Production and Characterization of 3-Methacryloxypropyltrimethoxysilane Modified Polyvinyl Acetate Dispersion

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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.¹ 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.^{2–6} 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.^{7–8} The hydrolization 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 successful 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.⁸ 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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Dispersion Disperzija	Compound Spoj	m/g	m(VAc) : r	m(GF31)
	vinyl acetate vinil-acetat	45.41		
oil phase		0	100:0	(F)
uljna faza	Geniosil GF31	0.454	100:1	(G)
		0.681	100:1.5	(H)
	ammonium persulphate amonijev persulfat	0.22		
water phase	water phase sodium tetraborate			
VOUEIId IdZd	Disponil SUS 87 SPCL	3.68		
	demineralized water demineralizirana voda	80		

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

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 threeneck 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 pripravu disperzije stabilizirane surfaktanatom. 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:

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

where τ is shear stress, $\dot{\gamma}$ is shear rate, η is viscosity, and τ_0 is yield stress or zero shear viscosity, which indicate the force required to start or stop the flow.

$$\tau = k \dot{\gamma}^n, \tag{2}$$

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 μ m – 500 μ m.

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 Konig from 6° to 3°).⁹ 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.¹⁰ For contact angle measurements, the dispersion was cast on a glass and dried at room temperature to a constant weight. Drops of (0.05 ± 0.01) cm³ 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⁻¹, temperature ramp from -20 °C to 220 °C under nitrogen flow 50 ml min⁻¹.

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.^{2,3,7,8,11–13} The higher stability and reactivity of silane radical are the main explanations given by authors. However, hydrolization 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 mater 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. Hydrolization 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 disperzijama PVAc

	PVAc dispersion Disperzija PVAc								
Parameter Parametar		P\ Stabili	Surfactant stabilized Stabilizirano surfaktantom						
	A	В	С	D	E	F	G	Н	
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 s⁻¹, and D at 2.2 s⁻¹



	31)	Viscosity/Pa s Viskoznost/Pa s				0 ⁻³ N cm ⁻² a/10 ⁻³ N cm ⁻²	Flow index Indeks tečenja			
Dispersion Disperzija	<i>m</i> (VAc) : m(GF31)	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/%
А	100:0	4.3	6.3	47	0.99	1.28	29	0.55	0.58	5
В	100:0.5	3.3	3.7	13	0.55	0.42	-24	0.43	0.46	7
С	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 hydrolization reaction could be expected.

Properties of polymer films

Generally, alkoxy groups of alkoxysilane 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,^{14,15} water resistance by polymer immersion in water,¹⁶ 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 – Svoistva čestica disperzije modificirane silanom GF31

	PVAc dispersion Disperzija PVAc							
Parameter Parametar		PVA sta Stabiliziran	Surfactant stabilized Stabilizirano surfaktantom					
	A	В	С	D	F	G		
<i>m</i> (VAc) : <i>m</i> (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/m² g ⁻¹ specifična površina/m² 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

	F31)	%/	T _g /	′°C	lations ija	e∕° t/°	on/% le/%	th of ↓ mm ⁻² jenog ∕ N mm ⁻²	f glued enog 'kN m ⁻¹
Sample Uzorak	m(VAc) : m(GF31)	Mass loss/% Gubitak mase/%	Initial Početni	After extraction Nakon ekstrakcije	Number of oscillations Broj oscilacija	Contact angle. Kontaktni kut,	Water adsorption /% Aposrpcija vode /%	Bond strength of glued wood/Nmm ⁻² Čvrstoća lijepljenog spoja s drvetom/Nmm	Bond strength of glued textile /kN m ⁻¹ Čvrstoća lijepljenog spoja s tekstilom /kN m ⁻¹
А	100:0	78.6	44	_	119	35	45	8.3	0.4
В	100 : 0.5	11.5	44	46	108	38	32	6.3	0.25
С	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 $T_{\rm g}$ 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_{σ} 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 dispersion (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.¹⁷ Only unmodified dispersion glue joints were able to reach applicable bond strength of 8 N mm⁻². Other samples collapsed during soaking. The wood gluing results could be explained by usage of low dry matter content dispersions.¹⁸ 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 unplastified 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

 differential scanning calorimetry diferencijalna pretražna kalorimetrija 3-methacryloxypropyltrimethoxysilane 3-metakriloksipropiltrimetokssiilan consistency index indeks konzistencije mass, g
– 3-metakriloksipropiltrimetokssiilan – consistency index – indeks konzistencije
– indeks konzistencije
– mass, g
– masa, g
– flow index – indeks tečenja
– polyvinyl alcohol – polivinil-alkohol
– polyvinyl acetate – polivinil-acetat
– glass transition temperature, °C – staklište, °C
– vinyl acetate – vinil-acetat
– shear rate, s ^{–1} – smična brzina, s ^{–1}
– viscosity, mPa s – viskoznost, mPa s
– contact angle, ° – kontaktni kut, °
– shear stress, N cm ⁻² – posmično naprezanje, N cm ⁻²
– yield stress, N cm ⁻² – granica razvlačenja, N cm ⁻²

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SAŽETAK

Priprava i karakterizacija disperzije polivinil-acetata modificiranog 3-metakriloksipropiltrimetoksisilanom

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U vodi je polukontinuirano emulzijski polimeriziran vinil-acetat (VAc) s komonomerom 3-metakriloksipropiltrimetoksisilanom (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-metakriloksipropiltrimetoksisilan, reološka svojstva, veličina čestica

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