

DISPERSION PRODUCTION BY SEMI-CONTINUOUS RADICAL VINYL ACETATE EMULSION POLYMERIZATION WITH SILANE CO-MONOMER AND CHARACTERIZATION OF FINAL PRODUCTS

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Abstract Vinyl acetate radical emulsion polymerization in water with GF51 silane co-monomer was performed by semi continuous way. The GF51 impacts on dispersion rheology as well on films and bonding strength properties were determined. It should be stated that even low quantities of GF51 (up to 6% from VAc) determined high viscosity of dispersions. The GF51 modified films have low water absorption and high affinity to glass. Molecular mass and thermal properties of GF51 modified polymers were determined accordingly.

Keywords: Semi-continuous vinyl acetate polymerization; Geniosil GF51; Triethoxy vinylsilane; Rheological behaviour; Wood bonding.

INTRODUCTION

Semi-continuous emulsion polymerization is an important process for the manufacture of latex products such as coatings, adhesives and synthetic elastomers. In all cases water emulsions are represented as product with low content of volatile organic compounds (VOC), which are very attractive in now days due to strict emission regulations by Western countries (EU and US).

Polyvinylacetate emulsion in water is a well known industry product, which finds its application in glue, paint and *etc.* compositions mainly because of low price. However, poor mechanical and water resistance properties of polyvinylacetate homopolymer need additional modification in order to satisfy end-users demands. During last two decades great interest in vinyl acetate emulsion copolymerization with organosilanes was noticed^[1, 2]. Organosilanes in polyvinylacetate modification are used for improvement of water resistance and elasticity of polymer. Inorganic material encapsulation into polymer is another rapidly expanding field in which organosilanes are used as adhesion promoters to inorganic/organic surfaces^[3–5].

Non-complicated dispersion production with applicable end properties is a main target for industrial dispersion producers. Therefore, optimal production conditions, as well as right proportions of components should be determined separately. The present paper deals with vinyl acetate radical emulsion polymerization in water in the presence of the industrial organosilane mixture Geniosil GF51 (herein after GF51). The influence of different proportions of GF51 on vinyl acetate emulsion polymerization as well on final dispersion and polymer film properties was investigated.

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EXPERIMENTAL

Materials

In order to simulate industrial production, commercial grade raw materials without further purification were used *i.e.* vinyl acetate (VAc) (Nevinnomyssky Azot, Russia), polyvinyl alcohol (PVA) Mowiol®23-88 (Kuraray, Germany), hydrogen peroxide (Sokolov, Czech), tartaric acid (Penta), sodium acetate (Fluka), demineralized water and Geniosil GF51 (Wacker Silicones, Germany). Geniosil GF51 is a mixture of triethoxy vinylsilane (50 wt%–80 wt%), alkylalkoxy siloxane (10 wt%–30 wt%) and 1,1,3,3-tetraethoxy-1,3-dimethyl-disiloxane (1 wt%–5 wt%)^[6].

Polymerization Procedure

Semi-continuous VAc radical emulsion polymerization was carried out using a 1 L five-neck round-bottom flask equipped with reflux condenser, plastic stirrer, two separate feed streams and digital thermometer.

At the beginning of the process water solution of PVA, sodium acetate and tartaric acid were loaded into the reactor. Stirring rate was set at 170 r/min, temperature was maintained at 60°C. Immediately after the temperature was reached, under nitrogen atmosphere, 10 wt% of VAc and 50 wt% of hydrogen peroxide of total amount were loaded. After induction period (approx. 5–10 min) the temperature increased up to 75–80°C and was kept until all hydrogen peroxide and VAc/GF51 monomer mixture (both mixed before use) were loaded continuously. Continuous monomer mixture loading was started 15 min. after beginning of polymerization. Monomer mixture feeding rate was 1.85 g/min. Formulations of prepared dispersions are given in Table 1. After all components were loaded, the reaction temperature was increased up to 80–85°C for final monomer conversion.

Table1. Formulations and components loading proportions for dispersion production

Compound	Initial charge (wt%)	Feed (wt%)	Total (g)
Vinyl acetate	10	90	260
Geniosil GF51	–	100	A. 0
			B. 1.3
			C. 3.9
			D. 7.8
			E. 15.6
Hydrogen peroxide 1% solution in water	50	50	40
Tartaric acid, 20% solution in water	50	50	4
Sodium acetate	100	–	0.28
PVA: Mowiol 23–88	100	–	20
Demineralized water	100	–	380

Note: Dispersions with different GF51 content are marked as A, B, C, D, E.

Analysis Techniques

Monomer conversion during polymerization

In order to determine the monomer content during 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 effected. The samples were dried until constant weight. The conversion was determined gravimetrically.

Monomer monitoring by gas chromatography

In order to determine free monomer content during polymerization, dispersion samples were removed with different time intervals. Hydroquinone was used for polymerization reaction termination. Dispersion samples were loaded into toluene (50 wt%:50 wt%), mixed and stored for 24 h. Toluene/VAc extract was characterized by gas chromatography. A Perkin Elmer (USA) Clarus 500 with FID detector and XL GC auto sampler as well as a capillary column (i.d.: 0.32 mm × 60 m) coated with 5.00 µm film of polydimethylsiloxane were used for this purpose. Sample volume — 1 µL, carrier gas — helium. Following conditions were set: column temperature

was programmed from 40°C (hold 5 min) to 250°C (10.5 K/min).

Viscosity measurements

Viscosity measurements were performed with a Brookfield viscosimeter DV-I model (Brookfield, USA), RV disc type spindle number 3, and test temperature (25 ± 1)°C. The shear rate and shear stress values were calculated according to a methodology given by Mitschka^[7].

Molecular weight measurements

It was determined that prepared polymers from GF51 modified dispersions have low solubility in various solvents such as toluene, benzene, xylene, dimethylsulfoxide and etc. In order to determine molecular weight differences among prepared polymers, samples were hydrolyzed with sodium hydroxide to PVA at boiling temperature for 1–2 h until full dissolution. Then, the polymer solution was cooled down, polymer was precipitated from water with acetone. Sodium hydroxide was washed from dried polymer by dissolution in demineralized water and further polymer precipitation with acetone. The procedure was repeated 3 times. After sodium hydroxide was washed out, polymer was dried to a constant mass, weighted and used for viscosity investigations. The viscosity-average molecular weight of polymers was calculated from intrinsic viscosity data measured with a Ubbelohde viscometer (Schott Duran, model 501 11/Ia). Analysis was carried out at 25°C, demineralized water used as polymer solvent. Viscosimeter was calibrated against demineralized water, and the K and α values¹ were 20×10^{-5} dL/g and 0.76 respectively^[8].

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 weighted before extraction. Extraction proceeded for 24 h. Rotation evaporator was used for solvent removal. After evaporation the flask was dried at 70°C to a constant mass and weighted. 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 Persoz method (chosen angle as per Konig from 6° to 3°)^[9]. Dispersion was cast onto glass and dried to constant weight at room temperature. Determined variation coefficients for oscillation value were $1.1 \div 1.7$.

Contact angle measurements

The contact angle measurements were done by Woodward^[10] methodology. For contact angle measurements, dispersions were cast on a glass and dried at room temperature to a constant weight. Drops of (0.05 ± 0.01 cm³) water were putted on surface of polymer, pictures were shot by a digital camera and contact angle was determined with Geola Virtual Protractor (Lithuania) software. Results are presented as average of 10 drops measures. Determined variation coefficients for θ value were $3.4 \div 5.4$.

Water adsorption ratio of the films

Dispersion was cast onto a preweighed glass substrate and dried to a constant weight at room temperature. Then, it was put into demineralized water and taken out time to time for weighing. The water adsorption ratio was calculated by gravimetric method.

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 K min⁻¹, temperature ramp from -20°C to 220°C under nitrogen flow 50 mL/min.

¹ Both K and α are constants associated with Mark-Houwink-Sakurada equation, $[\eta] = KM_v^\alpha$, where $[\eta]$ is the intrinsic viscosity and M_v the viscosity-average molecular weight of the polymer.

RESULTS AND DISCUSSION

Emulsion Polymerization

Experimental results are presented in Fig. 1, where the temperature is plotted against reaction time at different GF51 quantities used for dispersion modification.

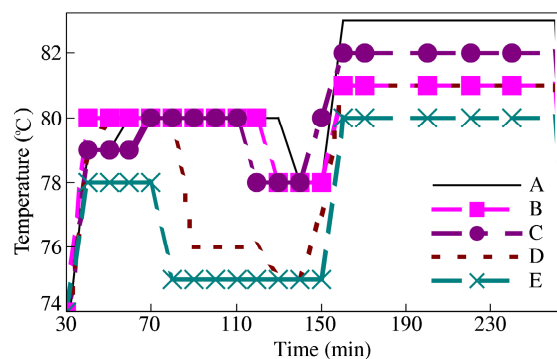


Fig. 1 Temperature variation during dispersions production

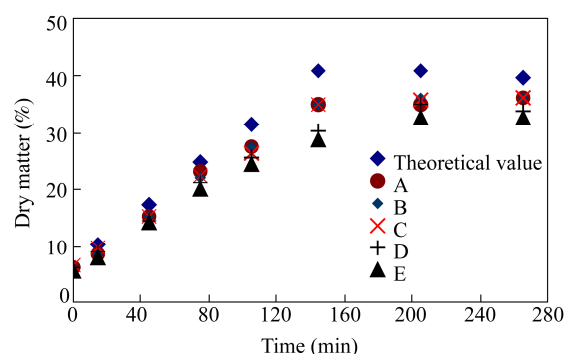


Fig. 2 Dry matter changes during vinyl acetate emulsion polymerization with different GF51 contents

According to Fig. 1, higher and earlier temperature drop during polymerization was determined with higher GF51 amounts. E dispersion with the highest amount of GF51 showed the earliest, longest temperature drop and monomer “over flooding” at the end of full component dosage. After that, dispersion E went into two separate phases. This gave uncontrollable polymerization reaction, consequently, high coagulum content in final dispersion was observed. Intensive coagulation of E dispersion particles forms solid and scraps on the reactor wall and agitator. This could become a serious problem in the plant production.

In order to determine free monomer conversion during polymerization, the dry matter measurements were done at selected time intervals. The following results are presented in Fig. 2.

According to Fig. 2, the higher amount of GF51 was used, the lower conversion of monomer was determined for each measured point. The theoretical value of dry matter for each point was calculated as per maximum monomer conversion. Therefore, all measured dry matter values are below the theoretical values.

The free monomer content in reaction media is a rather important parameter in order to maintain right monomer dosage rate and prevent monomer “over flooding” during continuous emulsion polymerization. The common and widely used method of free monomer content determination is the mass method (Fig. 2). However, it gives rather poor picture about monomer conversion processes, especially when more than one monomer is used in emulsion polymerization. Therefore, during emulsion polymerization of formulation D free monomer content was analysed by gas chromatography. The chromatogram of VAc/GF51 mixture in toluene is given in Fig. 3.

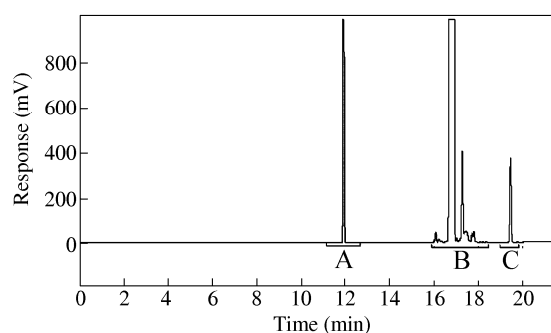


Fig. 3 Gas chromatogram of VAc/GF51 mixture in toluene: (A) VAc peak, (B) toluene peak and (C) GF51 peak

The components identification and verification according to gas chromatography method are presented in Fig. 3, where peaks of toluene (16–18 min), vinyl acetate (13.4 min) and GF51 (19.5 min) are obtained. Therefore, according to weight proportions of GF51 components (triethoxy vinylsilane (50 wt%–80 wt%), alkylalkoxy siloxane (10 wt%–30 wt%) and 1,1,3,3-tetraethoxy-1,3-dimethyl-disiloxane (1 wt%–5 wt%)) as well their boiling points (triethoxy vinylsilane (160°C), alkylalkoxy siloxane (not specified) and 1,1,3,3-tetraethoxy-1,3-dimethyl-disiloxane (227°C)) the peak at 19.5 min could be assigned to triethoxy vinylsilane (TEVS). Nevertheless, identification of each separate GF51 component by gas chromatography is not important for present investigations.

Calculations of monomer content were done as per monomer peak area. According to Fig. 4, following three periods were observed: (1) Stabilization (45–75 min); (2) Monomer content growing (75–150 min); (3) Monomer content decrease to final parameters during the so called dispersion “post cooking” (150–270 min). Obviously, that free monomer content detected by gas chromatography method reflected temperature variations during polymerization *i.e.* stable temperature period (45–75 min), temperature drop (75–150 min), and further temperature grow at “post cooking” procedure (150–270 min). It should be stated that monomer content for first VAc value (taken before continuous monomer mixture loading) is determined by rapid and highly exothermic polymerization reaction of initial VAc amount. Further VAc content grow up to stable values (45 min) could be determined by continuous VAc dosage from 15 min. During polymerization no TEVS monomer was determined by gas chromatography method. This could be due to a fast incorporation of TEVS into a polymer chain and/or rather small amount of TEVS used for dispersion modification.

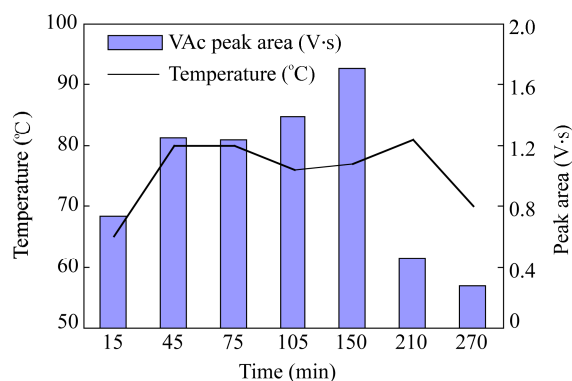


Fig. 4 Peak area and temperature changes versus time during emulsion polymerization of preparation D

GF51 modified system seems to have complex impact to emulsion polymerization reaction. Main GF51 component triethoxy vinylsilane (TEVS), according to a literature, is decreasing rate of radical polymerization^[11]. Naghash *et al.* explained it by higher stability of TEVS radicals in comparison to VAc radicals, which exist in the TEVS modified emulsion polymers. Due to a hydrolization of organosilanes in slightly acidic media and further formation of silanols^[12], different reactions, such as oligomerization, copolymerization and formation of cross-linked/dimensional structures, can proceed. Lower monomer conversion with higher GF51 content could be explained also by complicated macroradical's diffusion through high viscosity reaction media.

The influence of GF51 content on the final dispersion viscosity is presented in Fig. 5.

According to Fig. 5, dispersions with higher GF51 content have higher final viscosity. The E dispersion coagulated at the end of emulsion polymerization, so is not presented in viscosity and some further analysis. The influence of silane (TEVS) content to polyvinylacetate dispersion viscosity was investigated by Liu *et al.*^[13]. The higher TEVS content in dispersion determined higher dispersion viscosity, lower stability and larger particle size. Similar results were obtained with polyacrylate dispersions modified with TEVS^[14]. In our case GF51 modified dispersions properties agreed with Liu *et al.* results except latex storage stability (Table 2). The storage stability of prepared latexes was evaluated as per viscosity change during storage time.

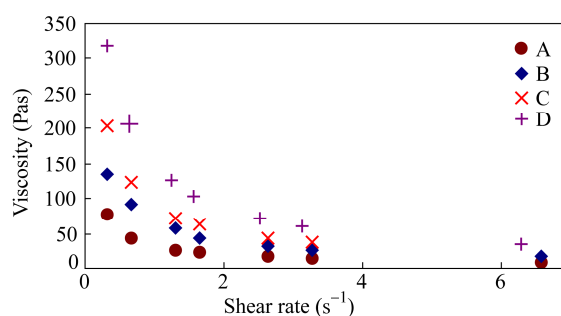


Fig. 5 Final viscosity of produced dispersions

Table 2. Storage stability of GF51 modified dispersions

Time (months)	Viscosity (Pas)				Initial viscosity increase (%)			
	A	B	C	D	A	B	C	D
0	14	27	38	59				
2	15	30	38	61	9	14	0	4
3	16	33	38	62	19	24	0	5

Shear rate for samples A, B, C at 3.290 s^{-1} ; D at 3.145 s^{-1}

According to Table 2, the best storage stability and unchanged viscosity during three-month storage time were observed for the C dispersion. On the contrary to Liu *et al.* results, better storage stability of dispersions with higher GF51 amounts was observed. This could be explained by different dispersion production technology (temperature, stirring rate, component dosage time, initiator system) and recipe, which have an impact to reaction kinetics as well dispersion final parameters^[15–17].

The dry matter of final dispersion is presented in Fig. 6.

According to Fig. 6, D and E dispersions could not fulfill the end users demand due to a low dry matter and high free monomer content.

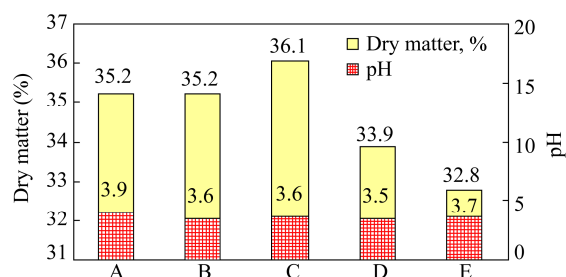


Fig. 6 Dry matter and pH values of final dispersions

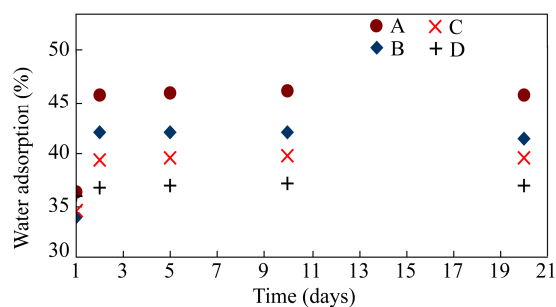


Fig. 7 Water adsorption of GF51 modified polyvinylacetate polymers

Properties of Polymer Films

Polyvinylacetate homopolymer is a well known polymer with certain properties that are widely published in polymer handbooks and different scientific papers. However, analysis and characterization of industrial polyvinylacetate homo and copolymer are a big issue for researchers due to the poor solubility of polymers. In order to prove polyvinylacetate copolymerization with various co-agents, different analysis techniques were published in literature, such as solubility of polymer in various solvents, graft polymer content determination by extraction^[18, 19], water resistance by polymer immersion in water^[20], mechanical properties (film hardness, tensile strength) and *etc.*

Poor solubility of silane modified polymer was indicated by Naghash *et al.*^[11] and Liu *et al.*^[13]. Both of them reported low solubility of TEVS modified polymer in various solvents such as toluene, benzene, xylene,

dimethylsulfoxide, THF and *etc.* Poor solubility of polymer was presented as an evidence of copolymer formation.

The water resistance of GF51 modified polyvinylacetate films is presented in Fig. 7.

According to Fig. 7, water adsorption of polymer films decreases with amounts of GF51. The unmodified polymer A adsorbed the highest amount of water under the same conditions. It could be stated that all films reaches their water adsorbance maximum during first two days, and then did not apparently change. After 20 days of immersion, decrease of polymers weight was determined. This could be explained by low molecular weight polymer as well as ungrafted PVA solubilization and diffusion into water media.

Despite the fact that GF51 modified polymer films showed higher water resistance, the tensile strength of wood joints glued with GF51 modified dispersions didn't show any improvement in glue joint water resistance. Tests with beech timber were carried out according to the second (resistant to moisture) series of EN 204 standard^[21]. Neither unmodified nor GF51 modified polymers glue joints were able to reach applicable bond strength of 8 N/mm². Samples collapsed during soaking. The wood gluing results could be explained by usage of low dry matter dispersions. In comparison dry matter of prepared dispersions was *ca.* 30 wt%–35 wt%, industry grades usually *ca.* 50 wt%–55 wt%. During gluing process water from dispersions should be absorbed by wood and further evaporated during storing. Higher water content in wood determines longer gluing time and higher wood deformations during drying. In order to have good mechanical interlocking between surfaces, dispersion particles should penetrate beyond the wood surface debris and damaged fibres into sound wood two to six cell deep^[22]. Dispersions with low dry matter cannot properly fill roughness of wood surface, thus formed gas pockets cause lower mechanical interlocking.

Different water repellence of polymer films was determined, and the result is presented in Table 3. Variation coefficient of contact angle results showed good repeatability and were below 5.5. Contact angle of GF51 modified films is higher in comparison to unmodified. These results agreed with polymer weight loss after extraction with toluene *i.e.* weight lost decreased with increasing GF51 amounts in polymer. Results could be explained by formation of cross-link polymer structures with siloxane bridges.

Silane moiety incorporation to polyvinylacetate chain should determine higher molecular weight polymers. Accordingly, the molecular weight of polymers A, B, C, D and E was determined. Due to low solubility of polymers A, B, C, D and E, the samples were hydrolyzed to PVA by sodium hydroxide until full dissolution. Viscosity-average molecular weight M_v (as per PVA) of prepared samples is presented in Table 3.

Table 3. Contact angle θ , weight loss, oscillation rate of initial polymers and intrinsic viscosity $[\eta]$, viscosity-average molecular weight M_v of hydrolysed polymers

Sample	θ	Weight loss (wt%)	Number of oscillations	$[\eta]$ (dL/g)	$M_v \times 10^{-4}$
A	35.90	78.6	119	0.17	2.2
B	45.52	38.3	116	0.24	3.4
C	60.11	13.8	111	0.30	4.6
D	63.36	7.9	73	0.31	4.8
E	–	3.4	–	0.32	5.0

According to results in Table 3, polymer molecular weight increases with increasing the amounts of GF51. This could be explained by TEVS moiety incorporation in polyvinylacetate polymer chain as well as formation of siloxane bridges between GF51 modified polymers chains.

The thermal properties of polymers are important for end user. Respectively, water based dispersions that are mainly used for glue and paint productions have certain polymer hardness and melting temperature values. GF51 modified polymers were evaluated by means of DSC. Following results are presented in Fig. 8.

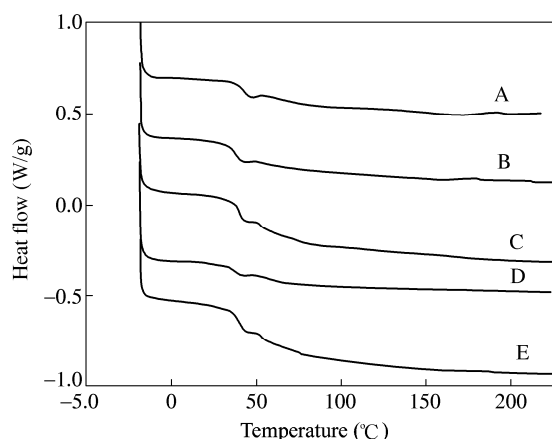


Fig. 8 DSC traces of unmodified and GF51 modified polymers
Data are reported for the second heating of the samples.

According to Fig. 8, the T_g range of samples was at 42–44°C. Polymer hardness, which is partially related to T_g value, was tested as well (Table 3). It was determined that increasing the amount of GF51 decreased polymer hardness. Similar results were published by Naghash *et al.*^[11]. TEVS moiety incorporation to vinyl acetate-acrylic polymer chain causes better thermal stability and lower T_g values. Nevertheless, in our case T_g values had small differences, so it is concluded that the used GF51 amounts have no significant impact to T_g values of B, C, D and E polymers.

CONCLUSIONS

Final properties of GF51 modified dispersions prepared by semi-continuous vinyl acetate radical emulsion polymerization in water highly depend on GF51 amount. Higher amounts of GF51 resulted in decreased polymerization rate, lower dry matter and higher viscosity of final dispersion. E dispersion with the highest amount of GF51 has the highest coagulum content and forms solid and scraps on the reactor wall and agitator. B and C dispersions have properties acceptable for end users.

Free monomer content was analysed by gas chromatography. The presented analysis technique is rather complicated to use, due to a sampling and an extraction of free monomer from dispersion. Nevertheless, upon our knowledge, a method was developed and used for this purposed first time and was not reported elsewhere.

Industrial polyvinylacetate dispersions are multi compound systems where components during radical emulsion polymerization are involved into path reactions (oligomerization, grafting and *etc.*). Poor solubility of GF51 modified polyvinylacetate polymer in various solvents was determined. Extraction with toluene showed higher cross-link structures in GF51 modified polymers. The water adsorption decreased with increasing the amounts of GF51. Modified polymers have better affinity to glass. Viscosity-average molecular weight M_v (as per PVA) of prepared samples increases with increase of the amounts of GF51. Presented differences between modified and unmodified polymer properties could be explained by TEVS moiety incorporation in polyvinylacetate polymer chain as well as formation of siloxane bridges between GF51 modified polymers chains. However, GF51 amounts used for polyvinylacetate modification have no significant impact to polymer T_g values.

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