

Stretch blow moulding of mineral filled PET

Noëlle Billon, Jean-Marc Haudin, Camille Vallot, Charles Babin

MINES-ParisTech, CEMEF, UMR CNRS 7635,

BP 207 06904 Sophia-Antipolis, France

^anoelle.billon@mines-paristech.fr, ^bjean-marc.haudin@mines-paristech.fr

Keywords: ISBM, Particles filled PET, Processing

Abstract: Injection Stretch Blow moulding is a two step processing that was designed and optimized mainly using unfilled PET resins. This study focuses on stretch blow moulding of a PET filled with a few percent of sub micronic mineral fillers.

Main effects of fillers are analyzed thanks to DSC, DMA, tensile tests, free blowing on prototype machine as well as stretch blow molding using industrial SBO1 machine. It is demonstrated that fillers increases crystallization kinetics resulting in a reduction of the processing range. Difference in strain hardening induced by fillers makes it necessary to adjust blowing temperature. However main effect occurs during heating phase. Temperature within the preform is much less homogeneous than in PET making thermal gradient totally different if heating protocol is kept unchanged. Once heating is controlled to reach to equivalent thermal gradients as for PET blowing is possible and rather equivalent to that of pure PET.

Introduction

Injection stretch blow moulding is a process that aims at the forming of hollow parts such as bottles. It starts with the injection of a thick preform that is further stretched and blown in a cold mould to obtain the final bottle through two main stages of variable relative importance:

- First, the pre-blowing (or low-blow) period decomposed into two sub-stages:
- The preform is first only (or mainly) stretched to a fraction of the total stretching distance (e.g., low-blow delay here expressed in percentage of total stretching length),
- Then air is inflated into the preform at low pressure (a few bars) during a few hundred of microseconds while the stretching goes on for a while and then stops.
- Second, a higher pressure (a few tens of bars) is imposed during a few seconds to enforce the material against the cold mould (typically 11 °C) and freeze the stretched material.

Prior to these stretch-blowing steps preforms are heated up, most often in a non uniform manner, thanks to IR ovens in which preforms stay by a few tens of seconds whilst electrical power delivered to the IR-lamps can be varied on demand.

To a certain extent, development of this processing technology has been tightly related to the development of PET applications and of PET resins.

Initially applied to pure PET, attempts were made to extend ISBM to filled resins in the recent years. Main objective for the uses of such filled PETs is to improve one property of the bottles (barrier, mechanical etc.) or another. Whatever, precise objectives are, ISBM conditions have to be adjusted to specific behaviour of these new blends.

In this study mineral sub micronic fillers were added to control UV barrier of bottles. It was our goal to analyze process ability of those resins in comparison to that of the matrix.

Material; Effect of the fillers

Blends were obtained with PET matrix of IV 888 using small amounts (a few 10 % in mass) of a master batch where fillers were introduced during synthesis. This resulted in a few percent mineral fillers reinforced PET supplied by Tergal Industry as injection moulded preforms the dimension of which are depicted in top of Fig. 1.

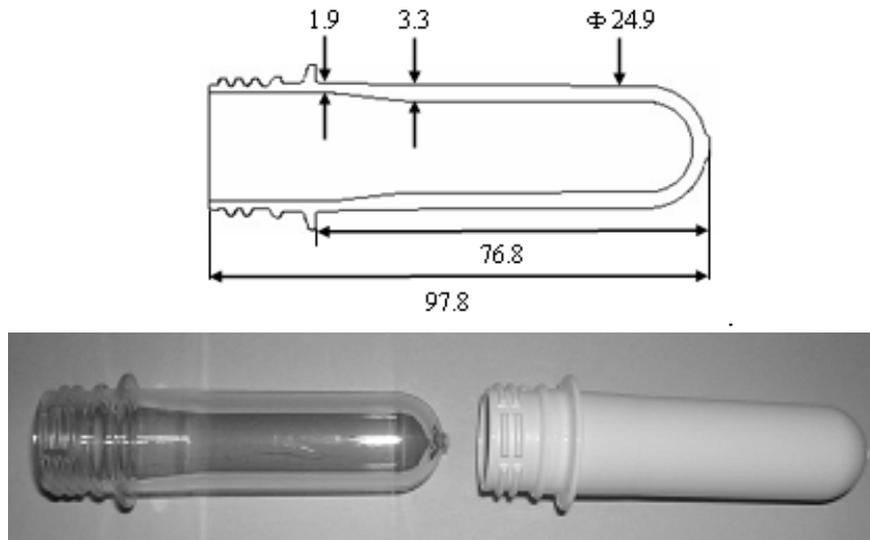


Fig. 1. Dimension of the preforms (top) and comparison between PET matrix (bottom left) and filled PET (bottom right).

As far as PET base materials are concerned, one considers that the material has to remain amorphous by the end of the injection and during heating stage for the bottle to be transparent and for the process to induce beneficial strain induced crystallization. In our case (reinforced PET, bottom right Fig.1.) transparency is no more a goal, but strain induced crystallization is still the way to control final properties of containers. So, first key issue is to ensure ourselves that the material in those preforms is still in the amorphous state.

In parallel, it is well known that inorganic particles such as TiO_2 , SiO_2 , kaolin and talc [1] can act as nucleating agent in PET. Mineral particles used in this study exhibited equivalent effects as demonstrated by DSC measurements (Fig. 2): cold crystallization temperature decreased and crystallization temperature from the melt increased significantly (by 15 °C) as a function of filler content.

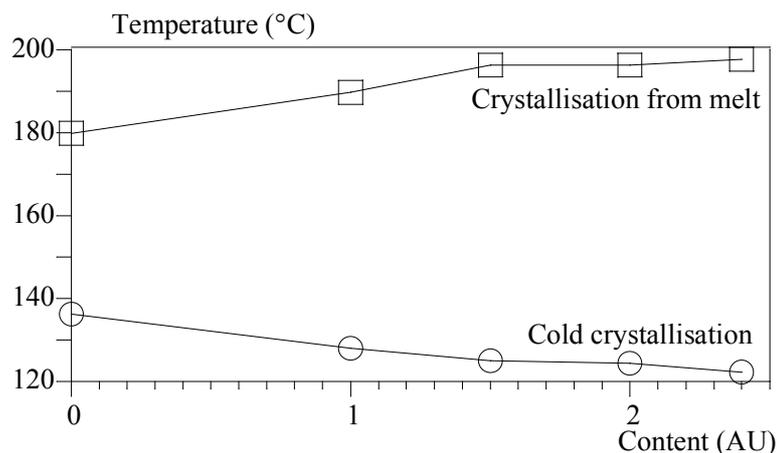


Fig. 2. Crystallization temperatures as measured by DSC with a 10 °/min cooling or heating rate.

Therefore it was more difficult to keep filled PET in the amorphous state and resulting preforms were a little more crystalline than PET ones. However, crystallinity ratio remained lower than 15 % (instead of 6 %, assuming a 120 J/g theoretical enthalpy for fusion), which was acceptable.

For their part glass transition as well as α transition temperatures as measured by DSC and DMA analysis, respectively, were found not to vary with the filler contents (Table 1).

Processing range is the range of temperatures lying above glass transition and below crystallisation temperature. In consequence, processing range can be reduced by almost 10 °C in case of filled resins.

Table 1. Glass and cold crystallisation temperatures for the PET and the blends for heating rate of 10 °/min compared to α transition and cold crystallisation temperatures observed in DMA for a heating rate of 1 °/min and three frequencies.

Content (AU)	DSC, 10 °/min		DMA, 1 °/min, 1Hz		DMA, 1 °/min, 10 Hz		DMA, 1 °/min, 100Hz	
	T _g (°C)	T _{cc} (°C)	T _{α} (°C)	T _{cc} (°C)	T _{α} (°C)	T _{cc} (°C)	T _{α} (°C)	T _{cc} (°C)
0	72	136	82	116	85	116	92	119
1	75	128	84	116	87	119	93	116
1.5	73	125	83	109	86	110	92	107
2	73	124	81	106	85	109	90	110
2.4	72	122	83	110	87	111	96	108

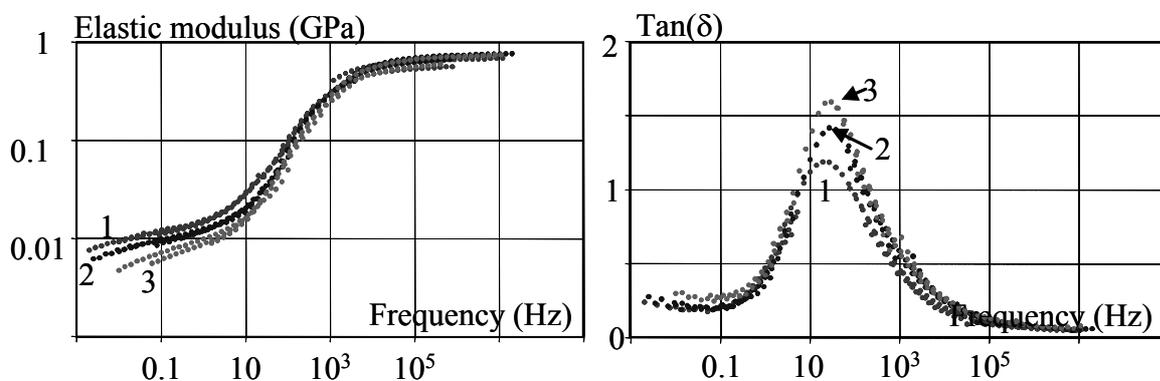


Fig. 3. Master curve for PET matrix (1) and the two extreme filled PETs of Fig. 2 (2, 3). Left: elastic modulus; Right: Loss angle. Reference temperature is 90 °C for the three materials

Additionally, rubbery modulus and damping was a little increased by the fillers (Fig. 3), which could be the trace that blend are a little less rigid and a little more visco elastic than initial matrix.

Finally, tensile tests were performed at constant strain-rate ranging from 10^{-4} to 10^{-2} s⁻¹ and using video extensometer. Those experiments unambiguously demonstrated that strain hardening was a little postponed by the addition of mineral fillers. This was already reported in the literature [2] and was explained by a loss of entanglement due to fillers. For our part it was difficult to totally exclude a possible decrease in average molecular mass due to addition of fillers.

Nevertheless, from these analyses one can conclude that fillers have only a weak effect on PET mechanical behaviour making filled PET a little softer in the processing range. Main effect is the fact that processing range for filled PET is a little narrower due to nucleating effects.

Process ability of filled PET

To address process ability free pre blowing phases were performed using a prototype machine developed and extensively used in previous studies [3-6] but also using a SBO1 industrial machine.

First apparatus allowed reproducing both heating (using IR oven) and stretch blowing of low blow period in conditions close to industry. However, as no mould was used this allowed a better analysis of true extensibility of the resins.

The heating was induced by 5 IR-lamps independently controlled leading to appropriate thermal profile in the preform. The neck of the preform was maintained at room temperature and was used to pick-up the preform from the oven to the stretch-blow apparatus in a way avoiding contact of the polymer with cold surfaces and deformation of the preform due to acceleration, and in a time enabling the stabilization of thermal gradients.

The heating time was initially 26 s as it was the optimal value for PET. In such a condition it was possible to form filled PET and PET matrix to the same final shape (an example is given in Fig. 4). However, processing conditions always have to be adjusted for each resin despite the fact that the resins were not very different according to our laboratory analysis.

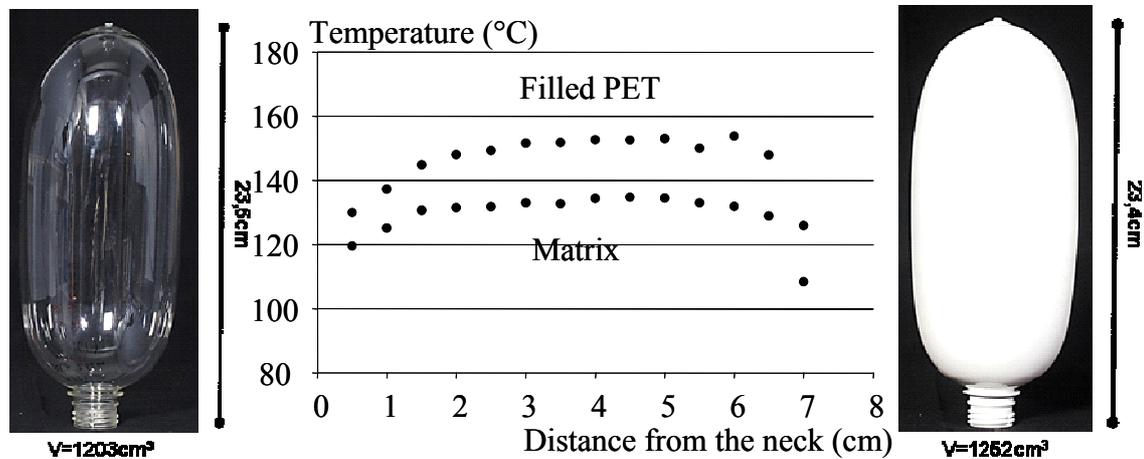


Fig. 4. Thermal profile on the external surface of the preform for free blowing of the matrix (left, higher content in Fig. 2) and of the filled PET (right). Stretching length and low blow delay are 75 mm and 10 %, respectively for both the two materials. Pressure is 7 bar for matrix and 8 bar for filled polymer.

In a general manner blowing of filled PET appeared possible *only if the external surface of the preforms were significantly hotter* than in the case of the pure matrix (Fig; 4). In addition, pressure had to be increased by one bar to blow the blends.

This tends to make blowing of filled PET more “difficult” and a little tricky as thermal crystallization could be possible by the end of heating of the preform. As an example, in the case depicted in Fig. 4 crystallinity ratio in the material at the external surface of the preform increased by 6 % (from 10 to 16 %) whereas crystallinity at the internal surface remained constant.

However, most important observation is the controversial results we obtained: as filled PET was less rigid they should be easier to deform whereas we needed more heating and more pressure?

The clue was the thermal gradient throughout the thickness of the preform. It was possible measuring temperature before blowing on both the external and the internal surfaces of the preform using tooled preforms according to a protocol described in [5] and [6]. Thermal gradient, which is usually of around 15 °C, reached values of 43 °C in case of filled PET. So that external surface was almost too hot whereas the inner surface of the preform was too cold, i.e. below glass transition temperature.

One can conclude that main difference between filled and unfilled resins was related to heating phase.

As a proof, by controlling the heating phase to control both the thermal profile and the thermal gradient, it was possible blowing filled PET in the equivalent manner as pure PET. To achieve that point two parameters were ruled: an increase of the residence time in the oven (Fig; 5) combined to a decrease in the heating power to make heating more progressive and more homogeneous. However, residence time cannot be increased to much as crystallization can constrain blowing (see Fig. 5 60 s).

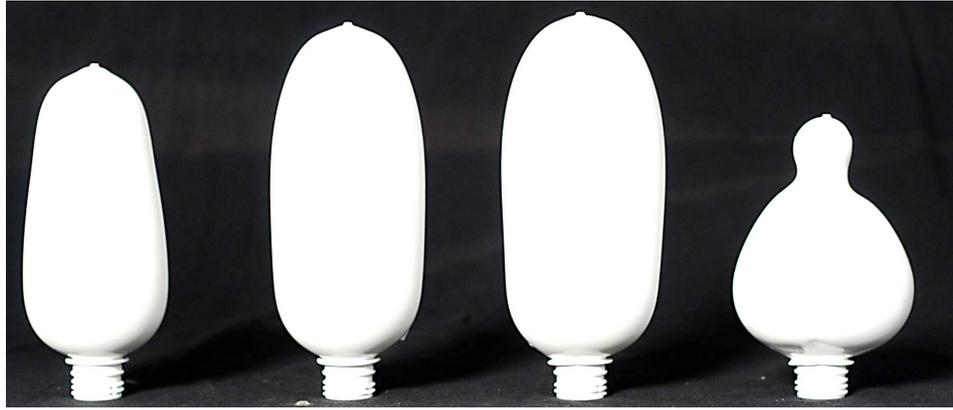


Fig. 5. Comparison between free blown part for the same heating parameters and same pressure but different residence times (45, 50, 55 and 60 s from left to right, respectively)

SBO1 machine is closer to industrial uses as it involves a mould and allows both pre blowing and blowing phases.

Same observations could be made using such industrial machine: once thermal profile and thermal gradient are controlled filled PET can be blown in conditions close to those used for pure PET. However, the presence of the mould tends to reduce a little the difference between the resins.

Discussion

Mineral fillers may appear to induce a drastic change in process ability of PET.

In fact, this can be due to a drastic change in heating kinetics. In our case, no difference in IR absorption could be evidenced. We assume that multiple scatterings, due to fillers, increase the optical path in the material. This makes the heating much more efficient on the external surface and reduces the penetration depth of the IR beams.

So heating protocol has to be adjusted as a function of the resins or, one heating protocol does not allow the correct forming of all the resins.

This latter point is summarized in Fig. 6 where heating process of the lower content-filled resin is applied to pure PET and higher-content filled PET. Obviously, pure PET is a little overstretched whereas higher-content filled PET is under deformed.

This analysis prove, as a secondary conclusion, that relevant study of stretch blow moulding of materials must involve in situ temperature measurements as controlling the oven does not allow controlling temperatures

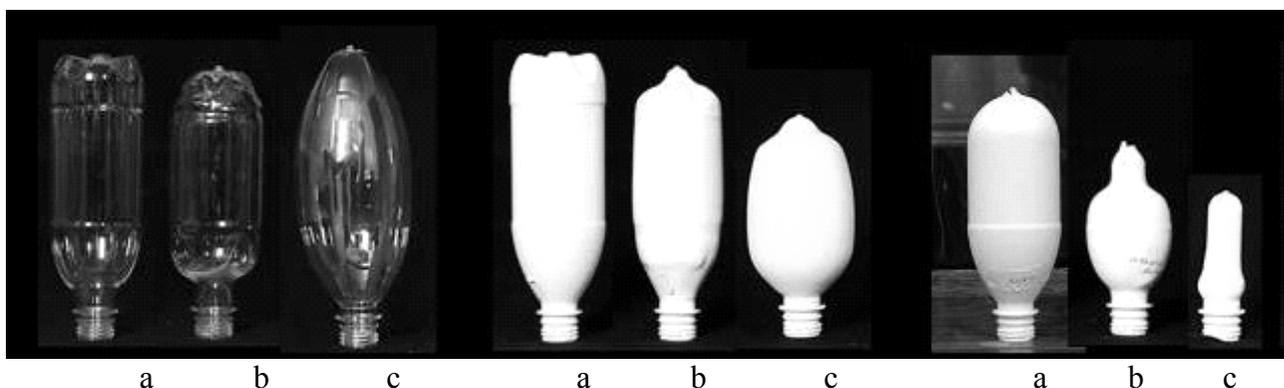


Fig. 6. Comparison between the shapes of bottles after pre blowing and blowing within a mould (a), pre blowing within a mould (b) and free blowing (c) for pure PET (left), lower content filled PET (middle) and higher content filled PET (right).

References

- [1] G. Groeninckx, H. Berghmans, N. Overbergh and G. Smets, *J. polym. Sci.*, 12 (1974) 303-316.
- [2] A. Taniguchi and M. Cakmak *Polymer*, 45(2004) 6647-6654
- [3] E. Gorlier, PhD ENSMP, France (2001)
- [4] E. Gorlier, J-M. Haudin, J-F Agassant, J-L Lepage, G. Perez, D. Darras and N. Billon, *Proc. The 4th ESAFORM Conf.*, (2001) 23-25
- [5] E. Deloye, PhD Mines ParisTech, France (2006)
- [3] M. Picard, PhD Mines ParisTech, France (2008)

Material Forming ESAFORM 2012

10.4028/www.scientific.net/KEM.504-506

Stretch Blow Moulding of Mineral Filled PET

10.4028/www.scientific.net/KEM.504-506.1099