

166 Assessment of stretch ability of polymers above Tg: a comparison between poly(ethylene furandicarboxylate) (PEF) and poly(ethylene terephthalate) (PET)

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Abstract

This study aims at developing a rapid protocol to assess and compare stretch abilities of polymers. Two polymers of the same family (polyesters) and designed for food packaging (e.g., injection stretch blow moulding (ISBM)) are used. One is a biosourced polymer named poly(ethylene 2,5-furandicarboxylate) (or PEF) and the second is a petroleum-based polymer named poly(ethylene terephthalate) (or PET). Based on linear viscoelastic analysis as a function of temperature and strain rate (DMTA) relevant range of stretching conditions can be suggested among which, some should lead to equivalent behaviour for the two polymers. This phase relies on typical master curve and time temperature superposition principle. Then, uniaxial tensile tests are performed using DIC analysis up to draw ratio of 10. This paper shows the efficiency of such protocol (previously developed) and allows clear comparison between intrinsic stretch abilities of polymer avoiding artefacts due to different temperature or strain rate sensitivities.

Introduction

Some polymer processing technologies are based on very large deformation. To achieve such forming, the material must exhibit a very specific behaviour that exists only when it is in rubbery state. This requires ruling, both the temperature and the strain rate and their coupling effects. Starting from an unknown material, a simple trial can be unsuccessful and the definition of the optimal stretching conditions can be long. In this study, a protocol developed in the past at CEMEF is used. It is based on the use of time temperature superposition principle and on the reading of classical master curves to adjust stretching conditions. Protocol is validated with two polyesters, PEF and PET, that have a really close chemical structure but a significantly different glass transition temperature. Up to now, PEF uniaxial mechanical behaviour and its microstructure development have been explored by only few authors [1,2,3] whereas PET is now well understood. In industrial process such as films stretching, blowing or thermoforming, polymers have to be highly stretched and draw ratios above 4 are most of the time reached. They are difficult to reach and fit with a really narrow thermoforming range. Depending on the viscoelastic behaviour of these polymers, it is necessary to identify a couple temperature-strain rate ($T, \dot{\epsilon}$). Even for two close polymers, such as PET and PEF, the thermoforming range leading to an equivalent mechanical response is different and the process parameters are difficult to optimize. As the α -relaxation temperature (related to glass transition) measured during a 1 Hz-tensile loading is different for PEF and PET (85°C for PET whereas 100°C for PEF) a simple use of known conditions for PET to PEF is unsuccessful. The goal of this presentation is to show how the use of a master curve can be relevant for providing interesting temperature-strain rate couples ($T, \dot{\epsilon}$), necessary for optimised stretch ability.

Time/temperature principle

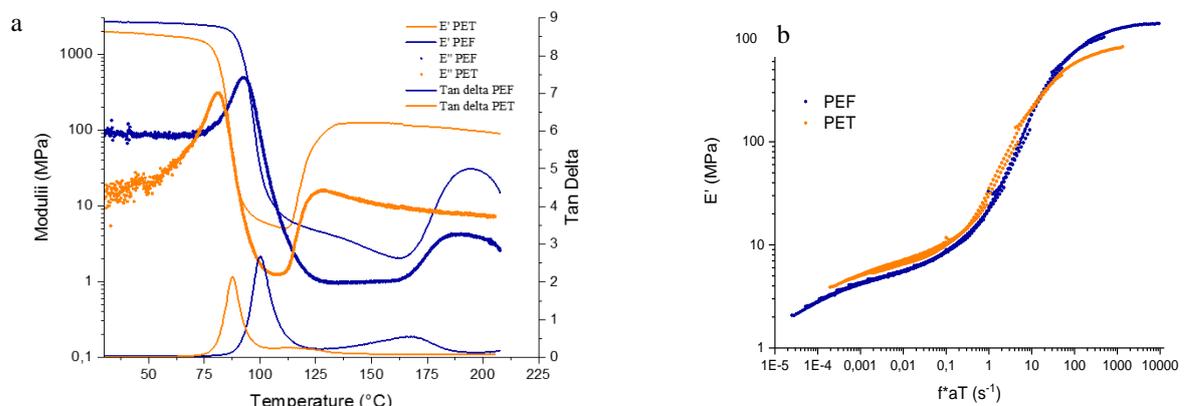


Figure 1: a) DMTA measurement from 25°C to 250°C at 1°C/min at and for 1Hz.

b) PEF and PET master curves at reference temperatures of 100°C and 85°C respectively; E' is the elastic modulus, aT the shift factor and f the frequency.

Linear visco elastic domains of PEF and PET was studied by DMTA (Fig. 1a). A master curve presented on Fig. 1b was built for each polymer, with two different reference temperature close to glass transition temperature. The master curve allows describing the material in the same reference state compared to their specific glass transition. When PEF and PET are compared in the more relevant scale, they exhibit a close

behaviour. Using time/temperature superposition principle, different technological stretching conditions in terms of temperature and strain rate can be chosen, assuming to lead to the same mechanical response. Thus, the master curve and the associated equivalent strain rate chosen can be interesting starting points to determine relevant stretching conditions to be explored, with only very few mechanical testing. This approach is also crucial for experimental facilities use, available in given constrained ranges, playing on the coupled effects of temperature and strain rate.

PEF and PET mechanical behaviour

Based on the time/temperature principle, PET and PEF have been uni-axially stretched using the same equivalent strain rate of $0,1 \text{ s}^{-1}$. Two different temperatures and strain rates have been used to validate the equivalence time/temperature principle (Fig. 2). Digital Image Correlation (DIC) allows the building of true strain/stress curves, arguing that deformations are homogeneous in the sample useful zone (Fig. 3). It may sound that difference in temperature is not that important (e.g. 3 degrees) but owing to thermal sensitivity of behaviour in that range (Fig. 1b), they can represent a significant change in rigidity. It is shown that adjusting strain rate according to Fig. 1a allows to compensate this effect. The mechanical curves are well superimposed for the two materials: the equivalence time/temperature principle is validated at large strain for PET, as previously shown [4] but also for PEF. It means that, for this equivalent strain rate, these two conditions of time and temperature lead to the same mechanical behaviour. This relative new result was also found by a previous author [2], but with other stretching conditions and without local strain measurements. As anticipated, two different technological conditions can be defined easily to make initial behaviour of PEF equivalent to that of PET. Extrapolated to processing this could enable to guide re-adjustment of processing conditions when passing from one material to another. Last new contribution is the direct comparison between PEF and PET. One can observe that both materials exhibit strain hardening but PEF strain hardening is postponed to higher draw ratios. This is a clear illustration of differences in strain induced crystallisation kinetics, which of course is not ruled by time temperature superposition principle.

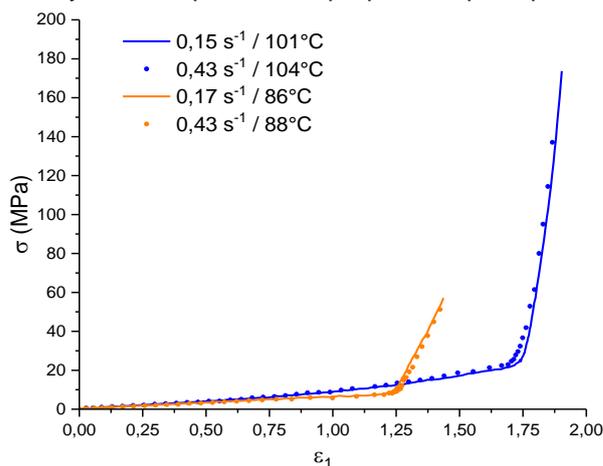


Figure 2 : PET and PEF true strain/stress curves obtained for the same equivalent strain rate of $0,1 \text{ s}^{-1}$.

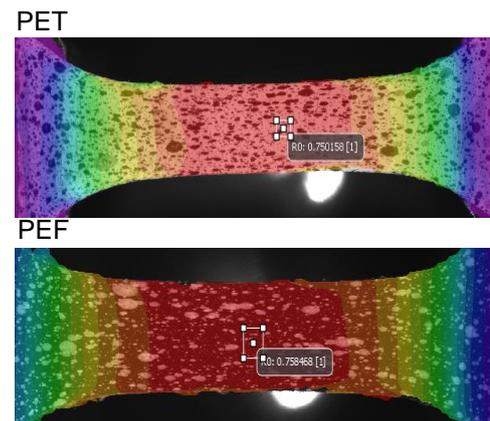


Figure 3 : PET and PEF deformation fields at $\epsilon_{xx} = 0.75$

Conclusion

This work, based on well-controlled mechanical tests, proposes a direct comparison between PEF and PET mechanical behaviour. Even if the materials present very similar chemical structure, they cannot be stretched in the same technological conditions. The use of time temperature principle allows to design those conditions for first focus on stretching range and second compare the two material in the same “physical state” Once the appropriate stretching range has been found for each of them, the mechanical response can clearly be discussed which will be done in further steps of the study.

Acknowledgments

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