Preparation of poly(vinyl alcohol) as the dispersant for suspension vinyl chloride polymerizations

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The study of the influence of the reaction conditions of alkaline catalysed methanolysis or hydrolysis of methanolic poly(vinyl acetate) (PVAc) solution shows that for PVAc with an average degree of polymerization of ~1140 the optimal degree of hydrolysis for use as a dispersant in the suspension polymerization of vinyl chloride is ~71 mol%. Also, the cloud point of aqueous solutions with 1 wt% poly(vinyl alcohol) (PVA) is at 23–29°C. It is necessary to minimize the amount of water present during PVAc methanolysis. PVA samples produced under optimal conditions can be used as dispersants for the suspension polymerization of vinyl chloride.

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

INTRODUCTION

The wide range of chemical and physical properties of poly(vinyl alcohol) (PVA) and partially hydrolysed or alcoholysed poly(vinyl acetate) (PVAc) has led to their broad industrial use[1]. There is considerable interest in the use of PVA instead of cellulose derivatives as an aid for suspension homopolymerization or copolymerization of vinyl chloride[2]. Free-radical initiated suspension polymerization proceeds in the system with monomer highly dispersed in the aqueous phase. PVA acts here as a protective colloid and contributes to the emulsification and stabilization of aqueous vinyl chloride or poly(vinyl chloride) (PVC) dispersions. The physical and chemical properties of PVC produced by suspension polymerization depend on the conditions of polymerization (temperature, mixing, amounts of aqueous phase) and on the kind of polymerization aid used[3]. It is known, that not every grade of PVA resin is suitable. Because of the growing demand for PVC grades with precisely defined quality and behaviour, the study of the influence of the reaction conditions during preparation of PVA or partly alcoholysed PVAc resins on their qualities in the process of suspension vinyl chloride polymerization could be useful.

In the present paper we concentrate on such a study, using PVA resins or partially methanolysed PVAc with a degree of hydrolysis of 70–74 mol%.

EXPERIMENTAL

Chemicals

The PVA methanolic solution contained 20 wt% PVAc with a degree of polymerization (*DP*) of 1140, and 0.2 wt% water. The acid number was 0.2 mg KOH g^{-1}.

The vinyl chloride (Novaky Chemical Works, Novaky) used contained the following impurities (in 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, water 193. The polymerization initiator used was EHP-80 (Novaky Chemical Works, Novaky) and consisted of 50 wt% xylene, 35 wt% bis-(2-ethylhexyl)peroxydicarbonate, 14 wt% benzoylperoxy-2-ethylhexyl carbonate and 1 wt% dibenzoyl peroxide.

All other chemicals were of analytical grade.

Procedure

PVAc hydrolysis proceeded under the reflux of methanol. The cloud points of the aqueous solutions with 1 wt% PVA resin or partially methanolysed PVAc were measured with colorimetric apparatus (Specol 10, Carl Zeiss, Jena). The measuring cell, with controlled temperature and mixing, enabled the absorbance to be measured with respect to temperature (temperature gradient 2°C min^{-1}). From the data obtained the following parameters were evaluated: the cloud temperature t_0 (cloud point), the temperature of flocculation of the resin (t_f) and the total change in absorbance (ΔA) during heating.

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The average *DP* of PVAc was determined by capillary viscosimetry using 1 wt% aqueous solutions of samples obtained by washing and drying saponified PVAc (method JISK 6726).

Surface tensions of aqueous PVA solutions were determined by the stalagnometric method (ISO 304-1978).

The dynamic viscosity of PVA aqueous solutions was measured using a Hoepler viscosimeter (DIN 53 014).

Suspension vinyl chloride polymerization was carried out in a 50 dm^3 double-walled stainless steel autoclave with intense mixing. The polymerization proceeded for 5.5 h at 55 ± 0.1°C; the ratio of water to vinyl chloride was 1.35, and the reaction was initiated with EHP-80 (0.12 wt% with respect to vinyl chloride). PVA resins (0.1 wt% with respect to vinyl chloride) were used as the polymerization aid. After polymerization, the reaction product (PVC suspension) was washed with demineralized water and dried. The particle size distribution, bulk density and the absorption of plasticizer were measured for each PVC sample.

RESULTS AND DISCUSSION

It is known that the protective colloidal behaviour of PVA resins is influenced by the *DP*, the degree of and procedure used for PVAc hydrolysis or alcoholysis and depends on the distribution of unreacted acetate groups. The protective colloidal behaviour of PVA is better when the unreacted acetate groups are in a block arrangement[4]. This is influenced mostly by the solvent, temperature and the catalyst used for PVAc solvolysis.

Our study of the influence of NaOH concentrations (in the presence of small amounts of water) on the reaction rates of PVAc methanolysis shows that an increase in NaOH concentration increases the reaction rates (*Table 1*). The concentration of NaOH was calculated as the ratio of the number of moles of NaOH minus the acid number of PVAc to the number of moles of VAc units in PVAc. Water added into methanolic PVAc solution has a negative effect on the reaction rates and on the degree of methanolysis of PVAc. The concentration of water was calculated as a weight per cent with respect to PVAc.

The cloud point is the parameter which depends on the *DP* of PVA and gives[5] information about intramolecular block distribution and intermolecular distribution of unreacted acetate groups (*Figure 1*). The influence of reaction conditions during PVAc methanolysis on the cloud point of the PVA resins produced was studied by changing the reaction time and the amount of water used (*Table 2*). The results show that reaction time, over the time interval studied, practically has no influence. The influence of water concentration is significant in the case of PVA or partially methanolysed PVAc with a degree of hydrolysis of 70–71.5, 72–73.5 and

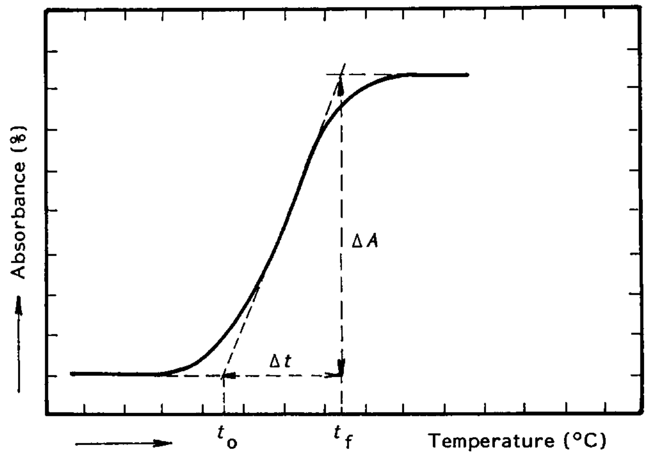

Figure 1 Typical shape of the clouding curve for a 1 wt% aqueous PVA solution

Table 1 Influence of the concentrations of water and NaOH catalyst on the rate and degree of PVAc methanolysis

		Degree of PVAc methanolysis (mol%)										
		Reaction time (min)										
NaOH[a] (×10^3)	Water[b] (wt%)	5	7	10	12.5	15	18	20	22	25	30	35
1.7	1.0	22.0	32.5	52.5	65.5	75.0	81.5	86.5	89.9	90.0	90.0	–
1.7	2.0	21.0	30.0	46.5	55.0	62.0	68.5	70.5	73.1	75.5	78.0	78.0
1.7	3.0	19.0	27.0	38.0	47.6	53.5	59.0	62.1	63.5	65.5	67.1	68.0
1.7	4.0	18.0	25.1	37.1	45.1	50.5	57.0	59.5	61.5	63.5	65.1	65.3
2.9	1.0	24.5	40.5	57.0	66.1	72.5	78.1	80.0	82.5	82.7	82.8	–
2.9	2.0	21.5	37.1	52.1	61.5	67.5	73.5	76.5	78.2	81.1	82.5	–
2.9	3.0	19.5	35.1	48.2	57.2	62.5	66.6	69.2	70.7	73.2	74.5	76.5
2.9	4.0	18.0	32.5	46.0	54.5	60.2	65.2	66.5	67.5	68.0	68.5	69.0
3.3	1.0	23.5	43.5	60.1	68.2	75.1	81.2	82.5	82.8	82.9	–	–
3.3	2.0	23.0	41.5	57.5	66.1	72.5	78.3	81.1	82.5	82.6	–	–
3.3	3.0	22.0	38.0	54.2	62.5	69.6	75.3	77.2	76.5	82.0	–	–
3.3	4.0	21.0	35.0	49.6	57.5	63.2	67.5	69.5	71.7	72.5	–	–
5.8	4.0	47.5	65.0	74.5	80.1	83.5	87.2	88.0	89.5	89.7	–	–
5.8	5.0	43.1	60.1	69.2	75.0	76.5	80.5	81.5	82.5	83.0	–	–
5.8	6.0	39.5	52.5	62.5	68.5	72.6	74.5	75.3	76.5	76.9	–	–
5.8	7.0	35.0	47.5	58.5	65.1	68.6	70.0	71.0	71.5	72.5	–	–

[a] Molar ratio of NaOH and vinyl acetate units in PVAc
[b] With respect to PVAc

74–75 mol%. By using increasing amounts of water during PVAc methanolysis the cloud point of the PVA resins produced decreases. This is probably the result of the NaOH catalyst being distributed inhomogeneously in the reaction mixture. The solubility of aqueous NaOH solution in methanolic PVA is low and therefore part of the catalyst is dispersed in the bulk liquid in the form of small droplets. Very high local concentration of the catalyst in the droplets causes higher rates of hydrolysis and methanolysis and is the reason for the hydrolysis of the methyl acetate formed, producing acetic acid and methanol. The acetic acid produced reacts with the NaOH catalyst and its concentration is decreased. Consequently, the alcoholysis of PVAc stops at a lower degree and the PVA resins produced have lower cloud points.

Table 2 Influence of reaction conditions during methanolysis on the cloud point (t_0) of the PVA resins produced

Degree of hydrolysis (mol%)	Water[a]	Reaction time (min)	t_0 (°C)
70.5	0.087	20	24
71.5	0.096	25	27
70.0	0.098	29	23
70.0	0.098	30	23
70.5	0.094	30	23
71.5	0.098	33	23

[a] Molar ratio of water and vinyl acetate units in PVAc

Table 3 Influence of reaction conditions during PVAc methanolysis on the cloud point and surface tension of the solutions of the PVA resins produced

Degree of hydrolysis (mol%)	Water[a]	Reaction time (min)	Cloud point (°C)	Surface tension[b] (mN m^{-1})
71.5	0.103	25	30	43.0
71.5	0.103	30	25	43.0
71.0	0.105	30	24	42.5
70.0	0.144	18	21	43.0
72.0	0.087	38	31	43.1
72.5	0.087	25	30	42.7
73.0	0.094	28	32	43.5
72.0	0.128	30	31	43.1
73.5	0.134	30	29	43.0
72.5	0.147	23	26	42.5
75.0	0.098	23	40	43.5
75.0	0.115	27	38	44.0
74.5	0.140	32	28	44.0

[a] Molar ratio of water and vinyl acetate units in PVAc
[b] Surface tension of 4 wt% solution of PVA at 20°C

As we have observed, the amount of water present in the reaction system during the methanolysis of PVAc causes the following in measurements of the cloud point: (i) differences in the temperature interval value (Δt) between the beginning of the clouding and the maximum absorbance; and (ii) differences in values of the total change in absorbance (ΔA). The results in *Tables 3* and *4* show that an increase in the amount of water during PVAc solvolysis causes an increase in Δt. A higher value of t is characteristic for PVA with a wider distribution for the value of the degree of hydrolysis. So, using greater amounts of water during PVAc methanolysis causes a wider distribution for the value of the degree of hydrolysis of PVA. Cloud point measurements are applicable as a tool for the characterization of PVA resins only for resins with a degree of hydrolysis or methanolysis within the range of $\sim$70–80 mol%. Resins with a higher degree of hydrolysis or methanolysis are completely soluble in water and no cloud formation was observed during the temperature changes. Grades of PVA resins with degrees of hydrolysis $< \sim 70$ mol% are insoluble in water.

As we have observed, the surface tension of PVA aqueous solutions is almost constant even if other characteristic parameters are changed. Therefore, measuring the surface tension cannot be used as a method for PVA characterization; other parameters (Δt and the ratio of Δt to ΔA) would have to be determined.

Solutions of the PVA resins prepared were tested as an aid in suspension polymerization of vinyl chloride. The size of the grain is an important parameter in the suspension PVC product and depends on the emulsification quality of the PVA resin used. The samples of PVC resins produced were sieved on grading sieves and were divided into four grades, according to the fraction (wt%) of particles which could not pass through a 0.25 mm sieve. The grades were: 0–5, 5–10, 10–50 and > 50 wt%. The last group of PVC grades is formed when the emulsifying activity of the tested PVA resins is poor or non-existent.

We have found a correlation between the value of $\Delta t/\Delta A$ and the quality of PVA as an aid in suspension polymerization of vinyl chloride. The use of PVA with a low value for this ratio allows the production of higher quality PVC grades (with sharp particle size distribution).

We can conclude (*Table 5*), that the best PVA resins as aids for suspension vinyl chloride polymerization are ones with a degree of hydrolysis of $\sim$71 mol%, a cloud

Table 4 Influence of reaction conditions on the parameters of the cloud point measurement, at constant mixing (120 rev min^{-1})

Degree of hydrolysis (mol%)	Water[a]	Surface tension (mN m^{-1})	Temperature interval, Δt (°C)	Relative change of absorbance, ΔA (%)	$\Delta t/\Delta A$
71.5	0.096	43.4	6	47.2	0.127
71.5	0.103	43.0	6	39.7	0.151
71.0	0.105	42.3	7	44.3	0.158
72.5	0.107	43.0	7	39.5	0.177
72.5	0.144	43.0	9	49.7	0.181
72.5	0.150	43.0	7	42.1	0.166
70.5	0.167	42.7	8	39.0	0.205

[a] Molar ratio of water and vinyl acetate units in PVAc

Table 5 Summary of the relations between the parameters of PVA resins and the ability of PVA to function as an aid in suspension vinyl chloride polymerization

PVC grade[a]	Degree of hydrolysis (mol%)	Reaction time (min)	Cloud point (°C)	Temperature interval, Δt (°C)	Relative change of absorbance, ΔA (%)	$\Delta t/\Delta A$
0–5	71.6±1	24.4	26.5±1	6.5	45.6	0.145
5–10	71.9±1	26.5	30.2±1	6.9	42.2	0.167
10–50	72.0±1	22.4	32.3±1.5	7.4	39.1	0.199
over 50	73.1±1	14.8	43.3±2	–	–	–

[a] PVC characterized by the fraction (wt%) of particles which could not pass through a 0.25 mm sieve

point below 30°C, a low t value and a low value for the $\Delta t/\Delta A$ ratio. The data obtained are relevant for PVA resins with an average *DP* of 1100. Other commercial PVA products (e.g. Goshenol KZ 06, Poval 9-EK and Alcotex 72.5) even with a degree of hydrolysis of ~70–72.5 mol% and a cloud point of 28–32°C give PVC resins with a low bulk density (470–480 $\mathrm{kg\,m^{-3}}$), when used as a polymerization aid. This can probably be overcome by using a mixture of the above commercial grades with PVA resins with a *DP* of ~2000 and a degree of hydrolysis of 84–88 mol%, which forms a 4 wt% aqueous solution with a dynamic viscosity 15–50 mPa s at 20°C.

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