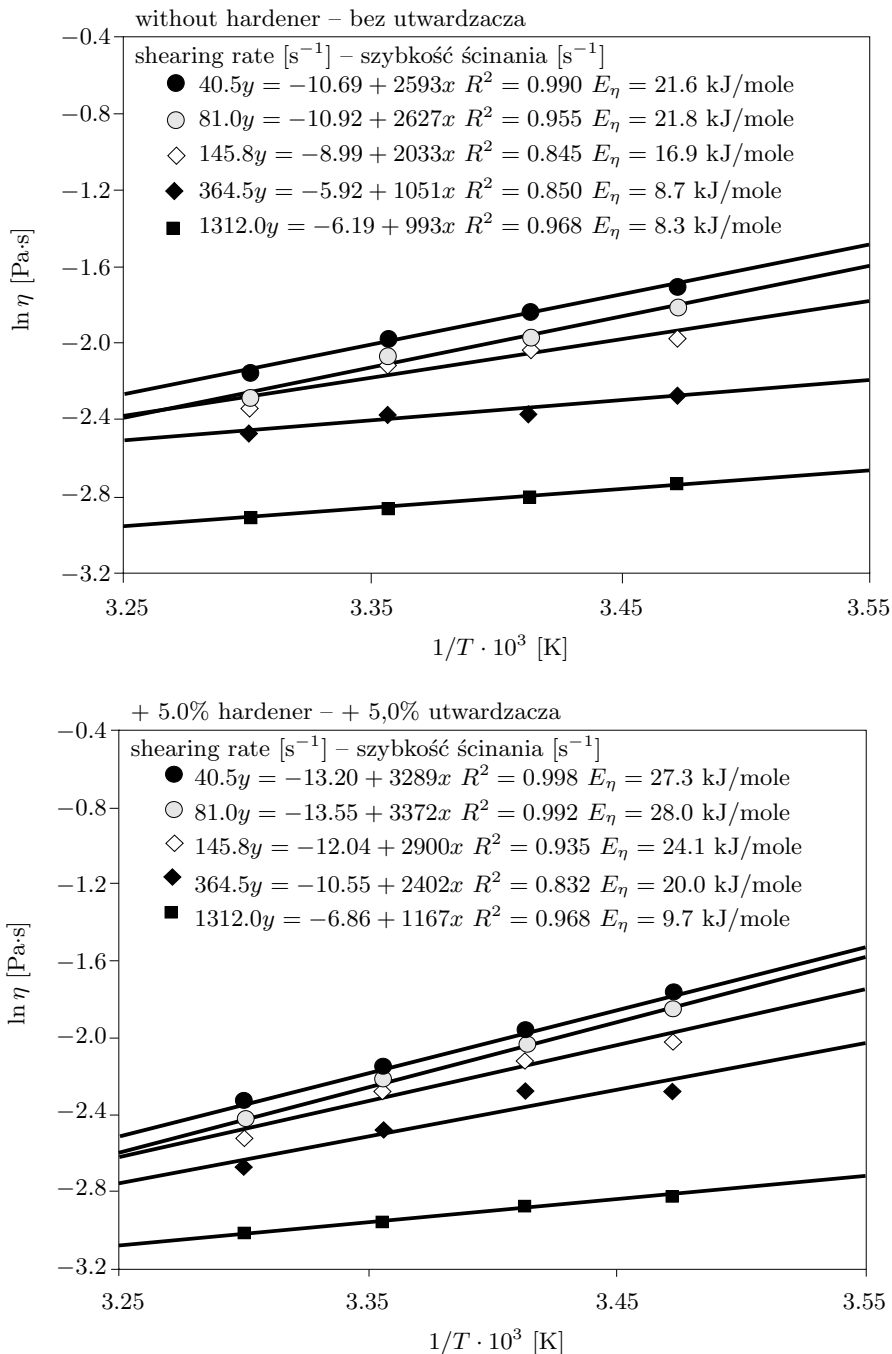


Fig. 2. Effect of hardener share in adhesion promoter on the course of E_η in function of selected shearing rate and temperature

Rys. 2. Wpływ udziału utwardzacza w promotorze adhezji na kształtowanie się E_η w funkcji wybranych szybkości ścinania oraz temperatury

2. It was proved that the best usability for the approximation of experimental data for the description of flow curves of tested adhesion promoter is shown by Ostwald de Waele rheological model. It was determined that the most sensitive parameter in that model is a coefficient of consistency, that indicates considerable changes in the scope of the analysed factors. Together with the increase of hardener share the increase of that coefficient took place.
3. For the approximation of the experimental data that describe the dependence of apparent viscosity on shear stress the highest usability was shown by Ellis model. The values of the characteristic time of liquid in that model, α_1 parameter were lowered together with the increase of system temperature and the amount of hardener.
4. The activation energy of viscous flow E_η were within a wide range (8-28 kJ/mol), and depending on hardener share. Together with the increase of shearing rate the values of that energy were significantly lowered. Moreover, the presence of hardener affected the increase of activation energy of the system's viscous flow.

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BADANIA WŁAŚCIWOŚCI REOLOGICZNYCH WODOROZCIEŃCZALNYCH SILANOWYCH PROMOTORÓW ADHEZJI STOSOWANYCH W PROCESACH KLEJENIA W PRZEMYSŁE MEBLARSKIM

Streszczenie

Przeprowadzono badania właściwości reologicznych wodorozcieńczalnego, silanowego promotora adhezji z różnym udziałem utwardzacza izocyjanianowego. Badania wykonano w reowiskozymerze rotacyjnym wyposażonym we współosiowe cylindry, prowadząc pomiary w zakresie temperatury 15-30°C, z odstopniowaniem co 5°C. Na podstawie wyników doświadczeń stwierdzono, że testowany środek proadhezyjny reprezentuje kategorię płynów reostabilnych, rozrzedzanych ścinaniem, nie posiadających granicy płynięcia. Wykazano, że największą przydatność do aproksymacji danych eksperymentalnych w zakresie opisów krzywych płynięcia wykazuje reologiczny model Ostwalda de Waele. Wraz ze zwiększaniem udziału utwardzacza następował wzrost wartości współczynnika konsystencji (k_1). Energia aktywacji lepkiego płynięcia (E_η) zawierała się w szerokim zakresie wartości, będąc uzależniona od szybkości ścinania oraz ilościowego udziału utwardzacza. Wraz ze wzrostem szybkości ścinania wyraźnie malały wartości tej energii. Obecność zaś utwardzacza wpływała na wzrost wartości energii aktywacji lepkiego płynięcia układu.

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