Modified poly(vinyl alcohol) as a dispersant in suspension polymerization of vinyl chloride: 3. Acetalized poly(vinyl alcohol)

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Poly(vinyl alcohol) (PVA) Sloviol R was modified to different degrees by acetalization reactions with aldehyde (formaldehyde, acetaldehyde, propionaldehyde and n-butyraldehyde) for 6 h at 60°C in the presence of HCl as catalyst. Samples of the modified PVA were tested as dispersants in vinyl chloride suspension polymerization. The grains of poly(vinyl chloride) (PVC) powder produced are more compact, not very porous, have a higher bulk density and lower plasticizer absorption. By increasing the degree of acetalization, the bulk density of the PVC produced decreases. Using a mixture of commercial PVA Alcotex 72.5 (which produces porous PVC with a low bulk density) and acetalized PVA, PVC with a grain morphology can be obtained.

(Keywords: poly(vinyl alcohol); vinyl chloride; suspension polymerization)

INTRODUCTION

In two previous papers[1,2] we have described two different methods for the preparation of modified poly(vinyl alcohol) (PVA). The products of such modifications can be used as the protective colloids or dispersants in vinyl chloride suspension polymerization. Our study of PVA modification by partial alcoholysis[1] revealed that the degree of polymerization of PVA and the amount of water present during alcoholysis are the most important parameters influencing the ability of the product to be a good dispersant. This ability can be predicted from the results of measurements of viscosity, surface tension, cloud point and flocculation temperature of the PVA produced.

In our study of either thermally or thermo-oxidatively modified PVA[2], we have observed the formation of aldehydic groups and partial acetals by previously known mechanisms[3-5]. There are some published studies of PVA acetalization to high degrees[6,7]. Six-member intramolecular acetal rings and intermolecular acetals are formed by the reaction of PVA with aldehydes in the presence of acids as catalysts[8]. This paper presents the results of a study preparing PVA partially acetalized with aliphatic aldehydes C_1-C_4 and its use as a dispersant in vinyl chloride suspension homopolymerization.

EXPERIMENTAL

Chemicals

Vinyl chloride and the peroxidic polymerization initiator EHP-80 were characterized in a previous paper[a].

Aqueous PVA Sloviol R (Chemical Works, Novaky) was prepared by alkaline saponification of a 16.1 mass% methanolic poly(vinyl acetate) (PVAc; degree of polymerization 1140, degree of hydrolysis 86.0 mol%, surface tension of 4 mass% aqueous solution 45.5 mN m^{-1}, dynamic viscosity 11.5 mPa s, acid number of dried sample 2.7 mg KOH g^{-1}).

The properties of the commercial PVA Alcotex 72.5 (Revertex, Harlow, UK) are as follows: degree of hydrolysis 71.0 mol%, degree of polymerization 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.

The aqueous 35.2 mass% formaldehyde (Chemko Strazske, Slovakia) contained 0.02 mass% formic acid.

Analytical grade acetaldehyde, propionaldehyde and n-butyraldehyde were distilled before use.

Procedures

Acetalized PVA was prepared in a 2.5 l jacketed autoclave equipped with a stirrer. The autoclave was flushed with nitrogen and aqueous PVA with aqueous (37.1 mass%) HCl was added and heated to the reaction temperature. The aldehyde was then added and after 6 h of reaction the product was cooled. Product samples were characterized by the methods described in detail in a previous paper[2].

Degrees of acetalization were determined by the oximation method, under boiling, in the presence of acid and hydroxylamine hydrochloride. The unreacted aldehydes were determined by oximation at laboratory temperature. The method described by ASTM D 1617-68

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was used to determine the number of unreacted acetate groups in PVA.

I.r. absorption spectra were measured at 400–4000 cm^{-1} on a Specord M80 (Carl Zeiss, Jena) and a Perkin-Elmer 398. Thin films (0.10–0.12 mm) were made for i.r. measurements by drying aqueous solutions of modified PVA on a polyethylene surface, at 50°C and 3 kPa pressure.

Vinyl chloride suspension polymerizations in the presence of modified PVA were carried out under the same conditions as in our previous work[1,2].

D.s.c. was carried out using a Perkin-Elmer DSC 7 according to ASTM D 3418-75 for the determination of the glass transition temperature (T_g).

Plasticizer absorptions were measured[9] with di(2-ethylhexyl)adipate at 75°C.

RESULTS AND DISCUSSION

With the aim of using modified PVA as a protective colloid in vinyl chloride suspension polymerization, a series of samples of PVA Sloviol R modified with formaldehyde, acetaldehyde, propionaldehyde or n-butyraldehyde were prepared (*Table 1*).

Very high conversions (95–99.5%) of the corresponding aldehydes were found, but the selectivities of the aldolization reactions were lower, especially when formaldehyde was used. This is caused by simultaneous unproductive reactions of the aldehydes, mostly by autocondensation reactions[10]. The determination of unreacted acetate groups of modified PVA and i.r. spectra measured for dried films of modified PVA show that with increasing degree of acetalization the amount of unreacted acetate groups in modified PVA decreases. The intensities of the i.r. spectral bands at 1740,1370 and 1250 cm^{-1} belonging to $C=O$, $—CH_3$ and $—C—O$ are reduced[11,12].

Samples of PVA modified with formaldehyde show intense bands at 1020, 1140, 1170 and 1239 cm^{-1}. The very low intensity of the band at 2770 cm^{-1} is probably the result of a low degree of acetalization with formaldehyde.

In the spectra of samples prepared by acetalization with acetaldehyde, bands at 940, 1098, 1240 and 1340 cm^{-1} can be observed. Modification using propionaldehyde yields bands at 1140, 1240 and 1338 cm^{-1}. The i.r. spectra of PVA acetalized with n-butyraldehyde show bands at 970, 1140 and 1380 cm^{-1}. The last band is

Table 1 Preparation of modified PVA and some characteristics (Sloviol R 100 g, HCl 6 g, aldehyde, 6 h, 60°C)

		Degree of aldolization			
Aldehyde[a] (mol)	Conversion (%)	Max.[b] (%)	Expt.[c] (%)	Unreacted acetate (%)[d]	T_g (K)
Unmodified[e]	–	–	–	16.5	343
F 0.07	95.1	3.9	1.5	1.3	350
F 0.15	97.2	8.7	3.5	1.7	354
F 0.30	98.7	18.1	5.6	1.1	361
AA 0.07	96.6	4.5	4.5	1.1	352
AA 0.15	97.0	8.9	8.9	1.5	353
AA 0.30	98.8	18.1	17.9	2.9	362
PA 0.07	98.9	4.2	4.2	1.6	–
PA 0.15	98.7	9.1	7.6	11.8	–
PA 0.30	99.3	18.3	16.2	2.0	–
BA 0.07	98.3	4.1	4.1	1.3	348
BA 0.15	98.9	9.1	6.8	2.3	352
BA 0.30	99.5	18.3	14.7	2.8	354

[a] F, formaldehyde; AA, acetaldehyde; PA, propionaldehyde; BA, n-butyraldehyde
[b] Maximum value calculated from the amount of reacted aldehyde
[c] Degree of acetalization found experimentally
[d] Unreacted acetate groups in modified PVA
[e] Unmodified PVA Sloviol R

Table 2 Acetalized PVA as a dispersant in suspension vinyl chloride polymerization and some properties of the polymers produced

	Sieve analysis of PVC[a] (%) on mesh (mm)							PVC bulk density (kg m^{-3})	Plasticizer absorption (min)
Degree of acetalization (%)	1.0	0.25	0.20	0.16	0.10	0.063	<0.063		
Unmodified[b]	–	–	–	–	–	–	–	–	–
F 1.5	0.7	20.8	19.8	23.0	23.0	5.5	7.9	670	>30
F 3.5	1.0	35.7	18.5	17.0	21.7	2.5	4.6	670	>30
F 5.6	0.5	21.2	29.7	20.0	20.7	4.2	4.2	585	30
AA 4.9	0.1	5.6	32.0	31.2	22.4	2.8	6.0	681	>30
AA 8.9	0.1	5.2	28.8	18.0	31.2	12.4	4.4	620	>30
AA 17.9	0.1	5.6	12.8	28.0	38.4	11.2	4.0	571	30
PA 4.2	0.3	14.6	12.9	22.0	35.4	9.7	5.4	640	>30
PA 7.6	0.2	15.6	43.6	15.6	17.2	2.8	5.2	638	>30
PA 15.2	0.1	20.8	19.3	17.8	30.9	6.3	4.9	608	30
BA 4.3	0.3	18.9	8.9	17.6	38.8	9.4	6.4	647	>30
BA 6.8	0.1	6.4	52.8	21.2	16.0	2.0	1.4	634	>30
BA 14.7	0.1	3.3	7.6	12.5	54.5	15.1	7.0	586	30

[a] Weight per cent of PVC which did not pass the mesh of stated size
[b] Unmodified PVA Sloviol R; block polymer formed

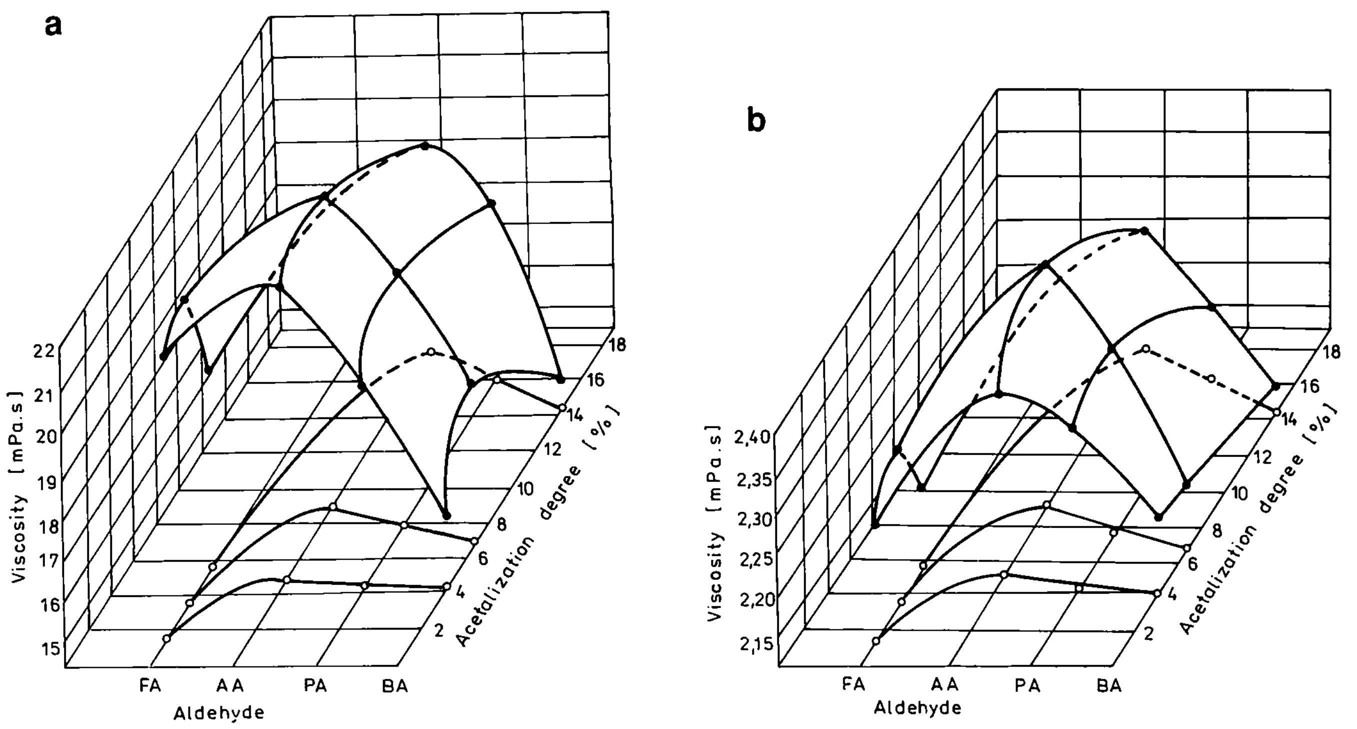

Figure 1 Influence of degree of acetalization and aldehyde used on the dynamic viscosity of aqueous solutions of acetalized PVA: (a) 4 wt%; (b) 1 wt%

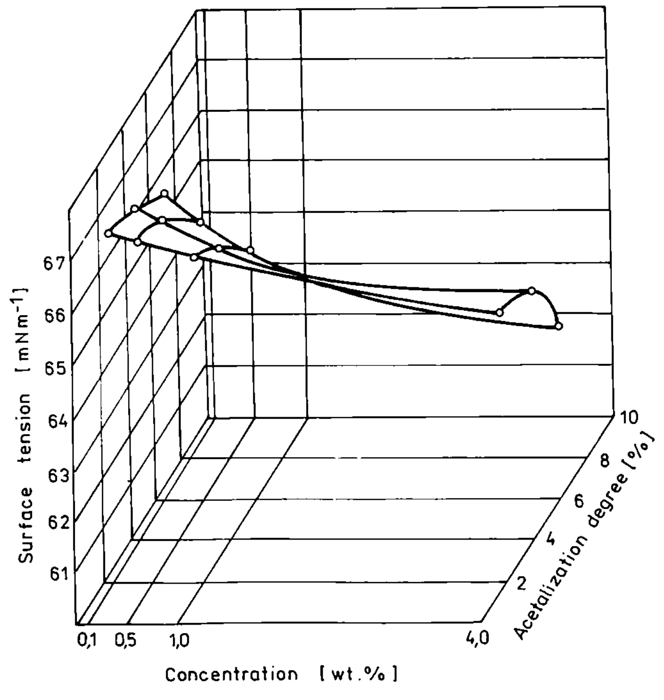

Figure 2 Influence of degree of acetalization and concentration of PVA modified with formaldehyde on the surface tension of aqueous solutions

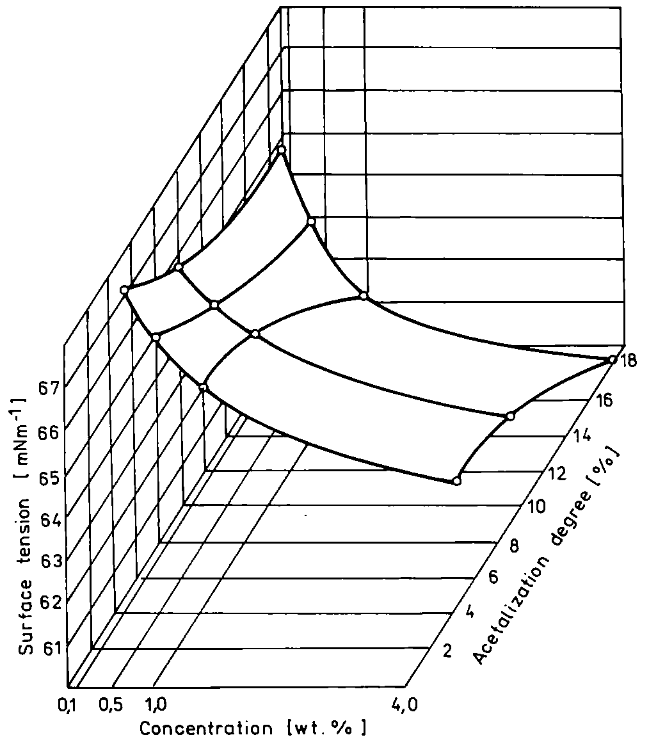

Figure 3 Influence of degree of acetalization and concentration of PVA modified with acetaldehyde on the surface tension of aqueous solutions

shifted to 1370 cm^{-1} in the samples with a higher content of acetate groups. This band is characteristic of CH_3 groups[11,12]. All these measurements show that the acetalization reaction of PVA proceeds under the conditions studied and that modified PVA is formed.

The dynamic viscosity measurements of 4 mass% (*Figure 1a*) and 1 mass% (*Figure 1b*) aqueous solutions of modified PVA show that the highest viscosity as a function of degree of acetalization and aldehyde used was observed for PVA modified with acetaldehyde. The lowest values were measured for PVA modified with formaldehyde. This is caused by the low degree of acetalization with formaldehyde. The rate constant of the acetalization reaction for formaldehyde is lower than those for acetaldehyde, propionaldehyde and n-butyraldehyde[13]. We assume that the smallest alkyl group coming from formaldehyde is not as hydrophobic as the longer alkyls from the higher aldehydes. PVA samples acetalized with

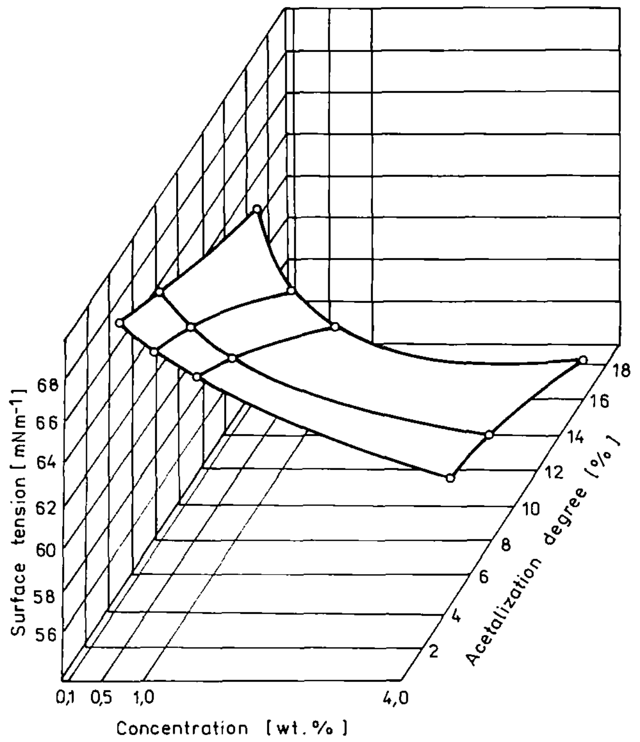

Figure 4 Influence of degree of acetalization and concentration of PVA modified with propionaldehyde on the surface tension of aqueous solutions

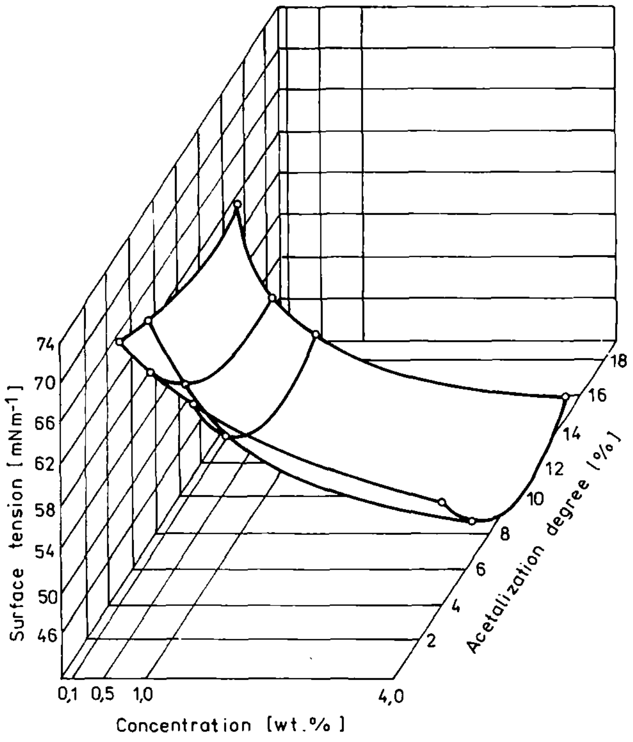

Figure 5 Influence of degree of acetalization and concentration of PVA modified with n-butyraldehyde on the surface tension of aqueous solutions

Table 3 Influence of the ratio of PVA acetalized with formaldehyde to unmodified PVA Alcotex 72.5 in a mixture used as a dispersant in suspension vinyl chloride polymerization on the quality of the PVC product

Dispersant (wt%)[b]		Sieve analysis of PVC[a] (%) on mesh (mm)							PVC bulk density (kg m^{-3})	Plasticizer absorption (min)
PVF[c]	AX[d]	1.0	0.25	0.20	0.16	0.10	0.063	<0.063		
0.10	0	0.1	37.1	16.7	25.1	13.6	2.3	5.2	693	30
0	0.10	0.1	8.5	33.6	36.7	12.5	8.5	1.6	472	9
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	15
0.03	0.07	0.4	11.2	45.8	20.0	13.0	8.4	1.2	503	9
0.04	0.06	0.1	13.2	36.2	28.0	18.8	1.2	2.4	500	8
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
0.09	0.01	0.1	26.3	23.1	29.2	13.1	4.4	3.8	639	>30

[a] Weight per cent of PVC which did not pass the mesh of stated size
[b] With respect to vinyl chloride
[c] PVA Sloviol R aldolized with formaldehyde (degree of aldolization 17.7%)
[d] PVA Alcotex 72.5

the higher aldehydes are more lipophilic and less soluble in water and produce more viscous solutions. Another reason may be due to the different ability of the aldehydes to react and form known intramolecular acetal rings or intermolecular acetals[8]. The lower aldehydes can produce both kinds of acetals; the higher aldehydes are less reactive and produce intermolecular acetals.

The influence of the aldehyde used for acetalization on the surface tension of aqueous solutions with different PVA concentrations can be seen from *Figures 2–5*. The results show that the value of the surface tension decreases with increase in the length of the alkyl group of the aldehyde used for acetalization. This is probably the result of the difference in the hydrophilic behaviour of the resultant acetals. This allows selection of the aldehyde and degree of acetalization for preparing modified PVA suitable to act as a dispersant in vinyl chloride suspension polymerization.

This is supported by the results (*Table 2*) of experiments, where PVA modified by acetalization was used in 0.1 mass% concentration (with respect to vinyl chloride) in vinyl chloride suspension polymerization. Using unmodified PVA Sloviol R as the dispersant the conversion of vinyl chloride was ~85%, which is comparable to the results obtained with modified PVA, but the polymer produced was mostly the result of bulk polymerization. To produce a suspension polymer it is necessary to use modified PVA as a dispersant.

PVA with a low degree of acetalization used as a dispersant produced a suspension polymer with slower plasticizer absorption (>30 min) and higher bulk densities. This means that the polymer grains are more compact and not very porous. More porous products with lower bulk density can be obtained by polymerization in the presence of PVA acetalized to a higher degree. This allows us to select the method of preparation of a suitable dispersant to produce PVC powder with the required morphology, and characterized mainly by porosity, absorption of plasticizer and bulk density.

Table 3 gives the results of polymerization experiments with commercially produced PVA Alcotex 72.5 and with PVA modified with formaldehyde (degree of acetalization 17.7%). Unmodified Alcotex 72.5 used as a dispersant in vinyl chloride polymerization produces porous PVC powder with lower bulk density. Addition of PVA modified with formaldehyde produces a less porous PVC powder with higher bulk density. Changing the ratio of the two dispersants yields a PVC powder with the required porosity.

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