



Spherical pellets exiting an SSP reactor

Influence of PET processing on preforms and bottles

based on an article by Brent Culbert, Senior Process Engineer, Polymetrix AG

Solid State Polycondensation (SSP) has been an integral part in the PET processing chain since the 1970s and is today considered a given in the manufacturing of PET bottles. It complements the melt phase by increasing the molecular weight of PET in the solid state above values that cannot be comfortably reached in continuous polymerisation, eliminates difficulties associated with the stirring of the viscous melt, limits degradation and removes byproducts such as acetaldehyde (AA) and oligomers.

Process parameters	Unit	Resin			
		1	2	3	4*
Intrinsic Viscosity (IV) by ASTM**	[dl/g]	0.785	0.768	0.779	0.800
Total modification (DEG+IPA)	[mol%]	4.65	4.19	3.88	4.57
SSP processing					
Medium	[-]	N ₂	N ₂	N ₂	dry air
SSP residence time	[h]	22	9	17	15-18
SSP temperature	[°C]	203	207	208	180-185
Pellet shape	[-]	spherical	spherical	cylindrical	spherical

Table 1: SSP processing conditions of various bottle grade resins

*SSP conditions not known and therefore estimated

**ASTM: American Society for Testing and Materials

Process conditions, such as temperature and residence time, can vary considerably during SSP. This can be due to differences in the starting IV after continuous polymerisation (CP) or the final IV, which depends on the bottle grade targeted - mineral water or CSD for example, or equipment constraints and throughput variation. To illustrate the influence of SSP on preforms and bottles, four bottle grade resins from four different commercial

production facilities were compared in a standard preform trial at Packaging Technologies & Inspection (PTI) European headquarters in Switzerland. The resins, shown as 1 to 4 in Table 1, all target the mineral water market and do not contain a reheating agent. Their IVs range from 0.77 to 0.80 dl/g (ASTM); level modification varies from 3.9 to 4.6 mol% (DEG+IPA). These differences do not significantly influence the preform results shown. Resins 1,

2 & 4 are all spherical pellets, crystallised directly from the melt; resin 3 is cylindrical and cooled below the glass transition (T_g) before storage and SSP processing.

Generally, the longer residence time and the higher the temperature during SSP, the greater the IV increase. Resins 1, 2 & 3 were all processed under nitrogen N₂ for between 9h and 22h at temperatures over 200 °C. Resin 4, from a Melt to Resin plant (MTR), has undergone a solid-state treatment ("conditioning"), which involves processing under dry air for an estimated 15-18h at 180-185 °C, to remove AA while SSP also occurs.

In Table 2, resin 4, the MTR resin, is clearly shown to differentiate from the other resins in several respects. It has a lower crystallinity, because of lower SSP temperatures, which is typified by a lower beginning of melting, although its melting point and

Resin quality	Unit	Resin			
		1	2	3	4
Pellet crystallinity (av.)	[wt%]	56.3	55.5	58.8	49.7
Colour L*	[-]	88.0	87.9	90.6	83.7
Colour b*	[-]	-2.3	-2.73	-2.14	-0.31
Residual AA	[mg/kg]	0.90	1.4	0.61	1.1
Residual MDO	[mg/kg]	0.67	1.0	0.82	7.7
Antimony (Sb) content	[ppm]	208	240	188	316

Table 2: Bottle grade resin measurements

end point of melting remain similar to the other resins. It is darker (lower L* colour), due to the very high Sb content (>300ppm) and is yellower (higher b* colour) due to processing under dry air at 180-185 °C for long periods of time. Yellowness is an indication of thermo-oxidative degradation. It is assumed that the high Sb content is required to boost reactivity in both the CP and SSP, for making higher IV in the CP and compensating for lower temperatures in SSP, which indicates a lack of flexibility during processing. Generally, the level of contaminants tends to decrease with increasing IV across SSP. Both Resins 1 & 3 easily reach the industry standard for residual AA of <1 ppm indicating sufficient SSP treatment. Resins 2 & 4 have AA values >1 ppm, due to reduced SSP treatment. 2-Methyl-1,3-Dioxolane (MDO) is referred to as "hidden AA", as it can be converted back to AA and ethylene glycol in the presence of water. The MDO level in the MTR resin is around 10 times higher than the other resins; this is thought to be caused by processing under dry air.

Preforming

43g preforms were made at PTI in Switzerland on an Arburg 370C mono-cavity moulding machine. Process parameters were kept the

same for all resins: drying for 5-6 h at 160 °C to less than 10ppm and injection moulding at barrel temperatures of 280 °C. The preform results in Table 3 can be used to compare the behaviour of the different resins, but the results cannot be compared directly to results from production scale preforming. All resins melted out without any issues during preforming. Neither the differing modification levels nor the level of crystallinity level influenced the melt out behaviour of the resins at 280 °C. No significant difference was observed in the melting behaviour of spherical and cylindrical pellets. An IV drop of around 0.02 dl/g was seen in all resins, regardless of solid-state treatment, which is typical during preforming as the resins were all well dried. This would suggest that moisture content, which was the same for all samples, had a more significant effect on IV drop than any difference in molecular weight distribution (polydispersity) between the samples.

The influence of SSP processing can be seen when comparing the combined AA and MDO (mmol/kg) loading of the preforms. Resins 1 & 3, with the longest SSP residence times and highest temperatures, have a much lower overall AA & MDO content, by 25-40%, compared to resins 2 (lowest SSP residence time) & 4 (lowest SSP temperature). A shift in

the MDO and AA balance can also be seen; this is due to equilibration.

The colour of the preforms is directly influenced by bottle grade resin quality. The MTR resin, with a long residence time under air and very high Sb content, results in darker (lower L* colour) and yellower preforms (higher b*). It also has a significantly higher haze level than the other resins; this could be caused by either the high Sb content or, possibly, degradation reactions from the long residence time under air at high temperature.

Summary

SSP continues to prove its value in the PET processing chain. Better management of the IV split between CP and SSP can allow more process flexibility, such as lower Sb contents, and improve preform and bottle quality. Longer SSP times and higher SSP temperatures under N₂ produce a cleaner resin, resulting in lower overall AA and MDO content in preforms and bottles while still maintaining good colour and low haze. SSP processing under dry air has limitations and leads to yellowness, an indication of oxidative degradation, as temperatures increase above 180 °C and residence times are extended to increase IV.

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Preform quality	Unit	Resin			
		1	2	3	4
IV (ASTM)	[dl/g]	0.765	0.747	0.759	0.778
IV drop (ASTM)	[dl/g]	0.019	0.023	0.019	0.021
Haze	[%]	8.89	8.60	8.17	10.69
Colour L*	[-]	82.03	81.56	84.28	76.10
Colour b*	[-]	2.60	3.69	2.70	4.85
Residual AA	[mg/kg]	6.2	9	6.2	6.7
Residual MDO	[mg/kg]	5.9	8.4	8.1	9.9
Total MDO & AA	[mmol/kg]	0.21	0.30	0.23	0.26

Table 3: Preform measurements - Note: Haze and colour measurements made directly on preform; glass preform used as zero reference for haze.