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What is This?

Polyvinyl Alcohol Melt Processing

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ABSTRACT: The melt processing behavior of polyvinyl alcohol (PVOH) acquired by polyvinyl acetate solution and suspension hydrolysis is studied. It is found that the PVOH obtained by suspension hydrolysis is much more suitable for melt processing because of the shape and size of the particles and of the chemical and morphological homogeneity. These advantages increase the practical importance of the suspension hydrolysis technology as compared to the solution.

KEY WORDS: polyvinyl alcohol, melt processing, solution hydrolysis, suspension hydrolysis.

INTRODUCTION

THE MOST KNOWN technologies for polyvinyl alcohol (PVOH) manufacturing are based on polyvinyl acetate (PVAc) hydrolysis, in methanol solution, in the presence of a small amount of sodium hydroxide or sodium alcoholate. The processes can be continuous and can be smoothly carried out in a powerful masticator, such as a Werner-Pfleiderer unit. After the synthesis, the PVOH is separated from the reaction mixture, dried, and milled [1,2]. This procedure presents drawbacks related to the degree of hydrolysis and equipment. The reaction cannot be controlled by preliminary analysis. In addition, alcoholysis should be conducted in a high-power unit that is able to

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break the gel, such as screw mixers. In addition, the concentration of PVAc lacquer subjected to hydrolysis cannot be higher than 20% [1,2].

These disadvantages were eliminated by using a suspension hydrolysis also in the methanol solution of PVAc to obtain beaded PVOH. In these conditions, hydrolysis occurs at the level of the beads formed by lacquer stirred dispersion, while the formation of compact gel and reactor blocking phenomena are fully eliminated. The method provides possibilities for controlling the degree of hydrolysis by the rapid determination of methyl acetate in the reaction medium. The other main advantage of this process is the decrease by three to five times of the power consumption due to the avoidance of the gel formation. Another advantage is that the procedure yields the desired bead size [2,3].

EXPERIMENTAL

PVOH obtained by PVAc solution (PVOH₁) and suspension (PVOH₂) hydrolysis was studied. First of all, for the two polymers, the particle size distribution was determined according to [4]. Then, considering the particle size distribution, using a classical routine, each type of PVOH was separated into fractions. Each fraction was characterized by determination of:

- the particle shape optical microscopy at 71,237, and 250 magnification;
- the saponification index in accordance with [5];
- the hydrolysis index in line with [5];
- the tacticity. According to [1,6], the absorption from 916 cm⁻¹ is correlated with a syndiotactic structure and those from 850⁻¹ with a frame vibration. By reporting the 916 cm⁻¹ IR absorption at those from 850 cm⁻¹, the polymer isotacticity and syndiotacticity can be determined. The report values of 0.3–1.2 demonstrate that 20–60% of the polymer is by an isotactic type and 43–68% by a synditactic type [6]. The IR spectrum was recorded on a Perkin Elmer 75 IR spectrophotometer in the 400–4000 cm⁻¹ range;
- the thermal properties by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements, in keeping with [7]. The DSC recordings were carried out on a Du Pont 990 DSC analyzer in a procedure with three steps: controlled heating (1), cooling (2), and a second controlled heating (3). The sample was heated from 30 to 220°C with a heating rate of 10°C/min. After 10 min holding at 220°C, the sample was cooled with the same ratio until 50°C. Then a new heating in the same condition was carried out.

The ATG curves were registered on a Q-1500 D derivatograph, in air, in the 20–500°C temperature range, with a heating rate of 10°C/min;

- the insoluble index defined as the reticulated or partially hydrolyzed polyvinyl acetate content – according to [5];
- the ash, naturism, insoluble, and volatile content in line with [5];

After formulation with the same plasticizing formula, the two types of PVOH were melt processed by:

- Brabender mixing with the recording of the temperature-time-torque dependence;
- extrusion into 0.7 mm tapes, on a Gottferd extruder, equipped with a screw by 687 mm length and 30 mm diameter. The extrusion temperatures were 100-120°C;
- blowing into film, with and without melt straining, on an Yvroud extruder equipped with a compressing screw by 792 mm length and 40 mm diameter and straining sieves with 200 or 600 eyes/cm^2 . The extrusion conditions: temperature $120-140^{\circ}$ C and the rate 40 rpm.

RESULTS AND DISCUSSION

Particle Size Distribution

The values presented in Table 1 show that the particle size distribution of the analyzed PVOH depends on the manufacturing procedure.

	Content (%)	
Sieve (eyes/mm)	PVOH ₁	PVOH ₂
1.0	0.22	_
0.5	20.33*	_
0.4	4.86	19.66*
0.315	14.4*	30.8*
0.25	6.208	12.25*
0.2	17.7*	21.84*
0.125	6.207	-
0.16	17.82*	6.74
0.1	9.067*	4.065
0.071	0.36	0.3886
0.063	0.61	0.4185
0.009	0.032	-
0.008	2.19	-

Table 1. Particle size distribution of PVOH₁ and PVOH₂.

*The main fractions.

The two types of PVOH have different particles size distributions. The solution hydrolysis-obtained PVOH (PVOH₁) has the broadest particle size distribution and contains 0.1% particles with small diameters (maximum 0.1 mm), 40% particles with 0.1–0.2 mm diameter, and 40% particles with \geq 0.25 mm diameter. The suspension hydrolysis-obtained PVOH (PVOH₂) contains mainly particles with a diameter >0.2 mm. These differences were determinated by the mechanical shredding of the polymer in the case of solution hydrolysis technology and by the special topo-chemistry of the hydrolysis reaction, governed by the interfacial tension in the case of suspension hydrolysis technology [8]. This broad size distribution will negatively affect the melt processing because of the dependence of the fusion heat on particle diameter.

The PVOH Particle Shape

Figures 1 and 2 present the optical micrographics of the two types of PVOH particles. It is observed that the particle shape depends on the PVOH manufacturing procedure. The PVOH₁ particles are strongly irregular and stretched, and those of PVOH₂ are spherical. Besides the particle diameter, their shape can settle important differences in the melt processing.

Chemical and Morphological Structure

The hydrolysis and saponification indexes of the two types of PVOH are slightly different (Table 2). These differences are within the limit of experimental error, and they can be a consequence of the way in which



FIGURE 1. The $PVOH_1$ particle shape.

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FIGURE 2. The PVOH₂ particle shape.

Table 2. The hydrolysis (HI) and saponification (SI) indexes of PVOH₁ and PVOH₂.

	PV	OH ₁	PVOH ₂	
Particle size (mm)	Н	SI	н	SI
0.040	88.57	131.38	88.26	135.37
0.063	89.47	122.02	87.18	145.62
0.500	89.86	118.04	87.12	146.29
1.000	89.16	125.18		

the hydrolysis reaction was carried out. It can be observed that $PVOH_1$ has a hydrolysis index greater than $PVOH_2$. The saponification index is high in the case of $PVOH_2$.

All the IR spectra have similar characteristics [9,10]. The analysis of these spectra demonstrates that the chemical structure of the solution hydrolysis-obtained PVOH is more homogeneous and, that there are small differences between the PVOH₁ and PVOH₂ chemical structures. These spectra confirm the greater hydrolysis degree and the smaller saponification index of PVOH₁, which was observed in chemical measurements. For both polymers, the spectra show small dependence on the particle diameter, especially for solution hydrolysis-obtained PVOH. Both PVOHs contain, in different numbers small ramifications, which are greater for PVOH₁, where the dependence of this number on the particle diameter is greater.

The tacticities of the two polymers is different and depend on the particle diameter especially in the case of $PVOH_1$ (Table 3). So, the $PVOH_1$ particles of sizes 0.04 and 0.063 mm have a chemical structure of syndiotactic type. Those of size 0.5 and 1.0 mm contain, in equal

	The $916 \mathrm{cm^{-1}}/850 \mathrm{cm^{-1}}$ rapport value / PVOH type		
Particle size (mm)	PVOH ₁	PVOH ₂	
1.0	0.39	_	
0.5	0.31	0.20	
0.063	0.28	0.21	
0.04	0.41	0.24	

Table 3. The tacticity estimation of PVOH₁ and PVOH₂.

quantities, syndiotactic and isotactic macromolecule. $PVOH_2$ has a prevalent syndiotactic chemical structure.

Considering the particle size distribution, the particle shape, and the chemical and morphological structure, it can be appreciated that suspension hydrolysis leads to a more homogeneous PVOH.

Sodium, Insoluble, and Ash Contents

The 1560 cm^{-1} peak from the IR spectra of both polymers is determined by the NaC₂H₃O₂ presence produced following the CH₃COOCH₃ reaction with the catalytic excess. This absorption is greater for PVOH₁ and smaller for PVOH₂. This is confirmed by the Na content, which is three times greater for PVOH₁ as compared to PVOH₂ (Table 4).

If the melting point of $Na_2C_2H_3O_2$ is $324^{\circ}C$, the extrusion is only $140^{\circ}C$. That is why, at the extrusion temperature $Na_2C_2H_3O_2$ is solid. For this reason $Na_2C_2H_3O_2$ can break the obtained film, generated in this way, new melt processing difficulties of PVOH.

The ash content (Table 4) is three times greater for solution hydrolysis-obtained PVOH. The insoluble content does not depend on particle size (Table 5) and is greater for $PVOH_2$ (Table 4).

From the sodium and ash contents, it can be appreciated that the inverse suspension hydrolysis-obtained PVOH is more suitable for melt processing as compared to the other PVOHs.

Thermal Properties

As already mentioned, the DSC analysis was carried out in three steps: controlled heating (1), cooling (2), and a second controlled heating (3). In Figure 3, representative thermograms for $PVOH_1$ and $PVOH_2$ are presented. The differences between the melting temperature

	Content [%] / PVOH type		
Content	PVOH ₁	PVOH ₂	
Natrium	0.42	0.14	
Insoluble	0.08	0.34	

Table 4. The ash, natrium, and insoluble content of the two type of PVOH.

Table 5. The particle diameter (size) dependence of the insoluble content.

Property	PVOH _{1 - 1.0}	PVOH _{1 - 0.5}	PVOH _{1 - 0.063}
Insoluble (%)	0.088	0.089	0.07

along heating curves 1 and 3 are determined by the fact that these curves represent thermal behavior of the polymer with thermal history (curve 1) and without thermal history (curve 3). All the DSC thermograms have similar characteristics [9,10].

It is well known that, even an atactic PVOH, has a greater crystallinity because of the greater number of hydrogen bonds between the hydroxyl groups from different macromolecules (Figure 4) [1]. The values of the main transition temperature for the two polymers are compared in Table 6. The dependence of the thermal behavior on the particle diameter is presented in Table 7. The PVOH₁ melting temperature seems to be more dependent on the polymer thermal history. The glass transition temperature has values of $68-73^{\circ}$ C. The melting takes place over a very large temperature range of $36-39^{\circ}$ C if the particles have greater diameter, and of $45-48^{\circ}$ C if the particles have smaller diameters (Table 8). These results demonstrate great differences between the melting behaviors of particles with small diameters as compared to those with great diameters. This thermal behavior dependence on the particle diameter will determine difficulties in the PVOH melt processing.

Crystallization is a low-intensity process, and takes place at temperatures dependent on the particle diameter. The crystalline content is 15% for PVOH₁ and 22% for PVOH₂. PVOH₂ has a higher crystallization and melting temperature as compared to PVOH₁ (Table 6). Even if PVOH₁ and PVOH₂ have approximately the same $T_{\rm g}$, the crystallization temperature of PVOH₁ is considerably smaller (16°C, Table 7).



FIGURE 3. The DSC thermograms of $PVOH_1$ (a) and $PVOH_2$ (b). (ENDO: a process of thermal energy absorption during a DSC measurement.)



FIGURE 4. Crystalline structure of atactic PVOH [11].

All these data demonstrate significant differences between the thermal behavior of the two studied PVOHs, which will have notable consequences on the melt processing and on the properties of the obtained films. The two studied PVOHs contain 5-6% volatiles

PVOH type	7 _g (curve 3) (°C)	7 _{cryst} (curve 2) (°C)	7 _m (curve 1) (°C)	7 _m (curve 3) (°C)
PVOH ₁	73	123	194	163
PVOH ₂	70	139	187	164

Table 6. Thermal properties of the PVOH fraction with particle size of 0.063 mm as a function of the synthesis procedure.

 T_{g} : glass transition temperature; T_{cryst} : crystallization temperature; T_{m} : melting temperature.

Fraction	7 _g (curve 3) (°C)	7 _{cryst} (curve 2) (°C)	7 _m (curve 1) (°C)	7 _m (curve 3) (°C)
PVOH _{1 - 0.04}	68	136	187	151
PVOH1 - 0.063	73	123	194	163
PVOH _{1 - 0.5}	73	125	197	169
PVOH _{1 - 1.0}	72	129	195	166

Table 7. The thermal properties of the $PVOH_1$ as a function of the particle size.

 T_{g} : glass transition temperature; T_{cryst} : crystallization temperature; T_{m} : melting temperature.

	The melting temperature interval			
Particle diameter (mm)	Beginning (°C)	Melting (°C)	End of melting (°C)	
PVOH _{1 - 0.04}	156	187	204	
PVOH _{1 - 0.063}	161	194	206	
PVOH _{1 - 0.5}	168	197	207	
PVOH _{1 - 1.0}	169	195	205	

 Table 8. The dependence of the melting temperature range on the particle size for PVOH1.

(Table 9), one in the case of PVOH and two for $PVOH_2$. These volatiles which leave the polymer at temperatures between 60 and 140°C (Figure 3, curve 1). That is why the studied PVOH melt processing will require a devolatilization step.

Melt Processing

POLYMER DRYING

The polymer volatiles must be removed in a controlled drying stage that must precede the entire melt processing sequence. Otherwise,



FIGURE 5. The torque dependence on the processing time for PVOH at 190°C.

Particle size (mm)	PVOH ₁	PVOH ₂
0.040	5.48	6.13
0.063	5.78	5.48
0.500	5.89	5.13
1.000	6.28	

Table 9. Volatile content (%) of the studied PVOH as a function of the particle size.

the first difficulties come into view even in the solid-state mixing of the polymers with plasticizers when, at 60° C, the first volatilization takes place. In addition, the calender rolling melt processing cannot be made until ~10 min, when the volatiles are eliminated. If the PVOH is first dried, the mixing of polymer with the plasticizers and the calender rolling can be made in good conditions.

THE BRABENDER PLASTICORDER MELT PROCESSING

The Brabender torque required for PVOH melt processing depends on the particle diameter and mixing temperature (Figures 5–8). Because $PVOH_2$ is mainly isotactic, has spherical particles, and narrow particle size distribution as compared to $PVOH_1$, which is an atactic polymer



FIGURE 6. The torque dependence on the processing time for PVOH at 210°C.



FIGURE 7. The torque dependence on the processing time and particle size for $PVOH_1$ at $190^\circ C.$



FIGURE 8. The torque dependence on the processing time and particle size for $\rm PVOH_2$ at 210°C.

with fibril particles and large particle size distribution, the required energy for $PVOH_2$ melt processing is smaller than that required for $PVOH_1$ (Figures 7 and 8). With an increase of particle diameter, the required mixing energy increases.

PVOH Extrusion and Blowing Melt Processing

After the dry blend mixing of the polymer with plasticizers and other melt processing additives, the resulting blend was extruded into tapes and blown into films, with and without melt straining. It was observed that the polymer particle shape and size distribution induced a great distinction between the melt processing behavior of the two PVOHs.

If the unscreened $PVOH_1$ could not be melt-processed by blowing, the unscreened $PVOH_2$ could be blown, but the obtained film contained many unmolted particles. The blown behavior of the screened PVOH depends on particle diameter. Near the very well-blown polymer fractions that contain particles with small diameters, after a certain diameter, even if the melt processing is possible, the film is periodically perforated by unmolted particles. Depending on the melt temperature, the number of perforations is greater or smaller. If the temperature is increased, the number of unmolted particles decrease but the film becomes rough, probably because of the degradation of the melt appearing through the melting of the small-diameter particles. At small processed temperatures, the number of unmolted particles increases and the film is frequently perforated, even if it has a convenient surface. The film obtained from particles with small diameter of 0.1 mm has a suitable aspect.

It was concluded that, for melt processing into films with suitable aspect and properties, the maximum diameter of the PVOH₁ particle must not exceed 0.1 mm for PVOH₁ and 0.25 mm for PVOH₂. It can be appreciated that the blowing of PVOH₁ is unrealistic because only 10% of the particles have the required diameter. Considering the melt processing behavior, it can be concluded that the proper PVOH synthesis technology is the inverse suspension hydrolysis (PVOH₂).

CONCLUSIONS

- 1. The particle size distribution of the PVOH obtained from solution hydrolysis is much broader as compared to PVOH obtained from suspension hydrolysis. This polymer has 15% crystallinity and requires a smaller Brabender melt processing energy. The PVOH obtained from suspension hydrolysis has a chemical and morphological structure that is more homogeneous. It has 22% crystallinity and requires a greater Brabender melt processing energy.
- 2. The advantages of the suspension hydrolysis over the solutions are:
- better control of the degree of hydrolysis by the rapid determination of the methyl acetate in the reaction medium;
- decrease in power consumption by three to five times due to the avoidance of the gel formation;
- desired bead size; and
- better melt processing of the PVOH obtained.

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