

Thermally Modified Poly(Vinyl Alcohol) as a Protective Colloid in Suspension Polymerization of Vinyl Chloride

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Aqueous solution of poly(vinyl alcohol) or partially hydrolyzed poly(vinyl acetate) was modified either thermally or thermo-oxidatively at 140 to 240 °C. Samples of poly(vinyl alcohol) thus obtained were tested as protective colloids in suspension polymerization of vinyl chloride. As found, thermal modification under nitrogen was virtually ineffective; more advantageous was that in the presence of air, or even better in oxygen. The most suitable temperature at one hour exposition was 180–200 °C. Important was the formation of an unsaturated conjugated system

$$\text{—}(\overset{|}{\text{C}}=\overset{|}{\text{C}}\text{—})_n\text{—CO—} \quad (n = 1\text{—}3)$$
 in macromolecules of poly(vinyl alcohol). Poly(vinyl alcohol) modified in this way, in contrast to an unmodified one or that exposed to the above-mentioned temperature in inert atmosphere, is an effective dispersant of suspension polymerization of vinyl chloride.

Poly(vinyl alcohol) (PVAL) belongs together with water-soluble derivatives of cellulose to the most used protective colloids of suspension polymerization or copolymerization of vinyl chloride (VC). Of importance are PVAL types ranging from extremely low-molecular to high-molecular ones and those with various content of acetate groups [1]. Combinations of two or more types of PVAL are frequently applied; some of them can be, however, modified variously [2–5]. Thus, PVAL or partially saponified poly(vinyl acetate) (PVAC) were functionalized with carboxyl, carbonyl or formyl groups; their protective colloid properties were thereby improved. Copolymers of vinyl acetate (VAC) with suitable comonomers were frequently employed for preparation of PVAL modified in this way [1, 6], or PVAL was treated individually. Ormondroyd [7] and Smalwood [8] investigated the influence of heating and unsaturation of primary types of PVAL on the magnitude of particles in the poly(vinyl chloride) (PVC) suspension and found that hydrogenation of the aqueous solution of PVAL was reflected in lowering of absorbance in UV spectra at $\lambda = 280$ and 320 nm belonging to chromophoric $\text{—}(\text{—CH=CH—})_n\text{—CO—}$ group with $n = 2$ to 3 . Use of such a hydrogenated PVAL as protective colloid in a suspension polymerization of VC is associated with a greater average size of PVC particles.

As evidenced in [9, 10] introduction of a carbonyl group into the molecule of PVAL or partially saponified PVAC not only narrows the size distribution of particles of the PVC formed, but also influ-

ences the bulk density and absorption of the plasticizer.

This paper presents the results of the study of the influence of conditions at the preparation of modified poly(vinyl alcohol) on the properties of suspension PVC produced in this way.

EXPERIMENTAL

Aqueous PVAL — Sloviol R (Chemical Works, Nováky) was prepared by alkaline saponification of 16.15 mass % methanolic PVAC (characteristics are given in Table 1).

Vinyl chloride (Chemical Works, Nováky) contained ($w/10^{-4}$ %): acetylene (1), propylene (3), 1,3-butadiene (11), chloromethane (49), chloroethane (7), 1,1-dichloroethane (3), 1,2-dichloroethane (4), vinylacetylene (12), water (193).

Polymerization initiator EHP-80 (Chemical Works, Nováky), formed from 50 mass % of xylene, 35 mass % of bis(2-ethylhexyl) peroxydicarbonate, 14 mass % of benzoylperoxy 2-ethylhexyl carbonate, and 1 mass % of dibenzoyl peroxide.

Redistilled water, medicinal oxygen, fluorescent lamp nitrogen, and air conditioned by passing through granulated charcoal were used.

Ultraviolet and infrared spectra were measured with Specord M 80 and UV—VIS spectrophotometers (Zeiss, Jena), respectively and with Perkin—Elmer, model 398 apparatus in the region of $\tilde{\nu} = 400\text{—}4000$ cm^{-1} .

Polymerization of VC

Aqueous solutions of PVAL were thermally modified in a rotatory autoclave (3 dm³) with an electrically heated jacket. The autoclave content was blown either with oxygen or nitrogen, filled with nitrogen, air or oxygen and heated to the predetermined temperature for 1 h. The product was cooled and analyzed for saponification number, acid number in solution and in the dry matter, dynamic viscosity, surface tension of the 4 mass % aqueous solution of PVAL and polymerization degree.

The prepared modified PVAL was used as a primary protective colloid (PVAL and VC mass ratio 0.001) in the suspension polymerization of the aqueous solution of VC (H₂O and VC mass ratio 1.35) containing initiator (EHP-80 and VC mass ratio 0.0012) in a 50 dm³ jacketed autoclave equipped with a paddle wheel stirrer at (55 ± 0.1) °C for 5.5 h. The suspension of PVC was then centrifuged off, washed with water, dried under reduced pressure at 50 °C and the distribution of particle sizes, bulk density, and plasticizer absorption were determined according to the appropriate Czechoslovak State Standard.

RESULTS AND DISCUSSION

The aqueous solution of PVAL was modified by thermal or thermo-oxidative process in the presence of nitrogen, air or oxygen at 140 to 240 °C.

Preparation conditions and property differences of the modified samples of PVAL are presented in Tables 1 and 2. The thermal treating, mainly in the presence of oxygen was associated with an evident change in colour of the modified samples of PVAL due to the unsaturated system formed [11] or alternatively even with elimination of acetic acid from the partially saponified PVAC.

The unsaturated system can be produced also by transfer reactions during VAC polymerization [12].

The unsaturated system in samples of modified PVAL or partially saponified PVAC was evidenced in the UV spectra by the absorbance increase at $\lambda = 225$ and 280 nm (Figs. 1 and 2). The absorption band at 225 nm can be almost unequivocally ascribed to α,β -unsaturated ketone units, that at 280 nm can be attributed either to β -hydroxyketonic [13] or α,β -unsaturated ketonic units [14]. Origination of these structures is possible through transfer reactions even at polymerization of VAC with an admixture of acetaldehyde, further as a residue of the peroxidic initiator, by degradation reactions associated with cleavage of the chain and dehydration of β -hydroxyketone structures of PVAL [11]. Moreover, also oxidation of primary and secondary hydroxyl groups, etc. can occur in the presence of oxygen.

Relation between the degradation degree of PVAL and the thermal treating can be considered from the difference in the polymerization degree and viscosity of aqueous solutions of the modified PVAL. Increase of the acid number of modified

Table 1. Characteristic Properties of PVAL Modified in Various Reaction Atmospheres at 200 °C for 1 h

Reaction atmosphere	Viscosity ^a mPa s	Surface tension ^a mN m ⁻¹	DP ^b	Hydrolysis mole %	Acid number		Classification
					in solution	in dry matter	
- (without modification)	11.56	45.5	1140	86.0	0.406	2.69	unsuitable
Nitrogen	10.23	53.5	955	90.0	12.33	19.70	unsuitable
Air	9.02	54.0	933	93.0	12.91	20.33	suitable
Oxygen	8.90	52.5	912	92.0	10.93	18.00	excellent

a) 4 mass % aqueous solution; b) degree of polymerization.

Table 2. Influence of Temperature on Characteristic Properties of PVAL Modified under Oxygen for 1 h

Temperature °C ± 1 °C	Dynamic viscosity ^a mPa s	Surface tension ^a mN m ⁻¹	DP	Hydrolysis mole %	Acid number		Classification
					in solution	in dry matter	
140	11.43	46.0	1096	87.4	1.18	7.21	unsuitable
160	9.49	47.5	974	88.2	2.43	7.82	unsuitable
180	9.13	49.2	931	89.8	5.61	11.54	suitable
200	8.90	52.5	912	92.0	10.93	18.00	excellent
220	4.66	52.7	-	93.3	15.34	20.49	excellent
240 ^b	6.3	54.5	-	93.7	12.2	-	unsuitable

a) 4 mass % aqueous solution; b) The sample was considerably degraded, the measured values are ambiguous.

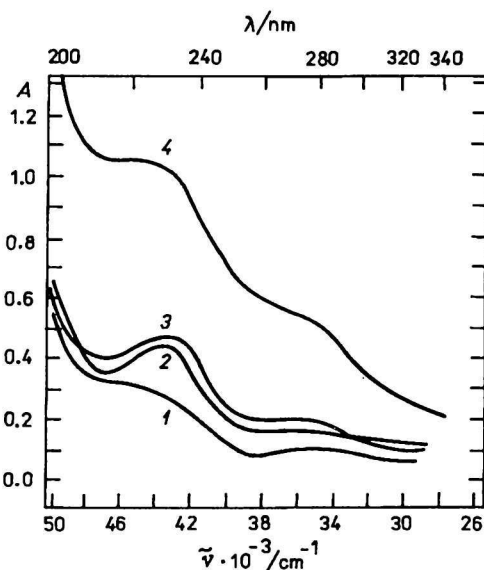


Fig. 1. Change in the UV spectra of aqueous (0.1 mass %) modified PVAL at 200 °C for 1 h in various atmospheres: 1. – (without modification); 2. nitrogen; 3. air; 4. oxygen.

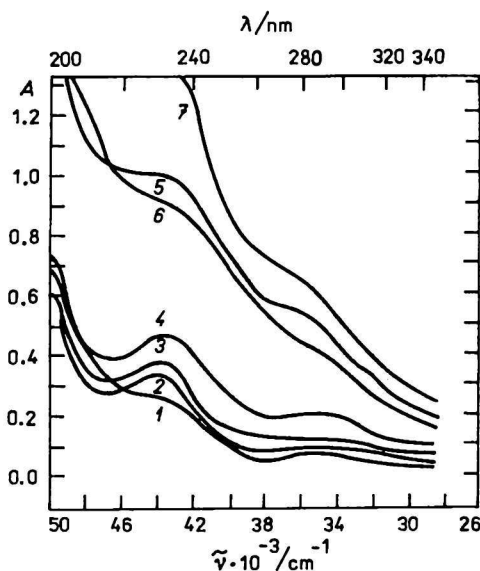


Fig. 2. Change in the UV spectra of aqueous (0.1 mass %) PVAL modified in oxygen for 1 h at θ /°C: 1. – (without modification), 2. 140, 3. 160, 4. 180, 5. 200, 6. 220, 7. 240.

samples of PVAL in solution or in dry matter indicates the elimination of acetic acid and oxidation of aldehyde groups.

Infrared spectra of the starting PVAL differed from those of the samples modified at 200 °C in relation to temperature and the gas applied as follows: the absorption band at $\tilde{\nu} = 1730 \text{ cm}^{-1}$ was shifted to 1705 cm^{-1} , intensity between 1650 and 1625 cm^{-1} increased, the band intensity at 1370 cm^{-1} decreased, the band shape and its distribution at 1430 cm^{-1} altered, the band at 1250 cm^{-1}

had lower intensity and was shifted to 1270 cm^{-1} , new bands originated at 1140 and 965 cm^{-1} and the band at 950 cm^{-1} was shifted to 920 cm^{-1} .

Not totally hydrolyzed samples of PVAC (to which the starting Sloviol R belongs) revealed an intense band at 1700 cm^{-1} characteristic of carbonyl groups; its shift between 1735 and 1705 cm^{-1} is due to elimination of acetate groups. Concurrently, absorption of carbonyl group of the acetate groups of the partially hydrolyzed PVAC was lowered. Nonetheless, hydrogen of the formyl group could not be evidenced either in the IR spectra at 2720 cm^{-1} , or in the ^1H NMR spectra. The presence of a ketone carbonyl was proved in the ^{13}C NMR spectrum and therefore, the band at 1705 cm^{-1} was ascribed to a ketone group.

Two bands at $\tilde{\nu} = 1600$ and 1650 cm^{-1} can be observed [15] for the conjugation of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups. Samples of the modified PVAL showed bands at 1650 and 1580 cm^{-1} belonging to $\text{C}=\text{C}$ and $\text{C}=\text{O}$ groups, respectively. The presence of an unsaturated system was evidenced by the band at 960 cm^{-1} belonging to $\text{C}-\text{H}$ vibrations of the double bonds. These results are in good agreement with those obtained by UV spectroscopy.

The lowering of the band intensity at 1735 cm^{-1} occurred parallelly with bands at 1370 and 1250 cm^{-1} , belonging to vibrations of CH_3 groups of the acetate groups and $\text{C}-\text{O}$ groups in the acetate groups, respectively. We suppose that the shift from 1250 to 1270 cm^{-1} and also the presence of the band at 920 cm^{-1} are associated with vibrations of COO^- group bonds because the acid numbers of solution and dry matter of samples prepared in the presence of oxygen rised with increasing temperature of thermal treating.

The polymerization tests displayed (Table 3) that the protective-colloidal properties of PVAL modified in this way and of partially modified PVAC samples were improved with increased modification temperature and presence of oxygen. This enabled us to prepare effective protective colloids from the starting partially saponified PVAC (Sloviol R). The most suitable temperature for modification of the above-mentioned partially saponified PVAC was found to lie between 180 and 200 °C as applied for 1 h in the presence of oxygen.

Ultraviolet and infrared spectroscopic measurements indicate that this improvement of protective colloidal dispersive properties of the modified PVAL samples can be attributed to the formation of an

unsaturated conjugated $-\text{C}=\text{C}-\text{C}=\text{O}$ system.

Application of modified PVAL samples of these properties as protective colloid in suspension homopolymerization of VC was associated (Tables

Table 3. Influence of Various Atmospheres on Characteristic Properties of PVC Obtained in the Presence of PVAL Modified at 200 °C

Atmosphere	Retention of PVC (%) over mesh size (mm)							Bulk density of PVC powder kg m ⁻³	Time of plasticizer absorption min
	1	0.250	0.200	0.160	0.100	0.063	0.063		
– (without modification)	N							–	–
Nitrogen	N							–	–
Air	1.1	31.4	46.2	11.6	7.4	1.6	1.8	539	30
Oxygen	0.1	1.6	4.8	9.6	22.6	26.0	35.4	605	30

N – the block polymerization proceeded (instead of suspension polymerization), the product was not characterized.

Table 4. Influence of the Temperature of Thermo-Oxidative PVAL Treating on the Distribution of the Particle Size of PVC

Temperature °C	Retention of PVC (%) over mesh size (mm)							Bulk density of PVC powder kg m ⁻³	Time of plasticizer absorption min
	1	0.250	0.200	0.160	0.100	0.063	0.063		
– (without modification)	N							–	–
140	N							–	–
160	0.7	63.6	14.2	10.7	6.4	3.7	1.6	460	18
180	0.4	31.2	25.2	17.4	8.7	7.3	9.9	517	30
200	0.1	1.6	4.8	9.6	22.6	26.0	36.4	605	30
220	0.9	2.8	4.0	12.8	40.0	24.6	15.8	579	30

N – the block polymerization proceeded (instead of suspension polymerization), the product was not characterized.

3 and 4) with diminution of the average particle size of PVC and increase of its bulk density. The PVAL sample modified at 240 °C was already remarkably degraded and therefore unsuitable for a polymerization test.

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