

Influence of the use of mechanically recycled pet in injection stretch blow moulding process (ISBM)

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Abstract. Different mechanically recycled PET issuing from different countries of origin have been studied and compared to a neat one, as a reference. Stretch ability above glass transition temperature was explored towards uni-axial tensile experiments or injection stretch blow moulding (ISBM) tests. It has been shown in that study that rPETs and virgin do present global mechanical behaviours. This similar trend is obvious either in low or large deformations domains. Master curves built for the 5 grades indicated equivalent behaviour between the grades from the glassy to the rubbery state. A controlled stretching campaign confirmed that all grades present visco-hyperelastic behaviours that are similar until the deformation for which the materials start to strain-harden. Uni-axial tensile tests were proved to be efficient to discriminate all grades especially regarding the Natural Draw Ratio (NDR) onset of all grades. The virgin PET does present a lower NDR that comforts the fact that strain-induced crystallization can be easier in the virgin case. This test campaign analysis is confirmed by the injected preforms blowing process where the virgin case grade develops lower blowing volumes because of a sooner NDR. It highlights the fact that forming behaviours of rPET must be slightly adapted compared to virgin PET. For rPET, the effects of loss of molar mass combined with the presence of contaminants could be at the origin of these discrepancies.

Introduction

In Europe, the use of PET has generated more than 4 million tons of waste in 2019 [1]. The “Single-Use Plastics” (SUP) European directive sets a target of collecting 90% of plastic bottles by 2029. The second objective will be to incorporate, from 2025, 25 % of recycled PET in bottles, and 30 % of recycled plastic in all plastic bottles [2]. PET accounted for 8% of plastic consumption in 2007 (15 MT) and only 4.5 MT were recovered, of which 3.6 MT were converted into flakes for recycling. PET used for bottles is the best recycled, however, it is estimated that half of these are not collected and only 7% are collected to make new bottles [3]. There are two main ways to recycle PET, mechanical and chemical. Mechanical recycling is not the most efficient way to recycle PET but is currently the most environmentally friendly [4]. To isolate PET from other polymers upstream of the recycling routes, it is first shredded. Then, PET is separated from other polymers such as polypropylene (PP), polyethylene (PE) and polyvinyl chloride (PVC).

Mechanical recycling of PET consists of regrinding, i.e., crushing, cleaning, melting, homogenizing, a second cleaning of contaminants, and extrusion filtration, all in one circuit. It is inexpensive but the quality is reduced [5]. It is traditionally done in a twin-screw extruder based on shear flow and requiring a long residence time. This results in severe degradation of the polymer [6]. Many impurities have to be removed from labels, adhesives or dust, metals etc. The first cleaning is not sufficient and therefore filtration of the melt is a key step. The removal of impurities must be controlled, especially those from PVC (contained in labels and adhesives) [7]. Finally, a last step called “post-condensation polymerization” at the solid state has to be included most of

the time so as to increase molar mass of the chains that have been degraded over the previous steps. The pellets issuing from this re-processing can be used again to produce new bottles or fibers.

It is necessary that the recycled PET (rPET) retains sufficient mechanical properties but also that it does not contain any hazardous substances. The latter can be derived from the degradation of PET or be unintentionally added substances (NIAS). Apart from their possible danger to human health, they can modify the properties of PET (mechanical, optical, thermal and/or crystalline).

Depending on the end use, from reuse to manufacture other bottles to downcycling (use for less demanding objects), the mechanical properties as well as the contamination of rPET must meet certain requirements. Some of them are listed below [8]: presence of metals (less than 3ppm), presence of polyolefins (less than 10 ppm), intrinsic viscosity (higher than 0.7 dl.g^{-1}), yellowing (less than 20)...

The presence of contaminants is regulated especially if the polymer has to be in contact with a food product. The mechanical properties must be sufficient for the recycled object to fulfill the same role as its counterpart made from virgin material. During the recycling cycle, PET comes into contact with degradation agents such as oxygen, light, mechanical stress, temperature and water. These can cause breaks in the chains and alter the formability and properties of the polymer [9].

The challenge of PET recycling appears today urgent: industrial issues must be understood from the synthesis of polymer to their re-processing, involving recycling steps. PET is a really good candidate for chemical and mechanical recycling. Nevertheless, the presence of contaminants in mechanically recycled PET, added to a possible loss of molar mass, tend to open new scientific and technological questions. The present study purpose is clearly in phase with such a current industrial context. Is stretch ability of these polymers, largely deformed above their glass transition is impacted by recycling? How can a process like Injection Stretch Blow Moulding (ISBM) be optimized regarding the use of recycled PET?

Materials

Two different mechanically recycled PET (rPET) have been chosen for this work. Pellets supplied by two manufacturers Ecolor® and Barik®, issuing either from Europe (named 100R1) or from outside Europe (named 100R2) were considered. The rPET used are transparent rPET. A comparison with a neat PET from Indorama®, acting as a reference, has also been proposed. Blends of both neat and recycled PET have been realized on half to half mass proportion. The blends are referred as “50R1” and “50R2”, involving either the rPET from Ecolor® (R1) or Barik® (R2). Pellets have been injected into square plates of 100x100 millimetres with a thickness of 3 millimetres. Preforms basically used for ISBM process were also injected. All the injection conditions were chosen to ensure the amorphous state of the PET. These conditions were identical for all the five grades (Virgin, 50R1, 100R1, 50R2 and 100R2), arguing on the fact that the rheological behaviour of all grades are very similar.

Results and discussion

In a first time, viscoelastic properties of the five grades were measured by DMTA. Master curves of the storage modulus (E') were built at a reference temperature of 85 °C for the five materials. They are presented in Figure 1.

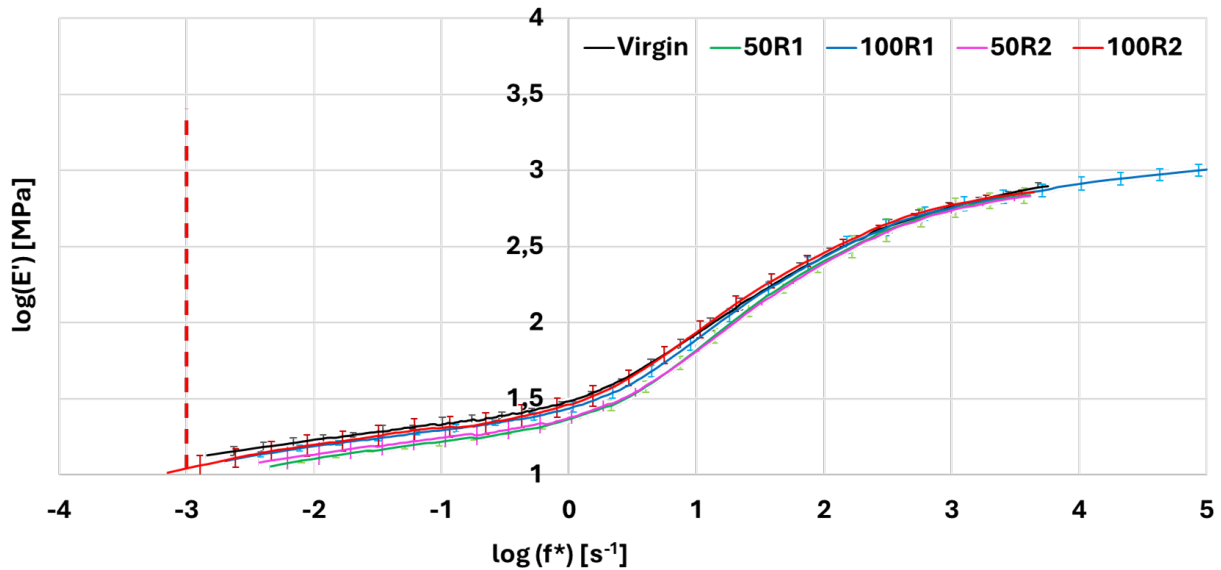


Fig. 1: Master curves of elastic modulus (E'), built at a reference temperature of 85 °C, for virgin, 50R1, 100R1, 50R2 and 100R2 PETs.

The five curves are very similar to each other, taking 85°C as a reference temperature. This reference is a temperature close to the α -transition temperature of each material, taken at the maximum of $\text{Tan}(\delta)$ peak, at a frequency of 1 Hz. To compare all grades, the rubbery plateau height cannot be used. All grades present an obvious transition from a rubbery behavior to a glassy one at the same equivalent frequency or reduced frequency. It is clear, considering all grades having the same inflexion point, that all materials should be sensitive to double effects of the temperature/strain rate couple with the same manner. For higher temperatures explored, it was observed that recycled PETs were able to crystallize easier in quiescent conditions than virgin PET. Lower molar mass combined with the presence of contaminants acting as nucleating agents may explain this phenomenon. The ability to develop strain-induced crystallization (SIC) in dynamic conditions was then investigated towards uni-axial tensile tests, as presented in the following paragraphs.

An equivalent frequency or equivalent strain rate ($\dot{\epsilon}_{eq}$) was chosen at 10^{-3} s^{-1} to explore the mechanical behaviour of the pure grades (Virgin, 100R1 and 100R2) in the large deformations domain. At the end of the rubbery-like plateau, the red dashed line illustrates the position selected, for which the material should be in a rubbery-like state. For this purpose, tensile tests were carried out for a controlled couple of temperature and strain rate associated to an equivalent strain rate of 10^{-3} s^{-1} . Figure 2 presents the true stress strain curves obtained for the three neat materials.

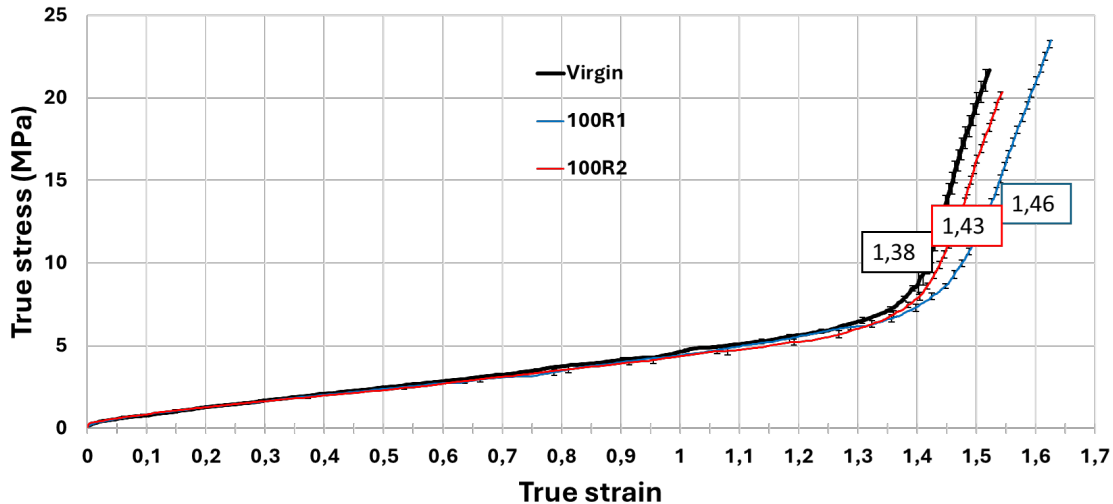


Fig. 2: True stress as a function of the true strain for an equivalent strain rate (ϵ_{eq}) of $10^{-3} s^{-1}$ for the three grades (Virgin, 100R1 and 100R2).

For the three grades presented, true stress strain curves illustrate the visco-hyperelastic response of PET, taken in its rubbery-like state. As expected, the induced crystallization begins at the slope change, and it corresponds to the natural draw ratio (NDR). Before the NDR, all responses are very well-superimposed testifying on the same ability of the three materials in being largely deformed. The stretching conditions that have been selected correspond to the same couple of temperature and strain rate, from a material to another. Equivalent mechanical behaviours that were obvious in the low deformations domain are clearly confirmed in the large deformations domain. As observed from DMTA analysis, the sensitivity to both temperature and strain rate remains equivalent from a grade to another. Moreover, as the α -transition temperature identified in the low deformations domain is the same from a grade to another, it appears that the physical state of the material is the same and clearly rules mechanical response either in low or large deformations domain. The gap from the α -transition is then crucial.

Nevertheless, differences appear for the three grades at the NDR onset. The NDR values are respectively of 1.38, 1.43 and 1.46 for the virgin, 100R2 and 100R1 PETs. Virgin PET is the first to strain-harden followed by 100R2. The last to strain-harden is the 100R1 grade. The dynamic crystallization kinetics that are ruling the strain-hardening are faster and more efficient in the case of the virgin material. Moreover, for deformations higher than the NDR, PETs do not behave in a similar manner. Strain-hardening which is involved by microstructural development such as strain induced crystallization (SIC) presents slight discrepancies as the slope decreases between the virgin, the 100R2 and 100R1. As SIC tends to be disturbed by thermal relaxation, it is possible to observe slight decreases of the strain-hardening slope as it is the case for the 100R1 grade. This behavior is observed when the relaxation phenomenon speed is comparable to the induced crystallization. SIC kinetics involved in 100R1 are obviously lower. Two main reasons may explain this phenomenon. The presence of contaminants or hetero elements can affect PET local chains organization necessary for SIC development. Another reason can be relative to the slight loss of molar mass and possible entanglements density necessary for molecular orientation and stretching.

To complete tensile tests performed at the laboratory scale, blowing tests were performed thanks to a prototype developed at Cemef allowing free blowing of injected preforms, in controlled conditions of temperature. Temperature measurements were carried out on the preform surface,

before blowing, thanks to an infra-red pyrometer calibrated for each grade. In fact, different process temperatures associated to different heating power of infra-red lamps were explored: the temperature varying between 85 °C (above the glass transition temperature) and 115 °C (before cold crystallization). The injection pressure of nitrogen gas was set at 6.5 bars, for a duration of 200 ms. A cooling with air was applied at the end of the blowing so as to simulate the contact of the material on an industrial cold mold. For the different blowing temperatures, the five grades were processed, and the volume induced were measured, after the cooling of the bubble. The Figure 3 presents the evolution of the volumes induced as a function of the process temperature.

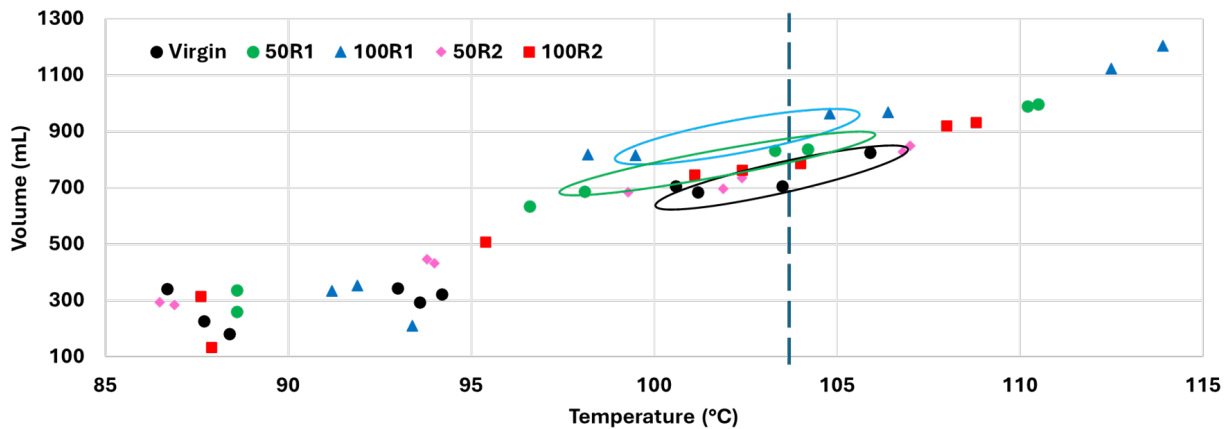


Fig. 3: Volume variation of blown preforms, as a function of blowing temperature, produced with ISBM process, for virgin, 50R1, 100R1, 50R2 and 100R2 PETs.

For the same blowing temperature, the behaviour of each grade does not appear equivalent. The volumes induced with the 100R1 grade are globally higher than the volumes of 100R2 that are higher than the virgin one. This comparison tends to comfort stretch ability of these materials for which the ability in developing SIC appeared easier in the virgin case. The fact that this material is able to crystallize easier will stop the deformation development, leading to lower blown volumes. The solicitations modes associated to ISBM process are mostly bi-axial tensile ones, but the tendency observed in uni-axial tensile mode was relevant enough to class the different materials in their ability to develop SIC.

An optimization of ISBM process could be to find a compromise between a later α -transition temperature and a sooner cold-crystallization temperatures, for recycled PET. Moreover, as recycled PET is less efficient in developing strain-induced crystallization compared to virgin PET, the process should be improved by choosing lower blowing temperature or higher strain rates.

Conclusion

As a conclusion, efforts were made on understanding the mechanical behaviour of recycled materials and their ability in being stretched above the glass transition temperature. The forming range of each material was identified and appears to be slightly reduced in the case of recycled PET according to an earlier cold crystallization. In the large deformations domain, mechanical behaviour was analysed with the same couple of temperature and strain rate, associated to the same equivalent strain rate ($\dot{\epsilon}_{eq}$). All PETs present very similar visco-hyperelastic responses, ruled by the initial physical state of the amorphous PET, ie their gap from α -transition temperature. The main discrepancies are obvious when the polyesters start strain-hardening, developing strain-induced crystallization (SIC). The natural draw ratios (NDR) are different from a material to another which means that the ability to developing mesophase or “organised” phase are not completely equivalent. As a result, both microstructures issuing from stretching or ISBM process

should not be totally equivalent in terms crystalline organization definitions and amorphous phase mobility.

References

- [1] PlasticsEurope, Plastics – the Facts 2020, 2020.
- [2] Directive (EU) 2019/904 of the European Parliament and of the Council of 5 June 2019 on “the reduction of the impact of certain plastic products on the environment”, (Text with EEA relevance) PE/11/2019/REV/1, *OJ L 155*, 12.6.2019: 1–19, *Juin 2019*.
- [3] MacArthur DE. The New Plastics Economy: Rethinking the future of plastics, 2016.
- [4] Majumdar A, Shukla S, Singh AA, Arora S. Circular fashion: Properties of fabrics made from mechanically recycled poly-ethylene terephthalate (PET) bottles. *Resour Conserv Recycl* 2020;161:104915. <https://doi.org/10.1016/j.resconrec.2020.104915>
- [5] Quentin J-P. PET ou polyéthylènetéréphtalate 2004:15. <https://doi.org/10.51257/a-v1-j6488>
- [6] Wu H, Lv S, He Y, Qu J-P. The study of the thermomechanical degradation and mechanical properties of PET recycled by industrial-scale elongational processing. *Polym Test* 2019;77:105882. <https://doi.org/10.1016/j.polymertesting.2019.04.029>
- [7] Aizenshtein EM. Bottle Wastes – to Textile Yarns. *Fibre Chem* 2016;47:343–7. <https://doi.org/10.1007/s10692-016-9691-8>
- [8] Awaja F, Pavel D. Injection stretch blow moulding process of reactive extruded recycled PET and virgin PET blends 2005. <https://doi.org/10.1016/j.eurpolymj.2005.05.036>
- [9] Badia JD, Strömberg E, Karlsson S, Ribes-Greus A. The role of crystalline, mobile amorphous and rigid amorphous fractions in the performance of recycled poly (ethylene terephthalate) (PET). *Polym Degrad Stab* 2012;97:98–107. <https://doi.org/10.1016/j.polymdegradstab.2011.10.008>