ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 19, No. 1. 2013

Impact of Industrial Grade Modified PVA to Vinyl Acetate Semi-continuous Emulsion Polymerization and Properties of Final Product

Mindaugas DUBININKAS [1] *, Gintaras BUIKA [1], Darius MINELGA [2]

[1] *Department of Organic Technology, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania*
[2] *Department of Wood Technology, Kaunas University of Technology, Studentų St. 56, LT-514241 Kaunas, Lithuania*

crossref http://dx.doi.org/10.5755/j01.ms.19.1.3823

Received 14 September 2011; accepted 15 February 2012

Successful vinyl acetate radical emulsion polymerization in water with different type of industrial grade poly(vinyl alcohol) were produced by semi continuous way. The poly(vinyl alcohol) type has crucial impact on dispersion rheological as well on films and bonding strength properties. It should be stated that the films containing modified poly (vinyl alcohol) has better water resistance and mechanical properties. Poly(vinyl alcohol) with higher ethylene moieties content and high hydrolization degree determines extremely low viscosity of final dispersion.

Keywords: poly(vinyl acetate) dispersion, poly(vinyl alcohol), semi-continuous polymerization, rheological behavior, wood bonding.

1. INTRODUCTION

Poly(vinyl acetate) (PVAc) dispersions are known as glue with poor mechanical and water resistance properties. Additional modifications are needed in order to produce water resistance glue described in EN204 standard [1]. The common way to increase water resistance of PVAc films is to modify dispersion with aluminum chloride, oxalic acid and etc. [2]. Nevertheless, modification process takes additional time and human recourse. Moreover, pH of acid modified glue is lower than normal and this cause faster hydrolyzation of polymer and poor storage stability, short “pot life” of the product.

In order to decrease PVAc dispersion production time, increase savings on raw materials and reach higher water resistance of PVAc films, we choose different type of protective colloid-modified and unmodified industrial grade poly(vinyl alcohol) (PVA) for radical semi-continuous VAc emulsion polymerization in water. The glue production and properties of final products are presented in this study accordingly.

2. EXPERIMENTAL

2.1. Materials

In order to simulate industrial production, commercial grade raw materials without further purification were used for dispersion production i.e. vinyl acetate (VAc) (Nevinnomyssky Azot, Russia), tartaric acid (Penta), sodium acetate (Fluka), sodium hydroxide (Fluka), plasticizer (Benzoflex 2088, Eastman), demineralized water. Five different industrial PVA grades (Kuraray, Germany/Japan) were chosen for PVAc dispersion production

2.2. Polymerization procedure

Semi-continuous radical VAc emulsion polymerization was carried out using 1L five-neck round-bottom flask equipped with reflux condenser, plastic stirrer, two separate feed streams, on-line thermometer. Successful semi-continuous VA emulsion polymerization was done with radical initiation system hydrogen peroxide-tartaric acid. At the beginning water solution of PVA, sodium acetate, and tartaric acid (TA) was loaded into the reactor. Stirring rate 170 rpm, temperature was maintained at 60 °C. Immediately after temperature was reached, under nitrogen atmosphere, 10 wt.% of VAc and 50 wt.% of hydrogen peroxide (HPO) of total amount was loaded. After induction period (approx. 5 min. – 10 min.) the temperature increased up to 75 °C – 80 °C and was kept until all HPO and VAc were loaded continuously. Continuous monomer loading and first load of TA was done ~15 min. after beginning of polymerization. Formulations of prepared dispersions are given in Table 2. After VAc and HPO were loaded, second load of TA was done. Then reaction temperature was increased up to 80 °C – 85 °C, for final monomer conversion. After dispersion production 15 wt.% sodium hydroxide solution in water was used for pH corrections up to 5. Before mechanical analysis of polymer film all dispersions were plasticized with plasticizer amount of 10 wt.% from dry matter of dispersion.

Table 1. Characteristics of used PVA

Commercial name of PVA	Viscosity, mPa·s	Degree of hydrolysis, mol%	Degree of polymerization/ molar mass (g/mol)
Mowiol®20-98	18.5–21.5	98.0–98.8	2800/125000
RS 1717[1]	23.0–30.0	92.0–94.0	1700/80000
RS 2117[1]	23.0–30.0	97.5–99.0	1700/75000
HR 3010[1]	11.0–15.0	99.0–99.6	1000/45000
R 1130[2]	20.0–30.0	98.0–99.0	1700/80000

[1] PVA containing ethylene moieties. Degree of ethylene moieties in PVA increases as follows: RS 1717 → RS 2117 → HR 3010.
[2] PVA containing silane moieties (grade of low modification degree).

---

*Corresponding author: ph.: +370-605-53711; fax: +370-349-56980.
E-mail: *dubininkas@achema.com* (M. Dubininkas)

Table 2. Formulations and components loading proportions for dispersion production

Compound	Initial charge, wt. %	Feed, wt. %	Total, g
Vinyl acetate	10	90	380
Hydrogen peroxide 1% solution in water	50	50	43.8
Tartaric acid, 20% solution in water	72	$15^{\text{1st. load}}$ $13^{\text{2nd load}}$	4.53
Sodium acetate	100	–	0.285
PVA: A. Mowiol 20-98 B. RS1717 C. RS2117 D. HR3010 E. R1130	100	–	28.5
Demineralized water	100	–	365

Note: dispersions with different PVA type are marked as A, B, C, D, E.

2.3. Analysis techniques

2.3.1. Viscosity measurements

Viscosity measurements were performed by Brookfield Digital Viscometer LVDV-II+ Pro (Brookfield, USA) with a small sample adapter, spindle number SC4-25, software – Wingather V2.2, test temperature was 20 °C ±0.5 °C.

2.3.2. Film hardness

The film hardness was examined using a pendulum hardness tester Pendulum Hardness Rocker Ref.707P (Sheen Instruments Ltd, England) by Persoz method [3]. Dispersion was casted onto the glass and dried to constant weight at room temperature.

2.3.3. Mechanical properties of polymer film

Sample films were made by casting glue on a flexible plastic sheet of polyester. The film thickness obtained after drying for 7 days at room temperature. Test specimens were prepared by cutting strips (50 mm × 5 mm). Specimens were tested by Zwick/Roell BDO-FB 0,5TH (Germany) machine. The speed of crosshead was maintained at 100 mm/min. Specimens were tested for tensile strength ($F_{\max}$), elongation (ε_R) and tensile stress (σ_B).

2.3.4. Contact angle measurements

The contact angle measurements were done by Woodward [4] methodology. For the contact angle measurements, dispersions were casted on glass and dried at room temperature to a constant weight. Pictures were shot by a digital camera and contact angle was determined with Geola Virtual Protractor (Lithuania) software.

2.3.5. Water resistance of the films/ /Water adsorption

Dispersion was casted onto a pre weighed glass substrate and dried to a constant weight at room temperature. Then, puted into demineralized water and taken time to time for weighing. The water adsorption ratio was calculated by a gravimetric method.

2.3.6. Particle size measurements

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

2.3.7. Bonding strength of wood joints

The glued wood pieces were prepared, conditioned, glued and the tensile shear strength of glued wood was carried out according to EN204 and EN205.

3. RESULTS AND DISCUSSION

3.1. Emulsion polymerization

Semi-continuous radical VAc emulsion polymerization was carried out using different type industrial grade PVA (Table 1) and according to formulations shown in Table 2.

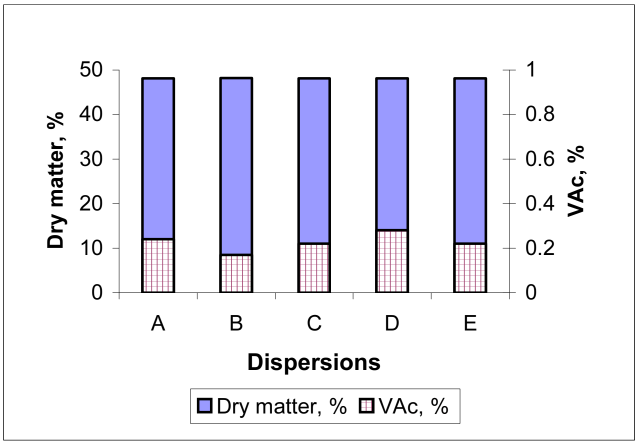

Fig. 1. Dry matter and free VAc values of final dispersions

According to Fig. 1 dispersions have almost the same total solid content and are acceptable for wood glue consumers. Nevertheless higher saponification of PVA determined slightly higher free VAc content. Gulbekian and Reynolds [5] examined the optimum properties of the PVA types (their degree of hydrolysis, the average molecular weight on the emulsion polymerization mechanism, and the stability of the final lattices) and stated that maximum conversion and minimum precipitate were obtained when 82.6 % – 91.5 % hydrolyzed PVA was used for PVAc dispersion production. Due to a block-distribution of residual acetyl groups, partially hydrolyzed ethylene modified PVA showed higher surface activity than used fully hydrolyzed unmodified and ethylene modified PVA. Respectively, lower monomer conversion i. e. higher free VAc content, were determined in dispersions produced with higher hydrolyzation degree PVA.

Hydrolyzation degree and molecular mass of PVA used for dispersion production have a major impact on particle size formation as well on viscosity properties of final product [6]. Viscosity data of produced dispersions are presented in Figs. 2 – 4.

Influence of different type PVA on dispersion rheological properties was published by Nakame et al. [7]. By them, hydrophobic hydration or interaction between hydrophobic groups of the ethylene in modified PVA (partially hydrolyzed grade) may contribute to the higher viscosity of the ethylene modified PVA. These interactions also stabilized emulsion as well particle diameter of ethylene modified PVA, which was slightly larger than for fully hydrolyzed unmodified PVA. According to Fig. 2 results, viscosity of different dispersions agreed with Nakame results i. e. fully hydrolyzed PVA grades determined lower viscosity of dispersion. Respectively, higher hydrolyzation degree of ethylene modified PVA dispersions determined lower viscosity of B, C, D dispersions. Dispersion E produced with silane modified PVA showed results rather similar to partially hydrolyzed PVA. Viscosity differences among B, C and D could be explained also by different molar masses of PVA. Higher molar mass of PVA determined higher viscosity values. Respectively, B and E dispersion had rather similar viscosities due to a similar molar mass of PVA.

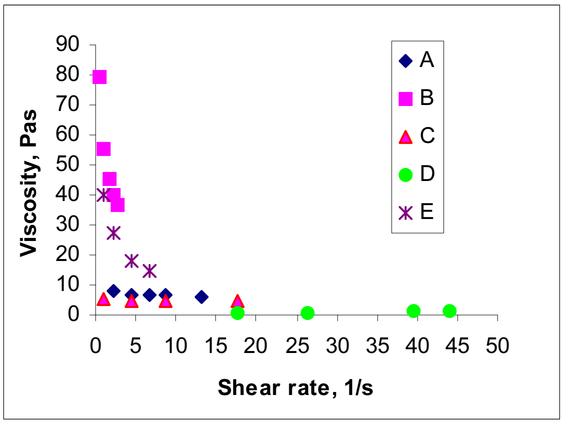

Fig. 2. Viscosity of produced dispersions

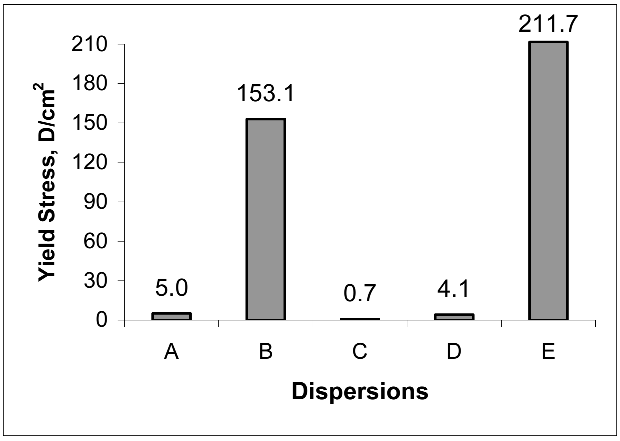

Fig. 3. Yield stress of dispersions

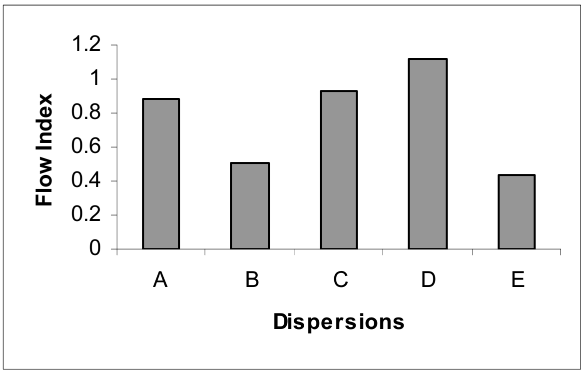

Fig. 4. Flow index of dispersions

Yield stress or zero shear viscosity, indicates the force required to start/stop flowing (molding, enrobing). This value is important for dispersion processing at production scale. According to Fig. 3 results, B and E dispersions have a highest yield stress value. This could be explained by higher interactions of PVA hydrophobic acetyl groups for B dispersion and silanol groups for E dispersion. High viscosity and yield stress values could cause serious problem during dispersion production as well transportation trough pipelines. Nevertheless, dispersions with high viscosity could find its applications in further modification in order to produce various products such as fertilizer anti caking agents or mastic.

The flow index (power law index) indicates dispersion dilatant or pseudoplastic behavior. Dilatant fluid values are above 1, pseudoplastic – below 1. According to Nakame et al. [7] dispersions produced with high hydrolyzation degree PVA are rather dilatant than pseudoplastic. Fig. 4 shows that dispersion D produced with highest hydrolyzation degree of ethylene modified PVA (so called "Super Hydrolyzed") was dilatant. Moreover, viscosity of D dispersion is much lower than normal and this could be a problem to use it in paints and wood adhesive production.

3.2. Morphology of dispersion particles

The particle size measurements are presented in Table 3.

Table 3 results shows that particle size of dispersion is highly dependent on hydrolization degree as well to chemical structure of PVA. Higher ethylene moieties content in PVA as well higher hydrolization degree determined higher particle size and lower polydispersity ($\overline{D}_w / \overline{D}_n$). Nakame et al. [7] explained it by higher surface activity of hydrophobic ethylene group in PVA, which forms larger and more even particles in dispersion.

Table 3. Morphology of particles prepared in presence of different type PVA

PVA type	Degree of hydrolysis, mol%	$\overline{D}_w$, μm	$\overline{D}_n$, μm	$\overline{D}_w / \overline{D}_n$
A	98.0–98.8	0.93	0.59	1.59
B	92.0–94.0	0.39	0.10	3.77
C	97.5–99.0	0.43	0.15	2.99
D	99.0–99.6	0.94	0.91	1.08
E	98.0–99.0	2.60	0.81	3.19

Wood glue produced from high particle size and low polydispersity dispersions have poor mechanical parameters. During wood gluing process large and even particles cannot properly fill roughness of wood surface, thus formed gas pockets cause lower mechanical interlocking.

3.3. Polymer film properties

In order to check different grades PVA impact on properties of the final polymer, different measuring techniques were applie. It should be noticed that industrial PVAc dispersions are multi compound systems where components during radical emulsion polymerization are involved into path reactions (oligomerization, grafting and etc.). Those produced with PVA as protective colloid have three different PVA fractions in dispersion: (1) free PVA in the water phase; (2) PVA physically adsorbed onto the polymer particles; (3) PVA chemically grafted into PVAc chain. Carra et al. [8] determined PVA fraction variation in dispersion composition. By him, grafted PVA fraction are relatively constant, however physically adsorbed fraction increased quite markedly with PVA blockiness. Variation of those three PVA fractions in final dispersion had crucial impact on dispersion rheological behavior as well on polymer physicochemical properties. The impact of PVA on final polymer properties was analyzed by various methods published in literature [9 – 11]. Water adsorption of produced polymers is presented in Fig. 5.

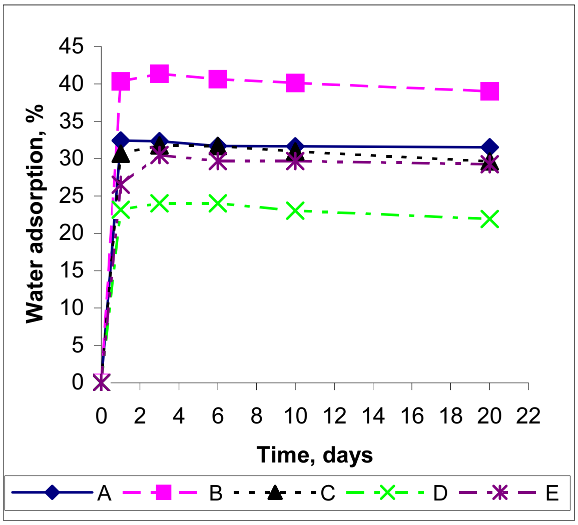

Fig. 5. Water adsorption of produced polymers

According to Fig. 5 highest water adsorption had sample B produced with partially hydrolyzed PVA. Respectively, polymer D with highest hydrolyzation degree PVA adsorbed lowest amount of water under the same conditions. Polymers A, C and D, which contain similar hydrolyzation degree PVA, had more or less the same water adsorption. Our findings agree with earlier published results where the increase in the degree of PVA hydrolysis increases water and solvent resistance, crystallinity, tensile, and adhesive strength [12]. It could be stated that all films reach their water adsorbance maximum during the first three days, and then did not apparently change. Further film immersion up to 20 days determined weight loss of polymers. This could be explained by low molecular weight polymer as well physically adsorbed PVA solubilization and diffusion into a water media.

Table 4. Contact angle θ, oscillation rate data of produced polymers

Sample	θ	Number of oscillations
A	55	345
B	57	353
C	56	345
D	47	341
E	67	348

Contact angle analysis is widely used for dispersion wetting ability and polymer water repellency determination, whereas oscillation rate results show hardness of polymer film. According to the results presented in Table 4 lowest contact angle had D polymer, respectively E polymer had highest contact angle. All other A, B, C polymers had more or less the same contact angle.

Polymer film B and E showed highest hardness, whereas ethylene modified PVA hardness decreased with higher PVA hydrolyzation degree. Nevertheless, hardness results were almost at the same level and didn't show significant variation. Hence, physicomechanical properties were further evaluated by testing polymers on tensile strength ($F_{\max}$), elongation (ε_R) and tensile stress (σ_B). The results are presented in Table 5.

Table 5. Mechanical properties of plasticized dispersion films

Sample	$F_{\max}$, kN/m	σ_B, MPa	ε_R, %
A	1.8	18.0	212
B	1.5	13.0	257
C	1.8	17.7	244
D	2.2	15.8	223
E	1.8	12.3	177

According to Table 5 results, tensile strength of polymers containing fully hydrolyzed PVA (A, C, D, E) was higher in comparison to sample with partially hydrolyzed PVA (B). Highest tensile strength value showed polymer D with "super hydrolyzed" PVA. It should be noticed that no significant changes in tensile strength of fully hydrolyzed ethylene and silane modified PVA containing polymer (C, E) and unmodified PVA containing polymer (A) were determined. Elongation of B, C, and D polymers decreased with higher hydrolization degree of PVA. Nevertheless, elongation results were higher in comparison to A and E polymers.

3.4. Bonding strength of latex

In order to find out possibilities to use prepared dispersions for wood industry, all dispersions were plastified and tested according to EN204 and EN205 standards. Water resistance of glue was tested according to sequences No. 2 and No. 3.

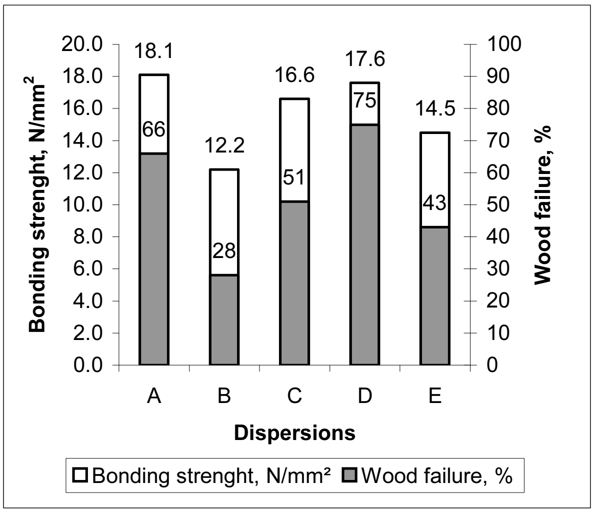

Fig. 6. Dependence of bonding strength and wood failure of samples according to sequence No. 2

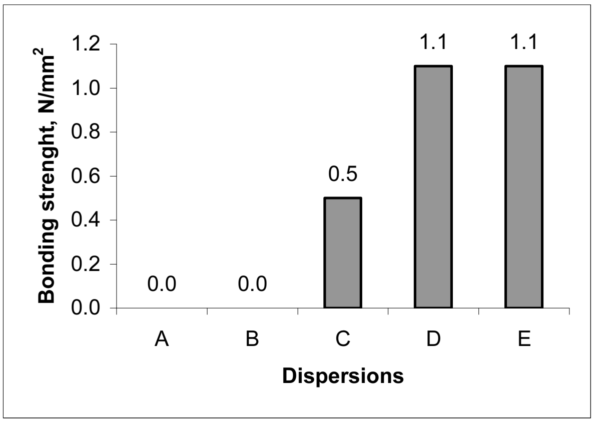

Fig. 7. Dependence of bonding strength of samples according to sequence No. 3

According to Fig. 6 and Fig. 7 results, water resistance of glue bond increased with higher content of ethylene moieties in PVA. It should be stated that hydrolysis degree of PVA had crucial impact as well. Samples with fully and super hydrolyzed PVA had highest water resistance. All samples didn't pass sequence No. 3 requirements i. e. bonding strength below 2 N/mm^2 and zero wood failure was observed. In order to reach D3 glue requirements prepared dispersions should be additionally modified.

4. CONCLUSIONS

Stable dispersions with various type and hydrolization degree PVA were produced via semi-continuous radical emulsion VAc polymerization. Influence of PVA on final dispersion characteristics was investigated accordingly. It was stated that ethylene modified PVA hydrolization degree has similar influence on dispersion viscosity properties as unmodified PVA i. e. higher hydrolization degree of PVA determine lower viscosity and close to dilatant behavior of final dispersion. Usage of "super hydrolyzed" ethylene modified PVA determine extremely low dispersion viscosity and dilatant behavior. Dispersion produced with fully hydrolyzed silane modified PVA had rheological properties rather similar to partially hydrolyzed PVA. Particle size of dispersions was highly dependent on PVA hydrolization degree as well to its chemical structure and molecular weight. The ethylene moieties in PVA determined formation of larger and more even particles.

Physicochemical properties of the plasticized films produced with different type of PVA were rather similar. It should be stated that tensile strength of the films increased with higher hydrolyzation degree PVA. Results of water repellence and bond resistance to water correlate to each other. Films with the high hydrolyzation degree as well high ethylene moieties content PVA showed higher water resistance. Nevertheless, all samples didn't pass sequence No. 3 requirements.

The issue reaching D3 requirements could be solved by PVA content variation during dispersion production. Lower content of water soluble compound i. e. PVA in dispersion formulations should determine higher water resistance of polymer film. Nonetheless, lower PVA amount in dispersion production could determine formation of high quantity of residue polymer and less stable dispersion. The gap between PVA quantity used in dispersion production and acceptable final product properties will be defined separately.

REFERENCES

1. **EN 204:2005**. Classification of Thermoplastic Wood Adhesives for Non-structural Applications.
2. **Santoemma, J.** US Patent. 5091458, 1990.
3. Sheen Pendulum Hardness Rocker Datasheet http://www.sheeninstruments.com/ datasheets/pen2.pdf
4. **Woodward, P. R.** Contact Angle Measurements Using the Drop Shape Method. http://www.firsttenangstroms.com/pdfdocs/CAPaper.pdf
5. **Gulbekian, E. V., Reynolds, G. E.** Polyvinyl Alcohol in Emulsion Polymerization. In: Polyvinyl Alcohol: Properties and Applications. Finch, C. A., Ed., John Wiley, London, 1973.
6. **Finch, C. A.** (Ed.). Polyvinyl Alcohol: Properties and Applications. John Wiley & Sons, London, 1973.
7. **Nakame, M., Ken, Y., Sato, T., Maruyama, H.** Preparation of Polymer Emulsion Using Poly(vinyl alcohol) as Protective Colloid *Colloids and Surfaces* A: *Physicochemical and Engineering Aspects* 153 1999: pp. 367 – 372. http://dx.doi.org/10.1016/S0927-7757(98)00458-0
8. **Carra, S., Sliepcevich, A., Canevarolo, A., Carra, S.** Grafting and Adsorption of Poly(vinyl) Alcohol in Vinyl Acetate Emulsion Polymerization *Polymer* 46 2005: pp. 1379 – 1384.
9. **Donescu, D., Gosa, K., Diaconescu, I., Mazare, M., Carp, N.** In: Emulsion Polymerization of Vinyl Acetate. El-Aasser, M. S. and Vanderhoff, J. W. (Eds.), Applied Science Publishers, London, 1981.
10. **Donescu, D., Gosa, K., Ciupitoiu, A., Languri, I.** Semicontinuous Emulsion Polymerisation of Vinyl Acetate. Part I. Homopolymerization with Poly(vinyl alcohol) and Nonionic Coemulsifier *Journal of Macromolecular Science, Chemistry* A 22 1985: pp. 931 – 940.
11. **Mingyue, Z., Weihong, Q., Hongzhu, L., Yingli, S.** Synthesis of Novel Polymerizable Surfactant and Its Application in the Emulsion Polymerization of Vinyl Acetate, Butyl Acrylate, Veova 10, and Hexafluorobutyl Methacrylate *Journal of Applied Polymer Science* 107 2008: pp. 624 – 628.
12. **Yildirim Erbil, H.** Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers, CRC Press LLC 4 2000: p. 25.