Modified Poly(Vinyl Alcohol) as a Dispersant in Suspension Polymerization of Vinyl Chloride
IV. Mixtures of Modified Poly(Vinyl Alcohol)

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The mixtures of poly(vinyl alcohol) (PVA) with thermo-oxidatively modified poly(vinyl alcohol) (B) or acetalized poly(vinyl alcohol) (D) were used as the dispersants in suspension vinyl chloride homopolymerizations in compositions at w_r(total, VC) = 0.1 mass %. Unmodified commercial PVA Alcotex 72.5 (A) produces porous poly(vinyl chloride) (PVC) grains with fast plasticizer absorption and low bulk density. Modified PVA B or D produce less porous PVC with substantially higher bulk densities. Defined mixtures of A with B or D can be used for the manufacturing of tailor-made PVC grades with required grain morphology, characterized by the grain size, porosity, and the bulk density.

Physical and chemical properties of PVC produced by suspension polymerization depend on the conditions of polymerization (temperature, mixing, amount of aqueous phase) and on the kind of polymerization aid used. There is considerable interest in the use of poly(vinyl alcohol) (PVA) instead of cellulose derivatives as an aid for suspension homopolymerization or copolymerization of vinyl chloride. We have studied [1, 2] the influence of the reaction conditions of the preparation of PVA, partially alcoholyzed PVAc resins and PVA thermally modified in inert or oxygen atmosphere on their ability to be good dispersants in the process of suspension VC polymerization. Our previous paper [3] presented the relations between conditions of PVA acetalization with aliphatic C_1—C_4 aldehydes and protective colloidal properties of such modified PVA or the grain morphology of produced PVC.

The PVA-based dispersants used in industrial suspension vinyl chloride homopolymerizations or copolymerizations are usually the combinations of minimum two different kinds of PVA. Thus [4], PVA with lower degree of polymerization 500—700 and degree of hydrolysis 70 mole % is combined with PVA with the degree of polymerization 2500 and the degree of hydrolysis 86—89 mole %. In many cases, one of the components is modified PVA. In this paper we present the use of the mixtures of PVA with thermo-oxidatively modified or acetalized PVA as the dispersant in suspension vinyl chloride polymerization.

EXPERIMENTAL

Vinyl chloride (Chemical Works Nováky), with impurities (w/ppm): acetylene 1, propylene 3, 1,3-butadiene 11, methyl chloride 49, ethyl chloride 7, 1,1-dichloroethane 3, 1,2-dichloroethane 4, monovinylacetylene 12, and water 193, was used.

Polymerization initiator EHP-80 (Chemical Works Nováky) consisted of 50 mass % of xylene, 35 mass % of bis(2-ethylhexyl)peroxydicarbonate, 14 mass % of benzoylperoxy-2-ethylhexyl carbonate, and 1 mass % of dibenzoyl peroxide. Aqueous PVA — Sloviol R (Chemical Works Nováky) was prepared by alkaline saponification of 16.1 mass % methanolic poly(vinyl acetate) (PVAc; degree of polymerization 1140, degree of hydrolysis 86.0 mole %, surface tension of 4 mass % aqueous solution 45.5 mN m⁻¹, dynamic viscosity 11.5 mPa s, acid number of dried sample a.n. (KOH) = 2.7 mg g⁻¹

Commercial PVA Alcotex 72.5 (Revertex, UK) has the degree of hydrolysis 71.0 mole %, polymerization degree 700, surface tension of 4 mass % aqueous solution 42.0 mN m⁻¹, dynamic viscosity 6.7 mPa s, and cloud point of 1 mass % aqueous solution 30.0 °C.

Thermo-oxidatively modified PVA (B) was made by thermo-oxidative treatment [1] of the above specified aqueous PVA Sloviol R in the presence of oxygen at 200 °C for 2 h. The degree of polymerization of such modified PVA is 931, degree of hydrolysis 92 mole %, surface tension of 4 mass % aqueous solution 52 mN m⁻¹, and dynamic viscosity 8.9 mPa s.

Acetalized PVA with 17.7 mole % degree of acetalization was prepared by the reaction of PVA Sloviol R with formaldehyde at 60 °C [3].

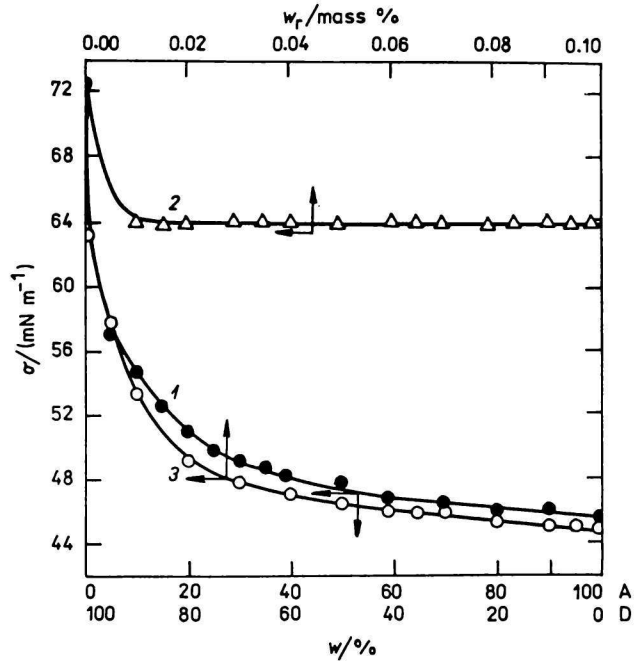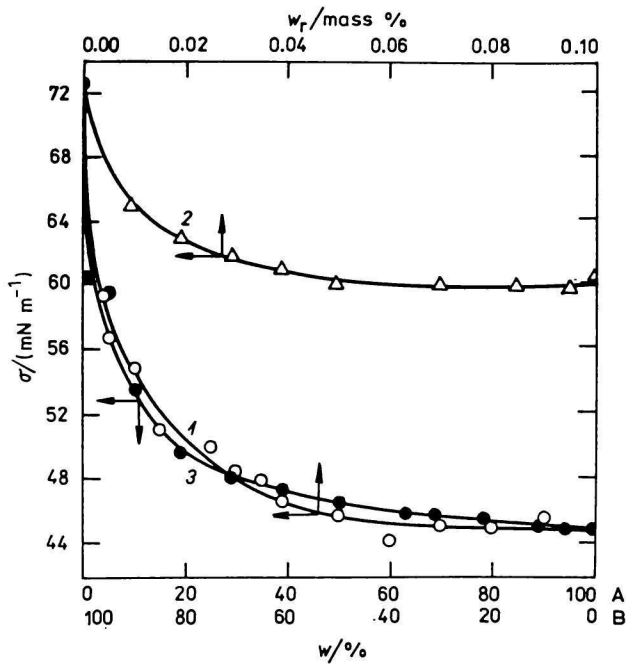* The author to whom the correspondence should be addressed.

Fig. 1. Surface tension of the aqueous solutions of dispersants (σ) *vs.* relative contents, relative to VC (w_r(dispersant, VC)) or *vs.* mass fractions (w(dispersant)) at w_r(total, VC) = 0.1 mass % when the mixtures were used. The curves belong to A + B (*1*), B (*2*) and A (*3*).

Fig. 2. Surface tension of the aqueous solutions of dispersants (σ) *vs.* relative contents, relative to VC (w_r(dispersant, VC)) or *vs.* mass fractions (w(dispersant)) at w_r(total, VC) = 0.1 mass % when the mixtures were used. The curves belong to A + D (*1*), D (*2*) and A (*3*).

All other chemicals were of anal. grade.

All procedures were described in our previous papers [1—3].

RESULTS AND DISCUSSION

One of the important parameters influencing the protective colloidal properties of PVA dispersant is the surface tension of their aqueous solutions. We measured this parameter for aqueous solutions of commercially produced PVA Alcotex 72.5 (A) and of different modified PVA. As a modified PVA we used thermally oxidized PVA Sloviol R (B) or Sloviol R acetalized with formaldehyde (D). Fig. 1 shows the influence of contents of A and B on the surface tension of the aqueous solution. Similar influence for the dispersants A and D is demonstrated in Fig. 2, when the mixture of dispersants was used. Figs. 1 and 2 show the surface tension *vs.* mass fractions of dispersants, while total content of the dispersants (related to vinyl chloride) is constant (w_r(total, VC) = 0.1 mass %). As we have observed (the curves *2* in Figs. 1 and 2) the increase of the surface-active properties is much more substantial in the case of PVA B compared to D.
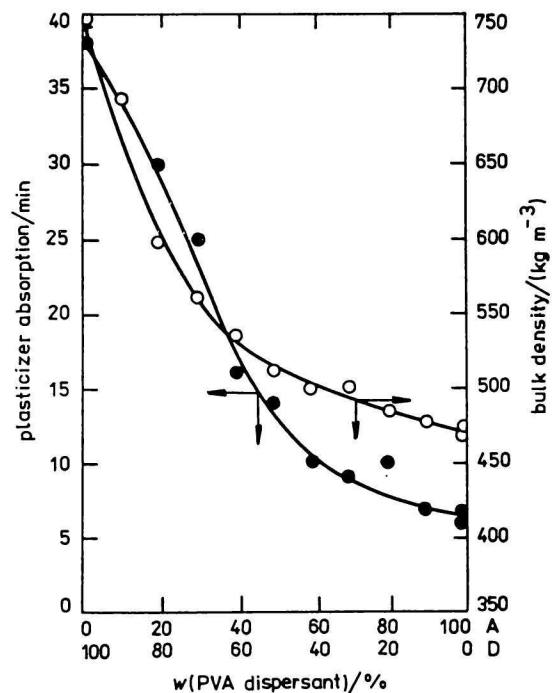

Fig. 3. Influence of the mass fractions of modified and unmodified PVA on the plasticizer absorption and the bulk density of produced PVC (w_r(total, VC) = 0.1 mass %).

Table 1. Influence of the Ratio of Thermo-Oxidatively Modified PVA (B) to Unmodified PVA Alcotex 72.5 (A) in a Mixture Used as a Dispersant in Suspension VC Polymerization on the Quality of PVC Product

Dispersant[a] mass %		Sieve analysis of PVC[b] (w/%) on mesh (ϕ/mm)							PVC bulk density	Plasticizer absorption
B	A	1.0	0.25	0.20	0.16	0.10	0.063	< 0.063	kg m^{-3}	min
0.00	0.10	0.7	0.2	2.4	26.8	60.8	8.4	1.4	474	6
0.01	0.09	0.6	0.2	10.8	33.6	50.4	2.4	0.8	495	10
0.02	0.08	0.3	1.2	18.8	40.0	19.6	3.2	17.2	488	8
0.03	0.07	0.4	1.2	22.8	41.6	26.8	1.6	6.0	492	9
0.04	0.06	0.5	16.0	37.6	28.8	15.2	1.6	0.8	509	11
0.05	0.05	0.6	43.2	28.0	19.6	8.4	0.4	0.4	513	12
0.06	0.04	N[c]	—	—	—	—	—	—	—	—
0.07	0.03	N[c]	—	—	—	—	—	—	—	—
0.08	0.02	N[c]	—	—	—	—	—	—	—	—
0.09	0.01	N[c]	—	—	—	—	—	—	—	—
0.10	0.00	0.3	3.6	9.2	16.1	33.0	27.6	13.6	560	30

a) With respect to vinyl chloride; b) Mass % of PVC which did not pass the mesh of stated size; c) Block PVC was formed and parameters were not measured.

Table 2. Influence of the Ratio of PVA Acetalized with Formaldehyde (D) to Unmodified PVA Alcotex 72.5 (A) in a Mixture Used as a Dispersant in Suspension VC Polymerization on the Quality of PVC Product

Dispersant[a] mass %		Sieve analysis of PVC[b] (w/%) on mesh (ϕ/mm)							PVC bulk density	Plasticizer absorption
D	A	1.0	0.25	0.20	0.16	0.10	0.063	< 0.063	kg m^{-3}	min
0.00	0.10	0.1	8.5	33.6	36.6	12.5	8.5	1.6	472	7
0.00	0.10	0.7	0.2	2.4	26.8	60.8	8.4	1.4	474	6
0.01	0.09	0.6	0.8	0.8	17.6	59.2	16.0	5.6	466	7
0.02	0.08	0.1	14.8	33.2	36.0	12.4	0.8	2.8	476	10
0.03	0.07	0.4	11.2	45.8	20.0	13.0	8.4	1.2	503	10
0.05	0.05	0.3	5.6	15.6	41.6	26.0	3.6	7.6	511	14
0.06	0.04	0.4	8.4	18.8	35.2	28.8	3.6	5.2	534	16
0.07	0.03	0.1	14.0	15.6	28.8	31.2	3.6	6.8	559	30
0.08	0.02	0.4	39.0	29.6	17.6	9.2	0.4	4.0	594	30
0.10	0.00	0.1	37.1	16.7	25.1	13.5	2.3	5.2	693	38

a) With respect to vinyl chloride; b) Mass % of PVC which did not pass the mesh of stated size.

The mixtures of A with B or D can decrease the surface tension in an extent similar to unmodified PVA Alcotex 72.5 (A) when used alone at the content related to VC, w_r(A, VC) = 0.01—0.10 mass %. But, as vinyl chloride suspension polymerization experiments using A, B, and D alone or their mixtures as a polymerization aid have shown, PVC products are with different grain morphology. Thus, in agreement with our previous results [2, 3] we can say that measuring of the surface tension cannot be used as a method for the characterization of protective colloidal properties of PVA only, and other parameters should be determined. Parameters, like the solubility, viscosity, and the cloud point are much more suitable [2, 3] for such characterization.

Solutions of the PVA resins prepared were tested as protective colloids in suspension polymerization of vinyl chloride in 50 dm³ autoclave. The size of the grain

is an important parameter of the suspension PVC product and depends on the protective colloidal quality of the PVA resin used. The samples of PVC resins produced were sieved on grading sieves and were divided into grades according to the mass fraction of particles which could not pass through a defined sieve. Large size PVC grains or blocks are formed when the colloidal protective activity of tested PVA is poor or nonexistent. Experimental results (Table 1) show that there are the differences in the morphology of PVC grains caused by different dispersant activity of A or B and of the mixtures of A with B. When unmodified PVA A is used alone as a polymerization aid, produced PVC grains are porous. This is supported by the plasticizer absorption parameter (6 min) and a low value of the bulk density (474 kg m⁻³). Thermo-oxidatively modified poly(vinyl alcohol) B used alone in suspension VC polymerization produced much less porous PVC grains

(plasticizer absorption 30 min) with substantially higher value of the bulk density (560 kg m^{-3}). When the mixtures of A and B in different ratios are used as the dispersants, the values of the parameters characterizing produced PVC grain morphology are additive from both qualitative and quantitative viewpoints. Similar situation we have observed when acetalized poly(vinyl alcohol) D was used alone or in the mixture with A (Table 2). Acetalized PVA D used alone acts similarly to the thermo-oxidatively treated B and produces PVC with less porous grains (plasticizer absorption 38 min) and with a very high bulk density 700 kg m^{-3} The mixtures of A and D produced PVC with different quality, depending on relative concentration of A and D during polymerization. Fig. 3 shows the correlation between relative concentrations of A, D and PVC grain characteristics (plasticizer absorption and bulk density).

We found poor reproducibility of PVC grain size distribution (Tables 1 and 2). The reason is probably in not high enough mixing of the polymerization reaction mixture in the reactor of volume 50 dm^3. This was supported by the experiments with less than 0.05 mass % of A (and more than 0.05 mass·% of B) being used as a polymerization aid (Table 1). In these experiments almost block PVC polymer with larger grains was formed. We can expect that with much more vigorous stirring of the polymerization mixture and higher concentrations of PVA dispersants a suspension PVC product could be obtained.

We can conclude that applying obtained correlations between relative concentrations of modified PVA B or D in the mixture with unmodified commercial PVA one can formulate a mixture of PVA-based dispersants to be used in suspension VC polymerization. Such a defined mixture of modified and unmodified PVA can be used for the manufacturing of tailor-made PVC grades with required grain morphology, characterized by the grain size, porosity, and the bulk density.

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