

# Comparative Characterization of Polyvinyl Alcohols for Vinyl Chloride Suspension Polymerization

## 2. Thermal Stability

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*Thermal analysis, mass spectrometry-coupled, of partially hydrolyzed polyvinyl alcohols, for suspension polyvinyl chloride technology, showed that the reduced blockiness of low hydrolyzed product induced a low thermal stability with three degradation stages. When high blockiness is obtained, thermal stabilities in excess of 273°C are attained, regardless the hydrolysis degree. Glass transition of polyvinyl acetate segments is always present for hydrolysis degree ranging from 47.8 to 88.7 mol %. The melting transition is exhibited only by samples with hydrolysis degree higher than 74 mol %.*

*Keywords: polyvinyl alcohol, TGA-MS, thermal stability, polyvinyl chloride*

The industrial production of poly (vinyl chloride) (PVC) is mainly achieved by suspension polymerization. In this process, vinyl chloride monomer (VCM) is dispersed in the aqueous phase and is polymerized by free radical initiation. The coalescence of VCM droplets is considerably reduced by the combined action of agitation and protective colloids, such as vinyl alcohol-vinyl acetate copolymers (PVAs). The degree of protection afforded to the vinyl chloride droplets during particle formation process depends on the type, properties and concentration of the protective colloids [1-5]. The molecular characteristics of PVAs, such as hydrolysis degree, molecular weight, length of acetate and alcohol segments and insaturation have a very important influence on the stability of the VCM/water emulsion and on the properties of the final PVC resin [6-11]. Previous studies [12-17], performed on samples having hydrolysis degree over 80 mol %, showed that the melting point of polyvinyl alcohols depends on the intramolecular distribution of chain units and particularly on the length of the crystallized units.

Thorough investigation of degradation pattern of partially hydrolyzed polyvinyl acetates was rarely performed. Infrared-coupled [18] or mass spectrometry-coupled [19, 20] thermal analysis revealed two stages processes, first being mainly dehydration and the second mainly deacetylating followed by chain scission.

Our in-deep comparative study on the structure of some polyvinyl alcohols, used in polyvinyl chloride technology, began in two previous papers. We presented the correlation of the degree of hydrolysis measured by the chemical method with the degree of hydrolysis determined from IR and NMR spectra [21] and the results of our investigation on the microstructure of some partially hydrolyzed polyvinyl alcohols used in PVC-S technology in terms of their degree of *blockiness via* UV and <sup>1</sup>H-NMR spectra [22].

In this paper, we present the thermal stability and the degradation pattern of partially hydrolyzed polyvinyl alcohols, discussed in correlation with their blockiness and hydrolysis degree.

### Experimental part

#### Materials and methods

Samples P1-P4, are commercially grades of water soluble PVAs, with 70-88 mol % degree of hydrolysis, used as primary suspension agents in PVC-S technology. Samples S1-S5 are alcohol soluble, commercially and in-house produced PVAs, with 40-60 mol % degree of hydrolysis, with the destination of secondary suspension agents in PVC-S technology. Among these, S3 has been obtained in laboratory by the alkaline alcoholysis of polyvinyl acetate in methanol, according to our method [23] and S5 was obtained in laboratory by the alcoholysis of polyvinyl acetate 50% in methanol in the presence of sulfuric acid (10%) at reflux temperature. Sample R1 is in-house produced PVA, used as reference for its high degree of hydrolysis of 88% mole. The composition and physical properties of the PVA samples listed in table 1 were determined according to the methods presented in our previous papers [21, 22].

Thermal analysis was carried out on dried, pressed and conditioned samples (24 h at 40°C and 0.1 torr) using a simultaneous TGA-DSC, MS hyphenated system, model NETZSCH STA 449C Jupiter /MS 403C Aeolos Mass Spectrometer, in He atmosphere, at a heating rate of 5°C/min.

### Results and discussion

The thermal behavior of PVAs depends only marginally on the average hydrolysis degree. As can be seen in table 2, the samples of PVAs, having a higher degree of hydrolysis (P1-P4 and R1), exhibit only two degradation stages (2 and 3), with an Onset 2 temperature lower by 10°C than the samples of PVAs having a smaller degree of hydrolysis (S1-S5).

At high degree of hydrolysis, the increased blockiness (samples P4 and R1) results in a reduced weight loss in Stage 2 but it increases in Stage 3.

In the degradation of S1-S5 samples series, the blockiness plays an important role. The samples with increased blockiness (samples S1, S3 and S4) behave

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**Table 1**  
CHARACTERISTICS OF PVA SAMPLES

Parameter \ Sample	P1	P2	P3	P4	R1	S1	S2	S3	S4	S5	
	Hydrolysis degree (mol %)	85.01	74.03	80.12	87.52	88.4	56.43	47.8	51.05	57.92	55.85
Average polymerization degree	1500	530	1850	1570	1185	185	215	184	206	218	
Average molar weight (SEC)	$M_w$	76100	29300	97700	77900	59100	11700	14400	12100	13200	13800
	$M_n$	42500	13200	53000	40800	28000	3230	4420	3540	3730	3990
	polydispersity	1.79	2.22	1.84	1.91	2.11	3.63	3.25	3.42	3.54	3.45
K value (viscosimetry)	70	46	79	71	63.7	20	26	25.5	25	24	
Absorbance of iodine complex		0.53	0.53	0.30	0.40	0.62	0.43	0.21	0.28	0.35	0.16
	$\lambda$ (nm)	639.9	631.2	635.9	638.6	626.1	622.4	603	604	620	590

Sample	Initial loss %	Onset 1 °C	Stage 1 loss %	Onset 2 °C	Stage 2 loss %	Onset 3 °C	Stage 3 loss %
P1	3.96	-	-	273.3	58.55	407.4	24.9
P2	3.08	-	-	276.0	62.69	419.2	23.64
P3	2.11	-	-	280.0	65.67	417.2	25.42
P4	2.42	-	-	281.9	58.79	414.0	33.08
R1	3.50	-	-	285.4	59.39	413.5	28.65
S1	3.60	-	-	288.2	63.29	394.4	24.13
S2	1.03	216.4	28.2	307.2	33.69	412.5	28.05
S3	2.64	-	-	286.8	63.64	413.6	25.48
S4	2.69	-	-	285.1	62.92	409.2	21.85
S5	3.22	224.9	25.19	308.9	35.05	411.3	28.14

**Table 2**  
WEIGHT LOSS STAGES AND DEGRADATION ONSET TEMPERATURES FOR THE ANALYZED PVAs

similarly to P1-P4 and R1 samples of PVAs with high blockiness, except the Onset 2, increased by 10°C. The PVAs with lower degree of hydrolysis and low blockiness (samples S2 and S5) present a completely different degradation pattern. The decomposition starts at very low temperature (around 220°C) with a supplementary stage, as if the Stage 2 is divided in 2 separate stages. The Onset of stage 2 increases by 20°C but the cumulate weight loss of stages 1 and 2 is equivalent to the weight loss of stage 2 of the other samples.

A closer look at the decomposition fragments, presented in figure 1 as representative example, shows a similar behavior for both types of highly hydrolyzed PVAs as well as for the PVAs with lower hydrolysis degree but with high blockiness (S1, S3 and S4).

In the initial stage, below 100°C, the associated water is liberated, the weight loss remaining below 4%.

Over 100°C begins the de-acetylating (fragments  $m/z=15$ ; 43 and 44) but the weight loss is below 0.2%. This process stops around 190°C. It is unclear if it is really de-acetylating or is a liberation of some trapped methyl acetate remained from alcoholysis.

Over 220°C a complex elimination of structural water ( $m/z=18$ ), formaldehyde ( $m/z=30$ ), de-acetylating ( $m/z=15$ ; 43 and 44) and elimination of benzene-like fragments ( $m/z=77$ ) represent the characteristics of the Stage 2 of degradation. This pattern indicates a main chain

scission at all types of units (acetate, alcohol or polyene resulted from eliminations).

In the Stage 3 of degradation the relative weight of the fragments of Stage 2 diminishes, the main fragment is  $CO_2$  ( $m/z=44$ ) accompanied by higher aromatic fragments, like toluene ( $m/z=91$ ).

In the case of low hydrolyzed and reduced blockiness samples S2 and S5, these not only exhibit a particular three-stage degradation, but the fragments evolved in each stage differ as well.

In the initial stage, below 100°C, no more associated water is liberated, consistent with diminished association in hydrophobic random copolymer.

The de-acetylating (fragments  $m/z=15$ ; 43 and 44) begins before 100°C and the weight loss is below 3%. This process stops earlier, around 150°C.

Over 200°C a complex elimination of structural water ( $m/z=18$ ), formaldehyde ( $m/z=30$ ), de-acetylating ( $m/z=15$ ; 43 and 44) and important elimination of benzene-like fragments ( $m/z=77$ ) represent the characteristics of the newly presented Stage 1 of degradation. This pattern indicates again the main chain scission at all types of units (acetate, alcohol or polyene). The presence of acetyl/acetic acid fragments ( $m/z=59/60$ ) is an indication that the frequent vicinity of acetate-alcohol units favors internal elimination of acetic acid. Almost all the structural water is eliminated in this first degradation stage. No higher aromatic fragments are formed in this stage.

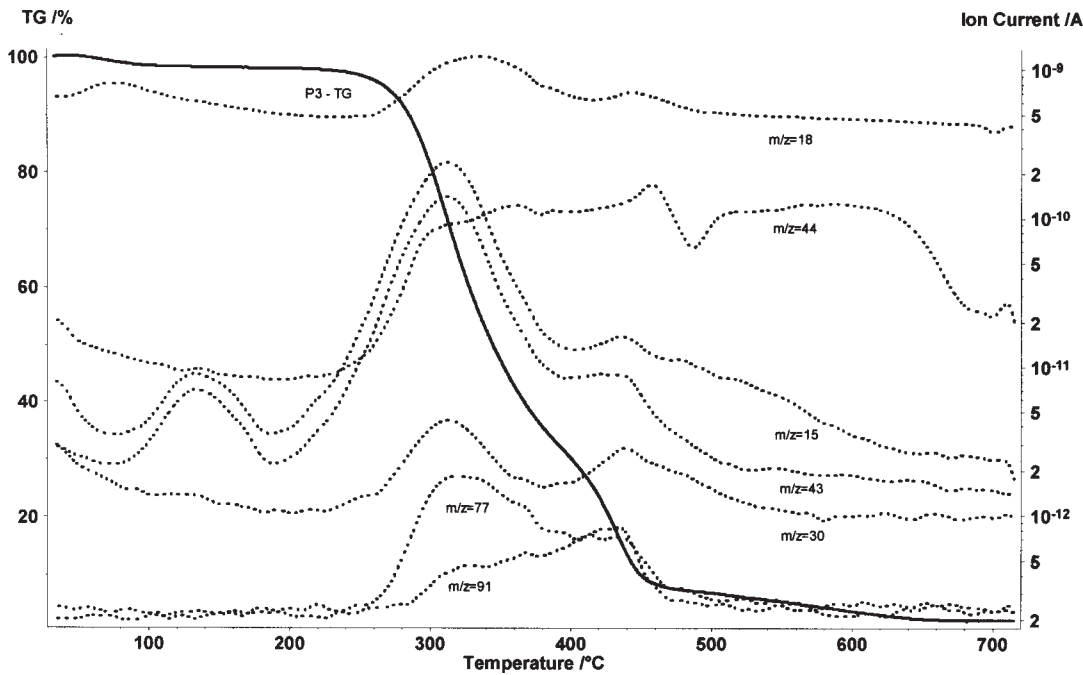


Fig.1. Typical thermogravimetric analysis of highly hydrolysed PVA with high blockiness  
TGA of sample P3 - continuous line; MS fragments - dotted lines, labels below curves

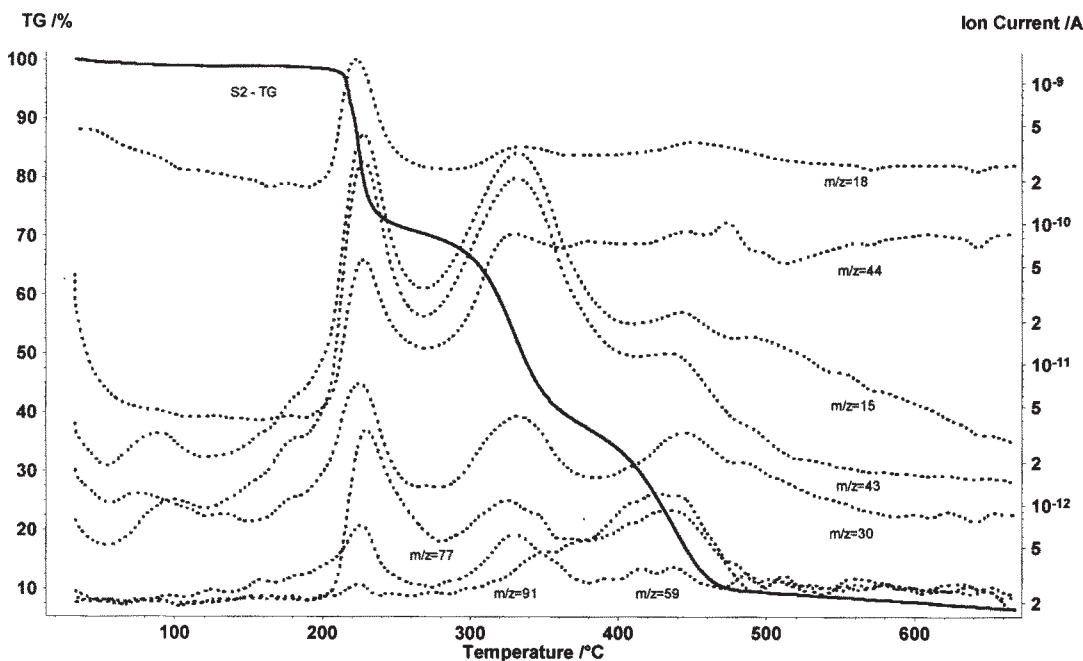


Fig. 2. Typical thermogravimetric analysis of low hydrolysed PVA with reduced blockiness:  
TGA of sample S2 - continuous line; MS fragments - dotted lines, labels below curves

Degradation in stage 2 continues following the same general pattern but water elimination is insignificant while higher aromatic fragments like toluene ( $m/z=91$ ) are present in low concentration

In the Stage 3 of degradation the relative weight of the fragments of Stage 2 diminishes but the fragments corresponding to acetate and alcohol are still present. Nevertheless, the main fragment is  $\text{CO}_2$  ( $m/z=44$ ) accompanied by higher aromatic fragments, like toluene ( $m/z=91$ ).

The degradation of this type of PVAs pays tribute to the high concentration of mixed triads, expanding the mixed fragments all over the degradation range. The multi stage process, very well defined, is more likely consistent with the large number of end groups and numerous molecular populations since the molar weight is quite low and the molar weight distribution is large (over 3).

The glass transitions of the polyvinyl alcohol segments were measured for all the analyzed samples and are presented in table 3. For both type of PVAs with high and

low hydrolysis degree, at a similar molar weight and degree of hydrolysis, samples P1 versus P4 and S1 versus S5 respectively, the Tg decreases when the blockiness increases. This is in agreement with the increased mobility of the longer polyvinyl acetate sequences.

The influence of the molar weight on Tg is somehow obscured but for PVAs with similar hydrolysis degree and blockiness, samples P4 and R1, the higher the polymerization degree the higher is the Tg. The attempt to fit the Tg versus hydrolysis degree using one of the monotonous correlations [24, 25], previously applied for copolymer compositions, failed probably because of the strong hydrophilic and hydrophobic interactions acting in PVAs.

The melting temperature of the PVA phase in highly hydrolysed samples of PVAs increases parallel to the hydrolysis degree while the melting enthalpy has a complex behaviour, depending on molar weight, blockiness and hydrolysis degree.

**Table 3**  
GLASS TRANSITIONS AND MELTING POINTS FOR THE  
ANALYZED PVAs

Sample	T <sub>g</sub> °C	Melting point °C	Melting enthalpy J/g
P1	49.8	187.2	22.65
P2	49.2	156.3	18.53
P3	50.0	177.0	28.91
P4	52.2	189.9	39.43
R1	49.8	190.3	25.85
S1	46.9	-	-
S2	49.8	-	-
S3	49.2	-	-
S4	51.5	-	-
S5	51.1	-	-

### Conclusions

The thermal stability of the PVAs is strongly influenced by the chain microstructure and the hydrolysis degree. All the samples with high blockiness or those with low blockiness but high degree of hydrolysis are quite stable over 220°C. Their degradation follows two stages as previously reported in literature.

The PVAs with low blockiness and low hydrolysis degree are more unstable, their three-stage degradation begins with a strong elimination of water and acetyl fragments before 200°C. This may impair on the melt processing of PVC.

Contrarily to previous reports, claiming that dehydration is the first elimination, the degradation starts at both acetate and alcohol units, regardless the hydrolysis degree or blockiness of the PVAs.

The DSC parameters, the T<sub>g</sub>, melting enthalpy and melting temperature, are under very complex influences of all molecular characteristics (molar weight and distribution, sequence distribution or blockiness and hydrolysis degree). No straight-forward correlation could be extracted from the available data.

At this point the TGA can be used as systematic method of characterization of PVAs but not the DSC.

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