

# Production and Characterization of 3-Methacryloxypropyltrimethoxysilane Modified Polyvinyl Acetate Dispersion

DOI: 10.15255/KUI.2014.034  
KUI-9/2016  
Original scientific paper  
Received November 11, 2014  
Accepted January 18, 2015

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## Abstract

Semi-continuous vinyl acetate (VAc) radical emulsion polymerization in water with 3-methacryloxypropyltrimethoxysilane (GF31) co-monomer was performed using protective colloid PVA and surface-active compound. The impact of GF31 on polyvinyl acetate (PVAc) dispersion physicochemical and production parameters were determined. Even low quantities of GF31 (up to 1.5 % of VAc mass) had crucial impact on PVAc dispersion and dispersion film's parameters.

## Keywords

*Semi-continuous vinyl acetate emulsion polymerization, 3-methacryloxypropyltrimethoxysilane, rheological behaviour, particle size*

## Introduction

Polyvinyl acetate (PVAc) dispersions are low price, zero formaldehyde emission products.<sup>1</sup> In the last decade, PVAc dispersions were used as an alternative to common formaldehyde based resins. However, poor mechanical and water resistance properties of PVAc homopolymer need additional modification in order to satisfy end-users demands. Mainly two technological routes of dispersion modification are used for this purpose. Chemical PVAc modification using various organic co-monomers were studied and published in literature. One other widely used method is preparation of PVAc dispersion blend with organic and inorganic materials. From the economical point of view, preparation of PVAc blends is more acceptable due to application of simple and low cost equipment. Nevertheless, preparation of PVAc blends causes stability issues of the prepared products due to incompatibility of initial raw materials. In this case, chemical modification of PVAc has a big advantage.

Application of silane compounds in order to modify specific parameters of polymers is widely published in literature.<sup>2–6</sup> However, chemical modification of PVAc dispersion using silane compounds has not been well studied. Despite positive silane impact on PVAc dispersion physicochemical parameters, negative quality aspects of prepared products were also pointed out in some publications.<sup>7–8</sup> The hydrolyzation of silane in water media, different reactivity ratios of vinyl acetate (VAc) and silane monomers are the main issues for production of stable and commercially success-

ful products. The present paper deals with semi-continuous VAc radical emulsion polymerization in water, in the presence of industrial co-monomer 3-methacryloxypropyltrimethoxysilane with a brand name of Geniosil GF31. The dispersion system was stabilized by using different industrial stabilizers – polyvinyl alcohol and surface-active compound.

## Experimental details

### Materials and polymerization procedure

Commercial grade raw materials without further purification were used for polymerization with protective colloid PVA, *i.e.* vinyl acetate (Nevinnomyssky Azot, Russia), polyvinyl alcohol (PVA) Mowiol®23–88 (Kuraray, Germany), hydrogen peroxide (Sokolov, Czech), tartaric acid (Penta), sodium acetate (Fluka), water and Geniosil GF31 – 3-methacryloxypropyltrimethoxysilane (Wacker Silicones, Germany). Vinyl acetate was purified using rotational evaporator R-114 (Buchi, Switzerland) in order to produce surface-active compound stabilized dispersions. Other raw materials used for this purpose: sodium tetraborate (Sigma Aldrich), ammonium persulphate (Sigma Aldrich), Disponil®SUS 87 Special (Cognis).

Semi-continuous VAc radical emulsion polymerization using protective colloid PVA was carried out by a method and recipes presented elsewhere.<sup>8</sup> The following VAc to GF31 mass ratios were used: A — 100 : 0 (blank), B — 100 : 0.5, C — 100 : 1, D — 100 : 1.5, E — 100 : 3. Formulations for surfactant-stabilized dispersions are given in Table 1.

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Table 1 – Formulation of surfactant stabilized PVAc dispersion  
 Tablica 1 – Sastav disperzije PVAc stabilizirane surfaktantom

Dispersion Disperzija	Compound Spoj	<i>m</i> /g	<i>m</i> (VAc) : <i>m</i> (GF31)	
oil phase uljna faza	vinyl acetate vinil-acetat	45.41		
	Geniosil GF31	0	100 : 0	(F)
		0.454	100 : 1	(G)
		0.681	100 : 1.5	(H)
water phase vodena faza	ammonium persulphate amonijev persulfat	0.22		
	sodium tetraborate natrijev tetraborat	0.22		
	Disponil SUS 87 SPCL	3.68		
	demineralized water demineralizirana voda	80		

VAc emulsion polymerization with surfactant was done in the following way: dispersion medium was prepared by dissolving surfactant (Disponil®SUS 87 Special), sodium tetraborate and initiator (ammonium persulphate) in water. The monomer emulsion was prepared by mixing VAc or VAc and GF31 mixture and dispersion medium in high performance mechanical mixer (Homogenizer MPW-302, Mechanika Precyzyjna, Poland) at 35 – 40 thousand revolutions per minute. The prepared emulsion was then loaded into a 150 ml flat bottom flask with plastic magnetic stirrer. During continuous mixing of prepared emulsion, nitrogen was purged for 10 minutes. The polymerization was performed under a nitrogen atmosphere in 150 ml three-neck round-bottom flask with plastic magnetic stirrer. The polymerization temperature was maintained at 60 °C – 65 °C, stirring rate was set at 250 revolutions per minute, and monomer emulsion was added in 10 shocks during 10 hours. The main equipment is presented in Fig. 1.

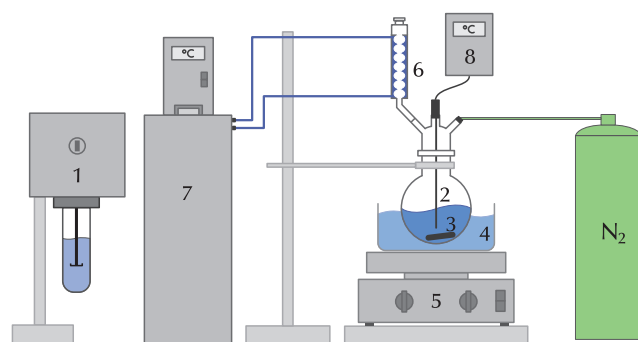


Fig. 1 – Production equipment of surfactant-stabilized dispersion. 1 – high performance mechanical mixer; 2 – three-neck round-bottom flask; 3 – plastic stirrer; 4 – water bath; 5 – magnetic stirrer with hot plate; 6 – condenser; 7 – cooling/heating water bath; 8 – digital thermometer.

Slika 1 – Aparatura za pripremu disperzije stabilizirane surfaktantom. 1 – mehanička miješalica visoke učinkovitosti; 2 – trogrla boca s okruglim dnom; 3 – plastična miješalica; 4 – vodena kupka; 5 – magnetska miješalica s grijalicom; 6 – kondenzator; 7 – vodena kupka za hlađenje/zagrijavanje; 8 – digitalni termometar.

## Analysis techniques

### Monomer conversion during polymerization

In order to determine the monomer content during the polymerization process, samples of reaction mixture were taken at different time intervals. These samples are relatively small, so that the overall composition in the reactor is not seriously affected. The samples were dried until constant weight. The conversion was evaluated gravimetrically.

### Viscosity measurements

Viscosity measurements were performed with a Brookfield viscosimeter LVDV-II+Pro. Test temperature (20 ± 0.5) °C. The parameters were calculated according to Wingather V2.2 software. The following equations, Eq. 1 (Casson) and Eq. 2, (power law) for non-Newtonian fluids were applied:

$$\tau^{1/2} = \tau_0^{1/2} + (\eta\dot{\gamma})^{1/2}, \quad (1)$$

where  $\tau$  is shear stress,  $\dot{\gamma}$  is shear rate,  $\eta$  is viscosity, and  $\tau_0$  is yield stress or zero shear viscosity, which indicate the force required to start or stop the flow.

$$\tau = k \dot{\gamma}^n, \quad (2)$$

where  $k$  is consistency index, and  $n$  is flow or power law index, which indicates dispersion dilatant or pseudoplastic behaviour. Values for dilatant fluid are above 1, and for pseudoplastic below 1.

### Particle size measurements

Samples were tested with Mastersizer Micro plus (Malvern Instruments, UK). Size range 0.5 μm – 500 μm.

### Mass loss after polymer extraction with toluene

Polymer extraction was carried out with a Soxhlet extractor. Toluene was used as solvent. Initial mass of flask was

weighed before extraction. Extraction proceeded for 24 hours. Rotation evaporator was used for solvent removal. After evaporation, the flask was dried at 110 °C to a constant mass and then weighed. The extracted polymer was evaluated gravimetrically.

### Film hardness

The film hardness was examined using a pendulum hardness tester Pendulum Hardness Rocker Ref.707P (Sheen Instruments Ltd, England) by the Persoz method (chosen angle as per König from 6° to 3°).<sup>9</sup> The dispersion was cast on a glass and dried at room temperature to a constant weight.

### Contact angle measurements

The contact angle measurements were done by the Woodward methodology.<sup>10</sup> For contact angle measurements, the dispersion was cast on a glass and dried at room temperature to a constant weight. Drops of  $(0.05 \pm 0.01)$  cm<sup>3</sup> water were put on the surface of the polymer, and the pictures were taken by a digital camera. The contact angle was determined with Geola Virtual Protractor (Lithuania) software.

### Water adsorption ratio of the films

The dispersion was cast on a glass and dried at room temperature to a constant weight. It was then put into demineralized water and taken out from time to time for weighing. The water adsorption ratio was evaluated gravimetrically.

### Thermal analysis

The thermal analysis of the polymers was determined using a DSC Q-100 (TA Instruments, USA) differential scanning calorimeter (DSC) for temperature scans. The scanning speeds of the heating and cooling cycles were 10 °C min<sup>-1</sup>, temperature ramp from -20 °C to 220 °C under nitrogen flow 50 ml min<sup>-1</sup>.

## Results and discussion

### Emulsion polymerization

Experimental results are shown in Fig. 2, where the temperature is plotted against reaction time at different GF31 quantities used for dispersion modification.

Retardation of radical copolymerization reaction using silane co-monomer was noticed elsewhere.<sup>2,3,7,8,11-13</sup> The higher stability and reactivity of silane radical are the main explanations given by authors. However, hydrolyzation of silane and further formation of silanol/siloxane compound could have crucial impact on polymerization kinetics as well. The increase of GF31 content caused temperature decreases during dispersion production (Fig. 2). Despite

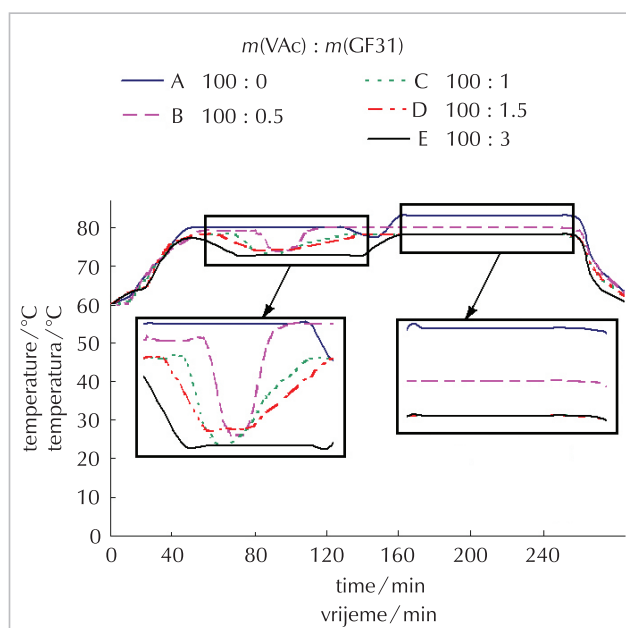


Fig. 2 – Temperature curve of dispersion production  
Slika 2 – Temperatura disperzije tijekom priprave

that, temperature in water bath was kept at constant. Dispersion (E) with the highest VAc to GF31 mass ratio coagulated and went into solid and water phases during production. The temperature drop in the reaction media during continuous monomer mixture dosage could be caused by back stream of unreacted and condensed monomers. In order to confirm this presumption, the dry matter content (monomer conversion) was analysed during dispersion production. The higher amount of GF31 was used, the lower conversion of monomer was determined for each measured point. The theoretical value of dry matter content for each point was calculated as per maximum monomer conversion. Therefore, all measured dry matter content values were below the theoretical values. The greatest differences in dry matter content between dispersions were observed at 145 minutes from the beginning of the dispersion production, *i.e.* at the end of continuous monomer mixture dosage. Lower polymerization temperatures caused dispersions with higher VAc and lower dry matter content (Table 2). Similar results for dispersions stabilized with surface-active compound were observed. Dispersion (H) coagulated during production, while (F) and (G) dispersions were rather stable during production and storage. Dry matter content of unmodified dispersion (F) was higher in comparison to (G) and (H). The results confirmed the presumption of retardation reaction, which proceeds in GF31 silane modified systems. Accordingly, the impact of dispersion system stabilizer on copolymerization kinetics could be assumed as minimal. According to the results presented in Table 2, the increase of mass fraction of GF31 in PVAc dispersion composition from 0 to 0.5 % decreases dry matter content at 145 minutes to about 1.9 %. Total calculated decrease in dry matter content, by increase in GF31 mass fraction from 0 to 3 %, reaches 6 %. However, a greater gain in dry matter content after so-called “post

cooking" procedure was determined for dispersions modified with higher GF31 content. This could be evidence of VAc polymerization reaction retardation by GF31 as well the necessity to prolong continuous monomer mixture dosage during PVAc dispersion production, if higher GF31 amounts are applied.

The rheological properties of dispersion are rather important for industrial application. Hydrolyzation of silane monomer and further condensation of silanols could be a key in retardation reaction in silane modified VAc systems. Formation of silanol derivatives as well as reaction between silanols and PVA could also be possible. Rheological parameters and stability of produced dispersion might change during modelled process. The influence of GF31 content on the final PVA stabilized dispersion viscosity is presented in Fig. 3. According to Fig. 3, the increase in dispersion final viscosity by using higher mass ratios of GF31 was determined. The highest viscosity was observed for PVA stabilized dispersion (D), at VAc to GF31 mass ratio 100 : 1.5. Dispersion (E), produced with highest VAc to GF31 mass ratio 100 : 3, coagulated at the end of emulsion polymerization, therefore viscosity and other analyses were not performed. The storage stability of dispersion was evaluated as per viscosity change during a storage time (Table 3).

PVA stabilized PVAc dispersions are pseudoplastic, *i.e.* the flow index values are below 1. Only a slight difference in pseudoplasticity for dispersions was determined. Lower viscosity change during storage indicates better storage stability of GF31 silane modified dispersions. Slight changes in yield stress and flow index values during dispersion storage were determined for dispersions modified with up to 1 % of GF31. However, GF31 content up to 1.5 % had changed yield stress and flow index values significantly. Contrary to GF31 modified dispersions, yield stress of unmodified dispersion (A) increase after 6 months of storage. This could be explained by polycondensation of silanol groups and decrease in hydrogen bonds in the dispersion system. Con-

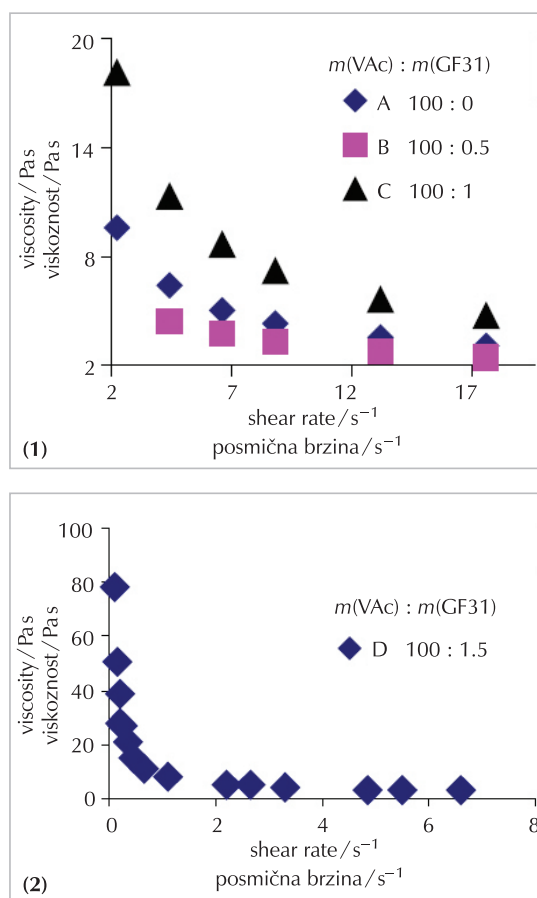


Fig. 3 – Final viscosity of dispersions  
Slika 3 – Konačna viskoznost disperzija

sequently, high rates of silanol polycondensation have negative impact on dispersion (D) storage stability.

The rheological parameters of dispersions greatly depend on dispersion particle size. The particle size parameters of

Table 2 – Parameters of GF31 silane modified PVAc dispersions  
Tablica 2 – Parametri silana GF31 modificiranog disperzija PVAc

Parameter Parametar	PVAc dispersion Disperzija PVAc								
	PVA stabilized Stabilizirano PVA-om					Surfactant stabilized Stabilizirano surfaktantom			
	A	B	C	D	E	F	G	H	
VAc to GF31 mass ratio maseni omjer VAc i GF31	100 : 0	100 : 0.5	100 : 1	100 : 1.5	100 : 3	100 : 0	100 : 1	100 : 1.5	
dry matter mass fraction at 145 min maseni udjel suhe tvari nakon 145 min	35.0	33.1	31.1	30.9	29.0	–	–	–	
final dry matter mass fraction / % konačni maseni udjel suhe tvari / %	35.2	33.8	32.0	31.2	30.2	33.6	32.7	25.0	
increase in dry matter mass fraction / % povećanje masenog udjela suhe tvari / %	0.2	0.7	0.9	0.3	1.2	–	–	–	

Table 3 – Rheological parameters and storage stability of PVA stabilized PVAc dispersions, at different mass ratio of VAc to GF31. Shear rate for A, B, C samples at  $8.8 \text{ s}^{-1}$ , and D at  $2.2 \text{ s}^{-1}$

Tablica 3 – Reološka svojstva i stabilnost disperzije PVAc stabilizirane PVA-om pri različitim masenim omjerima VAc i GF31. Smična brzina za uzorke A, B i C  $8,8 \text{ s}^{-1}$ , a D  $2,2 \text{ s}^{-1}$

Dispersion Disperzija	m(VAc) : m(GF31)	Viscosity / Pa s Viskoznost / Pa s			Yield stress / $10^{-3} \text{ N cm}^{-2}$ Granica razvlačenja / $10^{-3} \text{ N cm}^{-2}$			Flow index Indeks tečenja		
		Initial Početno	After 6 months Nakon 6 mjeseci	Diff. / % Razlika / %	Initial Početna	After 6 months Nakon 6 mjeseci	Diff. / % Razlika / %	Initial Početni	After 6 months Nakon 6 mjeseci	Diff. / % Razlika / %
A	100 : 0	4.3	6.3	47	0.99	1.28	29	0.55	0.58	5
B	100 : 0.5	3.3	3.7	13	0.55	0.42	-24	0.43	0.46	7
C	100 : 1	7.2	6.6	-8	2.37	2.02	-15	0.65	0.68	5
D	100 : 1.5	5.3	6.3	19	0.66	0.28	-58	0.30	0.40	33

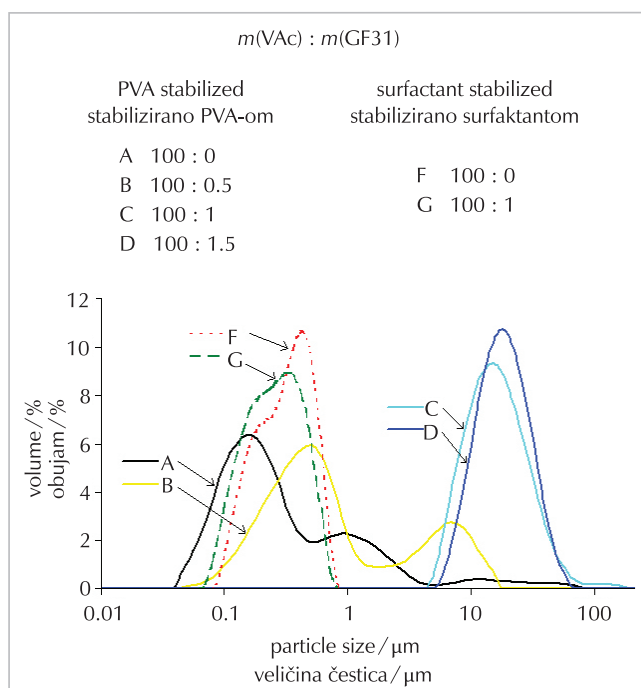


Fig. 4 – Distribution of dispersion particle size  
Slika 4 – Distribucija veličine čestica disperzija

GF31 silane modified dispersions are presented in Fig. 4 and Table 4.

According to particle size distribution curves presented in Fig. 4, PVA stabilized unmodified (A) and minimum amount of GF31 silane modified dispersions (B) have bimodal particle size distribution. Accordingly, further increase in GF31 silane content used for dispersion modification determines monomodal particle size distribution of dispersions (C) and (D).

According to Table 4 results, the increase in GF31 silane content in PVA stabilized dispersion composition caused formation of bigger and more uniform particles. Respectively, decrease in dispersity and specific surface area of particles were determined. On the contrary, GF31 had no impact on particle parameters of surfactant stabilized PVAc dispersions (F) and (G). Application of pre-emulsion produced by using high performance mechanical mixer, forms more uniform dispersion particles and minimal GF31 silane hydrolyzation reaction could be expected.

### Properties of polymer films

Generally, alkoxy groups of alkoxy silane monomer could be easily hydrolysed in water media. Further polycondensation of silanol groups form siloxane bonds and branched macromolecular structures. Accordingly, determination of rheological behaviour and particle morphology of GF31 silane modified dispersions characterizes possible routes of reactions, which proceeds in dispersion system. Another possible path of cross-linked macromolecule structure formation is polycondensation of silanols during dispersion drying. In order to prove this, different analysis techniques were published in literature, such as solubility of polymer in various solvents, graft polymer content determination by extraction,<sup>14,15</sup> water resistance by polymer immersion in water,<sup>16</sup> film hardness, etc. The results of film testing are presented in Table 5. Mass loss of films after extraction with toluene greatly decreases with increase in GF31 applied in PVAc dispersion modification. The weight loss difference between unmodified PVA stabilized dispersion film (A) and film cast from dispersion modified with highest content GF31 silane (E) reaches 52 times. The extraction results give clear evidence of branched macromolecular structure of GF31 silane modified PVAc. Dimensional macromolecular structures could also change  $T_g$  values of polymers.



Table 4 – Particle parameters of GF31 silane modified dispersion  
 Tablica 4 – Svojstva čestica disperzije modificirane silanom GF31

Parameter Parametar	PVAc dispersion Disperzija PVAc					
	PVA stabilized Stabilizirano PVA-om				Surfactant stabilized Stabilizirano surfaktantom	
	A	B	C	D	F	G
$m(\text{VAc}) : m(\text{GF31})$	100 : 0	100 : 0.5	100 : 1	100 : 1.5	100 : 0	100 : 1
dispersity disperznost	7.23	3.32	0.57	0.42	0.41	0.46
specific surface area/ $\text{m}^2\text{g}^{-1}$ specifična površina/ $\text{m}^2\text{g}^{-1}$	35.88	15.75	0.46	0.40	18.45	19.67

Table 5 – Parameters of PVA stabilized GF31 silane modified dispersion and dispersion films  
 Tablica 5 – Svojstva disperzije i disperzijskog filma modificiranih silanom GF31 i stabiliziranih PVA-om

Sample Uzorak	$m(\text{VAc}) : m(\text{GF31})$	Mass loss/% Gubitak mase/%	$T_g/^\circ\text{C}$		Number of oscillations Broj oscilacija	Contact angle/ $^\circ$ Kontaktni kut/ $^\circ$	Water adsorption/% Aposrcija vode/%	Bond strength of glued wood/ $\text{N mm}^{-2}$ Čvrstoća lijepjenog spoja s drvetom/ $\text{N mm}^{-2}$	Bond strength of glued textile/ $\text{kN m}^{-1}$ Čvrstoća lijepjenog spoja s tekstilom/ $\text{kN m}^{-1}$
			Initial Početni	After extraction Nakon ekstrakcije					
A	100 : 0	78.6	44	–	119	35	45	8.3	0.4
B	100 : 0.5	11.5	44	46	108	38	32	6.3	0.25
C	100 : 1	9.1	45	–	67	38	32	1.9	0.10
D	100 : 1.5	7.7	45	–	47	37	30	0	0.05
E*	100 : 3	1.5	46	49	–	–	–	–	–

\* E dispersion coagulated during production  
 \* disperzija E koagulirala je za vrijeme priprave

Film casted from GF31 silane modified dispersion was evaluated by means of DSC. According to Table 5 results, the  $T_g$  range of GF31 samples was 44 °C – 46 °C, surfactant stabilized at 41 °C – 44 °C. Slightly higher  $T_g$  values were observed for PVAc modified with higher GF31 content. Nevertheless,  $T_g$  values had small differences. GF31 amounts applied in dispersion modification had no significant impact on  $T_g$  values. The  $T_g$  values of dispersions (B) and (E) films are higher after extraction with toluene. Hence, low molecular weight and/or linear polymers were extracted. The difference between unmodified PVA (A) and surfactant (F) stabilized dispersions films  $T_g$  values were also determined. Branched PVAc-PVA polymer formation could be an explanation of higher  $T_g$  value for dispersion (A) film. Polymer hardness, which is partially related to  $T_g$  value, was tested accordingly. The increase in mass fraction of GF31 applied in dispersion modification from 0 to 1.5 % decreases dispersion film hardness more than twice.

Water based dispersions are widely used for glue and paint production. Basically, glue bond or paint coating during ex-

ploitation is influenced by air humidity and ambience temperature. Therefore, water repellence and contact angle analysis of dispersion coating was performed. According to Table 5 results, water repellence of GF31 modified dispersion film is slightly lower in comparison to unmodified (A). Results could be explained by formation of polymers with cross-link macromolecular structures with siloxane bridges.

Water adsorption is another widely used method for determination of film resistance to water. According to Table 5 results, water adsorption of GF31 silane modified dispersion films is lower in comparison to unmodified (A) and independent of dispersion stabilizer. Films, prepared from PVA stabilized PVAc dispersions, reached water adsorption maximum during first two days of immersion, and did not apparently change during further 18 days. Accordingly, surfactant stabilized dispersions films, reached water adsorption maximum after 16 days of immersion. The unmodified film, casted from PVA stabilized dispersion (A), had lower water adsorption (45 %) in comparison to film (55 %) casted from surface-active compound stabilized dis-

persion (F). Different water adsorption could be explained by different macromolecular structure of the film. Hydrophilic hydroxyl groups of protective colloid PVA influence faster, however branched structures of PVAc-PVA copolymers lower adsorption of water molecules. On the contrary, slower and higher water adsorption of surfactant stabilized PVAc dispersion film is influenced by hydrophobic acetyl groups and linear macromolecular structures.

Despite the higher water resistance of GF31 modified dispersion films, the tensile strength of glued wood joints showed no improvement in water resistance. Tests with beech timber were carried out according to the second (resistant to moisture) series of EN 204 standard.<sup>17</sup> Only unmodified dispersion glue joints were able to reach applicable bond strength of  $8 \text{ N mm}^{-2}$ . Other samples collapsed during soaking. The wood gluing results could be explained by usage of low dry matter content dispersions.<sup>18</sup> Another possible explanation is poor mechanical interlocking between surfaces due to the morphology of dispersion particles. Higher particle size and lower dispersity were observed for dispersions modified with higher GF31 content. Bigger and more uniform particles cannot properly fill roughness of wood surface, thus the formed gas pockets cause lower mechanical interlocking. Application of plasticizer could also have negative impact on tensile strength of glued samples. Consequently, textile was glued with unplasticized PVAc dispersions. According to results presented in Table 5, bond strength of both wood and textile samples decrease with application of dispersions produced with higher VAc to GF31 mass ratios.

## Conclusions

Modelling industrial semi-continuous polyvinyl acetate production process, acryl silane (GF31) modified polyvinyl acetate dispersion composition and production technology was developed. The mass ratios of vinyl acetate and GF31 for a product possessing acceptable physicochemical properties were determined.

The higher GF31 content, applied in VAc emulsion polymerization, determined:

- 1.1. increase in vinyl acetate content, *i.e.* lower dry matter content of final dispersion, particle size and dynamic viscosity of modified polyvinyl acetate dispersion;
- 1.2. decrease in modified polyvinyl acetate dispersion bond strength with wood and textile;
- 1.3. decrease in water adsorption and hardness of films as well as increase in water repellence of coating surface casted from modified polyvinyl acetate dispersion.

During drying of GF31 silane modified dispersion, silanol groups form Si–O–Si bond, accordingly branched macromolecular polymer is observed. Poor solubility of film in various solvents was confirmed. However, GF31 amounts used for polyvinyl acetate modification have no significant impact on polymer  $T_g$  values.

## List of abbreviations and symbols

### Popis kratica i simbola

DSC	– differential scanning calorimetry – diferencijalna pretražna kalorimetrija
GF31	– 3-methacryloxypropyltrimethoxysilane – 3-metakriloksipropiltrimetokssilan
$k$	– consistency index – indeks konzistencije
$m$	– mass, g – masa, g
$n$	– flow index – indeks tečenja
PVA	– polyvinyl alcohol – polivinil-alkohol
PVAc	– polyvinyl acetate – polivinil-acetat
$T_g$	– glass transition temperature, °C – staklište, °C
VAc	– vinyl acetate – vinil-acetat
$\dot{\gamma}$	– shear rate, $\text{s}^{-1}$ – smična brzina, $\text{s}^{-1}$
$\eta$	– viscosity, mPa s – viskoznost, mPa s
$\theta$	– contact angle, ° – kontaktni kut, °
$\tau$	– shear stress, $\text{N cm}^{-2}$ – posmično naprežanje, $\text{N cm}^{-2}$
$\tau_0$	– yield stress, $\text{N cm}^{-2}$ – granica razvlačenja, $\text{N cm}^{-2}$

## References

### Literatura

1. Composite Wood Product Stakeholder Meeting, California Environmental Protection Agency Air Resources Board, California, 2006. URL: <http://www.arb.ca.gov/toxics/compwood/presentation050206a.pdf> (1. 1. 2015.).
2. H. J. Naghash, S. Mallakpour, N. Mokhtarian, Synthesis and characterization of silicone-modified vinyl acetate-acrylic emulsion copolymers, *Prog. Org. Coat.* **55** (2006) 375–381, doi: <http://dx.doi.org/10.1016/j.porgcoat.2006.02.001>.
3. H. J. Naghash, S. Mallakpour, N. Kayhan1, Synthesis and Characterization of Silicone Modified Acrylic Resin and Its Uses in the Emulsion Paints, *Iran. Polym. J.* **14** (2005) 211–222.
4. Y. F. Zhang, L. Miao, C. L. Yang, M. G. Lu, Synthesis of ambient temperature self-crosslinking VTES-based core-shell polyacrylate emulsion via modified micro-emulsion polymerization process, *Polym. Bull.* **70** (2013) 1631–1645, doi: <http://dx.doi.org/10.1007/s00289-012-0867-y>.
5. G. J. Matison, Silane Coupling Agents and Glass Fibre surfaces: A Perspective. Silanes and Other Coupling Agents, vol. 5 (2009), Mittal, K. L. Ed. CRC Press, pp. 3–23, doi: <http://dx.doi.org/10.1163/ej.9789004165915.i-348.6>.
6. M. Bengtsson, K. Oksman, The use of silane technology in crosslinking polyethylene/wood flour composites, *Compos. Part A: Appl. Sci. Manuf.* **37** (2006) 752–765, doi: <http://>

- dx.doi.org/10.1016/j.compositesa.2005.06.014.
7. X. H. Liu, S. P. Yi, H. B. Li, C. Huang, Preparation of Poly(vinyl acetate) Modified by Triethoxyvinylsilane and Properties of Copolymeric Lattices, Iran. Polym. J. **16** (2007) 207–213.
  8. M. Dubininkas, G. Buika, Dispersion production by semi-continuous radical vinyl acetate emulsion polymerization with silane co-monomer and characterization of final products, Chin. J. Polym. Sci. **31** (2013) 346–354, doi: <http://dx.doi.org/10.1007/s10118-013-1220-0>.
  9. Sheen Pendulum Hardness Rocker datasheet. URL: <http://www.aguilarpineda.es/instrumentos/docs/folletoswebcontrol/SheenPendulo.pdf> (1. 1. 2015.).
  10. P. R. Woodward, Contact Angle Measurements Using the Drop Shape Method. URL: <http://www.firsttenangstroms.com/pdfdocs/CAPaper.pdf> (1. 1. 2015.).
  11. C. Y. Kan, X. L. Zhu, Q. Yuan, X. Z. Kong, Graft Emulsion Copolymerization of Acrylates and Siloxane, Polym. Advan. Technol. **8** (1997) 631–633, doi: [http://dx.doi.org/10.1002/\(SICI\)1099-1581\(199711\)8:11<631::AID-PAT691>3.0.CO;2-K](http://dx.doi.org/10.1002/(SICI)1099-1581(199711)8:11<631::AID-PAT691>3.0.CO;2-K).
  12. E. M. Petrie, Handbook of Adhesives and Sealants, vol. 2 (2007), The McGraw-Hill Companies, Inc., pp. 290.
  13. X. H. Zhou, W. P. Tu, Z. P. Xia, Preparation and performance of acrylate emulsion modified by vinyltriethoxysilane, J. Mat. Prot. **37** (2004) 21–23.
  14. D. Donescu, K. Gosa, A. Ciupitoiu, I. Languri, Semicontinuous Emulsion Polymerization of Vinyl Acetate. Part I. Homopolymerization with Poly-(Vinyl Alcohol) and Nonionic Coemulsifier, J. Macromol. Sci. **22** (1985) 931–940, doi: <http://dx.doi.org/10.1080/00222338508056645>.
  15. D. Donescu, K. Gosa, I. Diaconescu, M. Mazare, N. Carp, Emulsion Polymerization of Vinyl Acetate, (1981), M. S. El-Aasser, J. W. Vanderhoff (Eds.), Applied Science Publ., pp. 203–214.
  16. M. Y. Zhu, W. H. Qiao, H. Z. Liu and Y. L. Sun, Synthesis of a novel polymerizable surfactant and its application in the emulsion polymerization of vinyl acetate, butyl acrylate, Veova 10, and hexafluorobutyl methacrylate, J. Appl. Polym. Sci. **107** (2008) 624–628, doi: <http://dx.doi.org/10.1002/app.27123>.
  17. European Standard EN 204 “Classification of thermoplastic wood adhesives for non-structural applications”, 2005.
  18. J. Bikerman, Causes of Poor Adhesion: Weak Boundary Layers, Ind. Eng. Chem. **59** (1967) 40–44, doi: <http://dx.doi.org/10.1021/ie51403a010>.

## SAŽETAK

### Priprava i karakterizacija disperzije polivinil-acetata modificiranog 3-metakriloksiopropiltrimetoksisilanom

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U vodi je polukontinuirano emulzijski polimeriziran vinil-acetat (VAc) s komonomerom 3-metakriloksiopropiltrimetoksisilanom (GF31) uz PVA ili surfaktant kao zaštitni koloid. Određen je utjecaj GF31 na fizičko-kemijska svojstva i tijek priprave disperzija. Već i mala količina GF31 (do 1,5 % mase VAc) ima izrazit utjecaj na svojstva disperzije i filma.

#### Ključne riječi

Polukontinuirana emulzijska polimerizacija vinil-acetata, 3-metakriloksiopropiltrimetoksisilan, reološka svojstva, veličina čestica

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Izvorni znanstveni rad  
Prispjelo 11. studenoga 2014.  
Prihvaćeno 18. siječnja 2015.