Comparative Characterization of Polyvinyl Alcohols for Vinyl Chloride Suspension Polymerization

1. The Degree of Hydrolysis

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The paper presents a comparative study on the structure of some polyvinyl alcohols used in PVC-S technology. The obtained data clearly showed that the degree of hydrolysis can be determined, with the same high precision through chemical method, IR and ^{13}C-NMR spectra. The carbonyl content determined from the IR spectra also correlates with the carbonyl content determined from ^{13}C-NMR spectra. A fast and reliable IR method for checking the degree of hydrolysis as technological support can be provided, the normalized carbonyl content determined from IR spectrum being linearly correlated with the degree of hydrolysis.

Keywords: Polyvinyl alcohols, vinyl alcohol-vinyl acetate copolymers, IR spectra, ^{1}H-NMR spectra, ^{13}C-NMR spectra

The suspension polymerization of vinyl chloride is a complex process and requires elaborate formulations. These include suspending agents or protective colloids that play a key role in the particle formation process. In the suspension polymerisation of vinyl chloride the bulk monomer phase is dispersed in water by vigorous stirring and the droplets produced are stabilized against coalescence by the presence of suspending agents or protective colloids. The degree of protection afforded to the monomer droplets depends on the type, properties and concentration of the protective colloids [1-5].

The properties of suspension obtained polyvinyl chloride (PVC-S) depend largely on its particle structure or morphology, so significant changes in polyvinyl chloride characteristics can be achieved by changes in suspending agent systems [6-10].

Polyvinyl alcohols (PVA) are among the most used suspending agents or protective colloids. They are vinyl acetate - vinyl alcohol copolymers. The basic properties of polyvinyl alcohols depend on their degree of hydrolysis, degree of polymerization, average molecular weight and distribution of hydroxyl groups on the polymer chain. Little changes in polyvinyl alcohols structure can result in important changes of polyvinyl chloride morphology, hence of polyvinyl chloride properties [8-10]. For this reason we decided to perform an in-deep, comparative study on the structure of some polyvinyl alcohols used in polyvinyl chloride technology.

Here, we present the comparative determination of the degree of hydrolysis of different types of polyvinyl alcohols used in PVC-S technology as basis for a new method of characterization. For reproducibility reasons, complete standard characterization of all the samples used was also performed.

Experimental part

Materials

In this study we used different commercially available polyvinyl alcohols and some polyvinyl alcohols prepared in laboratory. Thus, P1-P4 and R1-R4 samples are commercially grades of water soluble polyvinyl alcohols (table 1).

Sample S1 is a commercial solution of polyvinyl alcohol (33.15%) in a mixture of water-isopropanol (Ineos). Sample S2 is a commercial solution of polyvinyl alcohol (41.5%) in methanol (3V Sigma SpA). S3 and S4 are polyvinyl alcohol samples obtained in laboratory by the base-catalyzed alcoholysis of polyvinyl acetate in methanol, according to our method [11]. S5 is a solution of polyvinyl alcohol obtained in laboratory by the alcoholysis of polyvinyl acetate 50% in methanol in the presence of sulfuric acid (2.5%) at reflux temperature (table 2).

Two samples of polyvinyl acetate in solution were prepared, special measures being taken for keeping these samples unhydrolysed for reference purposes.

Methods

The degree of hydrolysis (DH) was determined by saponification followed by the titration according to Japan Industrial Standard JTS K 6726-1977 [12].

The distribution of the hydroxyl and acetate groups on the polymer chain (blockiness) was measured according to previously published methods [13a-c] on a SPECORD 250-222A181 UV-VIS spectrometer (Analytic Jena, Germany).

K values were determined from measurements of the relative viscosity of the polymer solutions and calculated according to Fikentscher's equation multiplied by 1000 [14].

Molecular weight of polyvinyl alcohols have been measured in a mixture of water:methanol 1:1 on Ultrahydrogel columns using a Size Exclusion Chromatograph (or GPC) Waters equipped with a refractive index detector. The mobile phase was a mixture of methanol:water 1:1. Molecular weights were calculated against a calibration curve constructed using polyethylene glycol standards.

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Table 1
WATER SOLUBLE POLYVINYL ALCOHOL SAMPLES

Polyvinyl alcohols / Characteristics	P1 [a]	P2 [b]	P3 [c]	P4 [d]	R1 [e]	R2 [e]	R3 [f]	R4 [g]
Degree of hydrolysis (% molar)	84.51	74.03	80.12	87.52	88.4	87,89	90.63	99,31
PVA-iodine complex abs.	0.5316	0.5343	0.3005	0.4041	0.6194	0.5987	0.6531	0.6089
λ (nm)	641.6	631.2	635.9	640	626.1	625.4	631.9	623.1
K Value	70	46	79	71	63.7	64,04	64.4	50.1
Molecular weight (GPC)								
M_w	76124	29266	97706	77892	59102	62360	62134	27543
M_n	42524	13165	53016	40839	28031	27567	7368	5820
Polydispersity	1.7901	2,2230	1.8429	1.9072	2.1084	2.2620	8.4326	4.7327

[a] Celvol E 26/88 (Celanese); [b] Alcotex B72 (Harlow Chem. Comp. Ltd., UK); [c] Gohsenol KH 17 (Nippon Gohsei, JP); [d] Mowiol 26/88 (Kuraray, JP); [e] PVA sample from Loba Chemie; [f] PVA sample from Romacril, Rasnov, [g] PVA sample from Doljchim, Craiova

^1H- and ^{13}C-NMR spectra were recorded at 30°C on a VARIAN UNITY INOVA 400 instrument, operating at 400 MHz for ^1H- and 100 MHz for ^{13}C-NMR. Chemical shifts (d) are given from solvent peak. ^{13}C-NMR spectra were recorded in non-NOE conditions and recycle delay was optimised at 7 sec to insure reproducible integration of all signals. The acetate molar fraction (AC_{NMR}) was calculated as the sum of the carbonyl integrals (in the range of 169 to 174 ppm) plus methyl integral (at about 20 ppm) divided by 2 times the sum of CH integrals (in the range of 63 to 71 ppm).

FT-IR spectra were recorded on a Bruker Vertex 70 instrument equipped with a Harrick MVP2 diamond ATR device on dry samples. Evaluation of carbonyl normalized content (CO_{FTIR}) was made from peak areas of C=O signals divided by the integral of the C-H stretching vibrations (2800-3000 cm^{-1}) as normalization reference, according to our previously published method [15].

Results and discussion

Samples having various degrees of hydrolysis are clearly differentiated in ^1H-NMR spectra (fig.1). The assignments of the signals in ^1H-NMR and ^{13}C-NMR spectra along with investigations of sequence distributions of vinyl alcohol-vinyl acetate groups in different polyvinyl alcohols have been earlier reported [16-18].

Microstructure of polyvinyl acetate-polyvinyl alcohol copolymers and its dependency on degree of hydrolysis of polyvinyl acetate-polyvinyl alcohols copolymers are obvious in ^{13}C-NMR spectra (fig.2).

All ^{13}C-NMR spectra of polyvinyl alcohols samples recorded in DMSO-d_6 present the following general features:

- a sharp singlet at about 20 ppm attributed to methyl carbon atom of the acetyl side group;
- three methylene carbon resonance lines (39-46 ppm) attributed [16-18] to the three dyad sequences alcohol-alcohol (O,O), alcohol-acetate / acetate alcohol (A,O) and

Table 2
ALCOHOL/WATER SOLUBLE POLYVINYL ALCOHOL SAMPLES

Polyvinyl alcohols / Characteristics	S 1 (Inovol SA5)	S 2 (Polivic 202)	S 3 (lab sample)	S 4 (lab sample)	S 5 (lab sample)
Dry substance (%)	33.15	41.5	37.11	35.41	38.1
Degree of hydrolysis (% molar)	56.43	47.8	51.05	57.92	55.85
PVA-iodine complex absorbance,	0.4322	0.2077	0.2853	0.350	0.1574
λ (nm)	622.4	603	604	620	590
K Value	20	26	25.5	25	24
Molecular weight (GPC)					
M_w	11723	14376	12071	13210	13760
M_n	3227	4418	3536	3728	3989
Polydispersity	3.6326	3.2540	3.4139	3.5437	3.4494

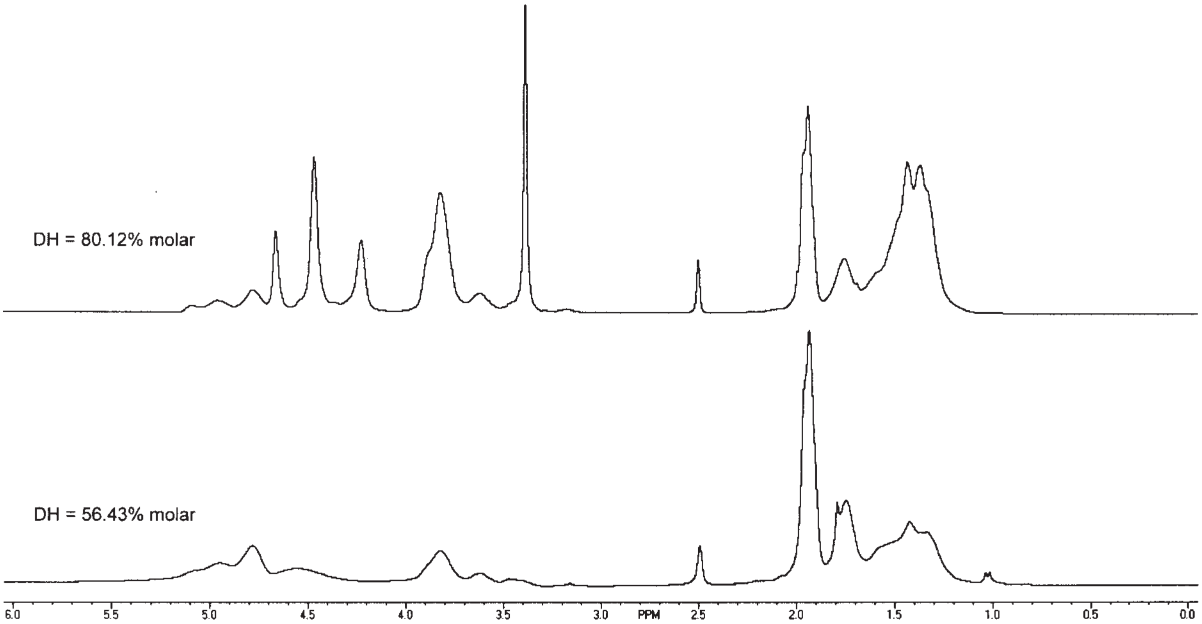


Fig.1. Typical ^{1}H-NMR spectra of water and alcohol/water soluble polyvinyl alcohols

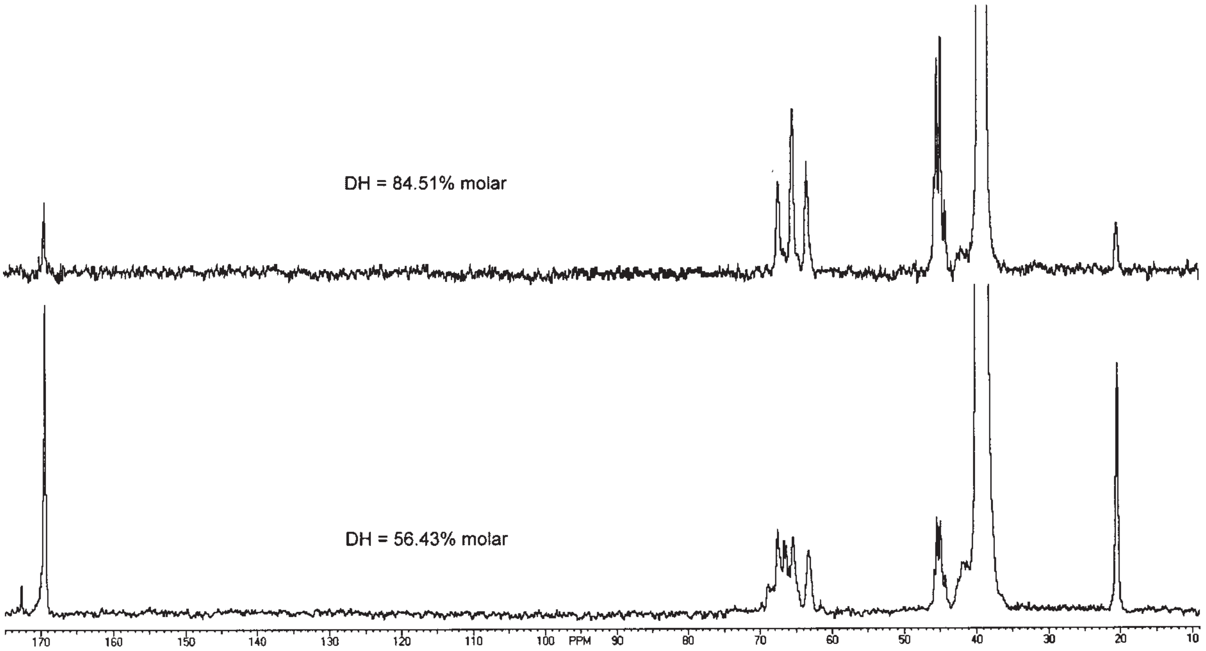


Fig.2. Typical ^{13}C-NMR spectra of water and alcohol/water soluble polyvinyl alcohols

acetate-acetate (A,A), but the last line is overlapped by the multiplet signal of the solvent;

- a broad complex signal in the 60-70 ppm region attributed to the methine carbons [16-18];
- three well resolved lines attributed to the carbonyl carbons at about 169-172 ppm.

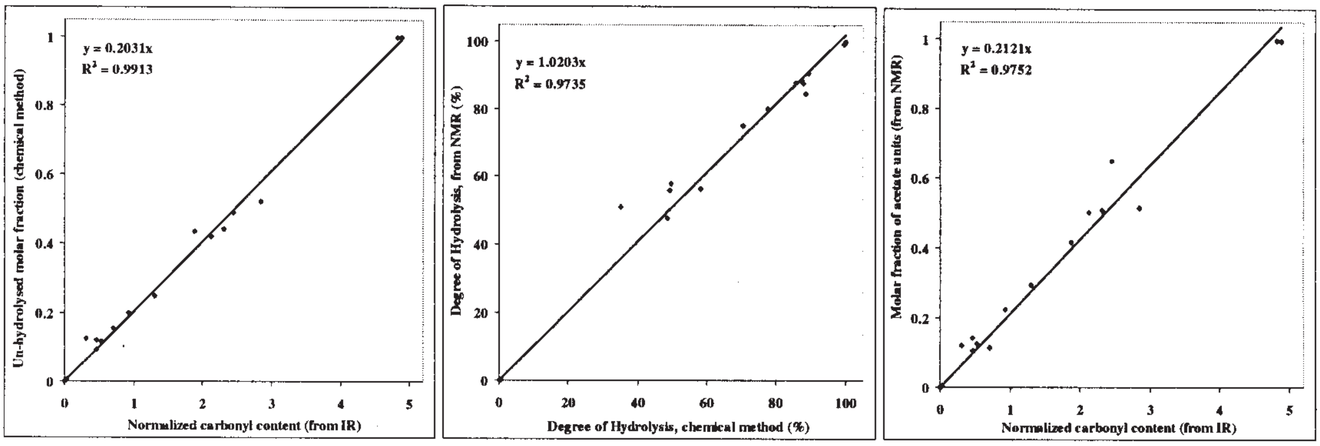
In the carbonyl carbons region, the high field peak corresponds to the carbonyl carbon atoms in acetyl side groups located within a vinyl acetate block. The low field peak was assigned to carbonyl carbon atoms located in isolated acetyl side groups surrounded by OH groups. Consequently, the central peak was assigned to carbonyl carbon atoms of acetate units in the centre of a transition triad (O,A,A) [16-18].

All ^{13}C-NMR recorded spectra of polyvinyl alcohols differ in relative intensities of the three peaks corresponding to the carbonyl and in number and intensities of the resonance lines in the methylene and methine regions.

For all samples, the degree of hydrolysis, measured using three different methods - chemically (DH), spectrophotometrically (IR) and spectrometrically (^{13}C-NMR) - gave values that correlated with a high degree of confidence (fig. 3 a-c).

Indeed, the un-hydrolyzed fraction (100-DH), as measured by the chemical method, correlate with the carbonyl normalized content CO_{FTIR} (fig. 3a). The degree of hydrolysis measured by the chemical method also correlate with the degree of hydrolysis determined from ^{13}C-NMR spectra (fig. 3b), calculated as ($100 - AC_{NMR} \times 100$). Moreover, the carbonyl content determined from the infrared spectra, CO_{FTIR}, also correlate with the acetate content, AC_{NMR}, determined from ^{13}C-NMR spectra (fig. 3c).

Since the correlation of the degree of hydrolysis (DH) with the normalized carbonyl content (CO_{FTIR}) has a R^2



a b c

Fig. 3. FT-IR, ^{13}C-NMR and chemical analysis correlations of the degree of hydrolysis

factor of 0.9913, the degree of hydrolysis can be safely calculated from infrared spectra using the formula:

$$DH = 0.2031 \times CO_{FTIR}$$

Conclusions

We performed a comparative study on the structure of some polyvinyl alcohols used in PVC-S technology.

The degree of hydrolysis measured by the chemical method correlate with the carbonyl content determined from the IR and ^{13}C-NMR spectra. Moreover, the carbonyl content determined from the IR spectra also correlate with the carbonyl content determined from ^{13}C-NMR spectra. All three correlations have high confidence coefficients.

Our data clearly showed that the degree of hydrolysis can be determined, with the same high precision, through any of the three presented methods. It means that we can provide a fast and reliable IR method for checking the degree of hydrolysis as technological support. This study will continue with the investigation of the molecular weights and molecular weight distributions and with the chain microstructure.

Acknowledgements: This work was partially achieved by means of the projects PN2 CNMP Parteneriate 71-029 "Nabieco" and 31-056 "Biopolact", financed by the Romanian Ministry of Education and Research.

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Manuscript received: 23.08.2009