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Embrittlement of Poly(butylene terephthalate) Induced by Injection Molding Process

Camille Loyer, Gilles Régnier, Vincent Duval, and Emmanuel Richaud*

Poly(butylene terephthalate) (PBT) dumb-bell samples are injection molded. Tensile tests reveal a brittle behavior for samples manufactured at high temperature (280°C) and long residence times contrarily to those processed at 240°C and 260°C with moderate residence times. Average weight molar mass and DSC measurements are exploited to derive an embrittlement criterion. The comparison with some literature data suggests that samples are mainly degraded by a thermolysis process with minor effect of oxygen.

1. Introduction

Poly(butylene terephthalate) (PBT) is a polyester polymer mainly used for its very good mechanical and electrical properties. Its degradation has been extensively studied through the chemical degradation products identification. Few authors studied PBT degradation during its processing.^[1,2] It is admitted that the degradation during process can be due to temperature, oxygen and water.^[2,3] It is actually well documented that polyesters such as PET and PBT can undergo a hydrolytic degradation^[4-7] but this can be avoided by cautiously drying pellets. Another issue is the thermal degradation in the processing conditions which is the aim of the present paper.

2. Results

2.1. Mechanical behavior

Injection molding gives the opportunity to study material ageing with temperature above the melting temperature. It was decided to perform uniaxial testing at different solicitation rates to study the influence of the later on mechanical behavior.

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Figure 1 depicts different behaviors depending on solicitation speed. Using a previously defined embrittlement criterion^[8] and the less severe injection molding condition (240°C – 4 min), it can be observed that regardless the solicitation rate, injected at 280°C with a 15 and 20 min residence time degrades too much PBT. For families in the “transition area,” 260°C with a 15 min residence time and 280°C with a 4 min residence time, solicitation speed has a greater influence probably because of chains scissions concentration is close to the critical one.

2.2. Macromolecular and morphological behavior

Gel Permeation chromatography (GPC) and DSC measurements showed that both number and weight average molar mass decrease meanwhile crystallinity ratio increases in line with previous studies^[9,10] showing that ageing induced chain scissions mechanism favors the reorganization towards crystalline state. In other words, injected samples are brittle either because of low molar mass and/or high crystalline ratio. This phenomenon is well displayed in Figure 2 where data for samples processed by injection molding are overlaid with data for hydrolytically or thermally oxidized thin films, and confirming the existence of a frontier (depicted by a dashed red line) between regions corresponding to ductile and brittle samples.^[8]

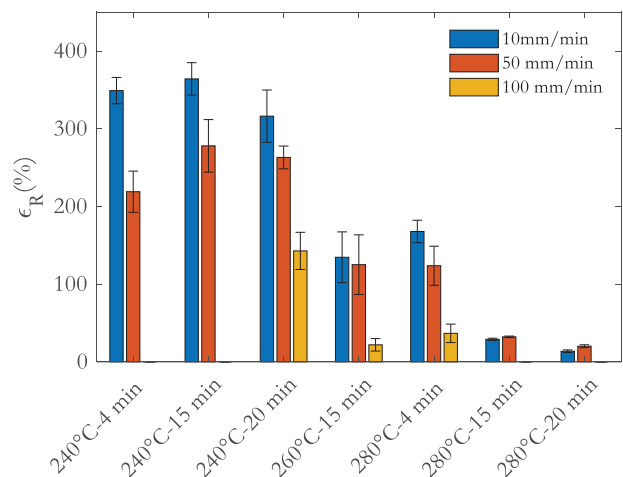


Figure 1. Elongation at break average and average standard deviation for dumb-bell specimens..

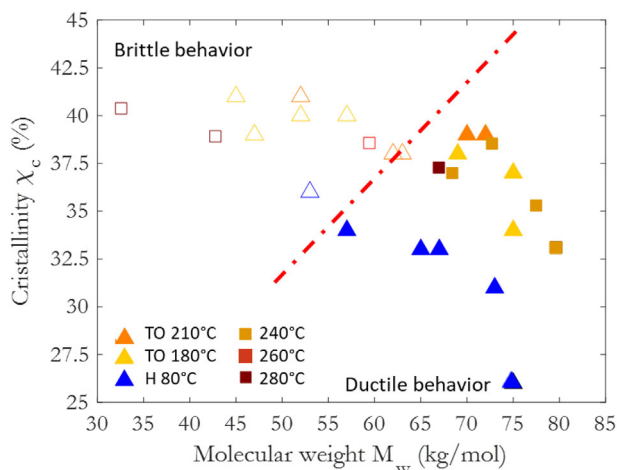


Figure 2. Crystallinity ratio – average weight molar mass map for pressed films from previous study^[8] ($\blacktriangle, \triangle$) and for samples from the current study (\blacksquare, \square). Open symbols correspond to brittle samples and closed symbols to ductile ones.

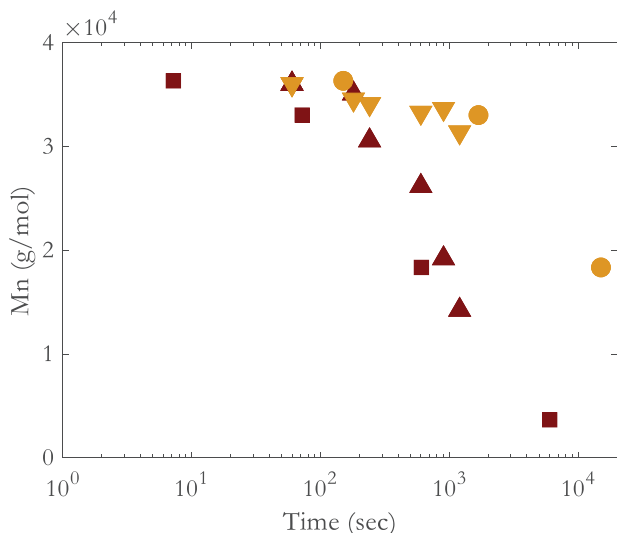


Figure 3. Number molar mass changes in function of time for Devaux's data^[11] (\bullet : 240°C, \blacksquare : 280°C) and experimental data (\blacktriangledown : 240°C, \blacktriangle : 280°C).

In order to better understand to which extent oxygen is involved in the injection induced degradation, it has been decided to compare weight molar mass obtained in this study with the one obtained by Devaux et al.^[11] during PBT thermolysis and exploited by Gervat.^[12] Results are given in Figure 3.

As it can be seen from Figure 3, the experimental data from this work match well with Devaux's^[11] data for pure thermolytical ageing (i.e., absence of oxygen). It can be concluded that injection

molding induces a thermolysis phenomenon, i.e., that the oxidation of methylene groups is here negligible. A possible mechanism is given in Figure 4. As a first approach, we could consider degradation path as followed:

A kinetic model was developed to describe the molar mass changes basing on the polymer decomposition by β -abstraction.

3. Conclusion

Injection molding leads to PBT degradation through chain scissions mechanism and then to material embrittlement. As a consequence, the chain scissions induce a higher crystallinity. Comparison with previous data allows us saying that injection molding degrades PBT mainly by thermolysis phenomenon. The next step will be to determine intermediate degradation product in order to construct kinetic modelling that would help predicting PBT degradation.

4. Experimental Section

Material: The PBT was an injection grade, which was injection molded into dumb-bell using a DK Codim 175/140 with a 36 mm screw diameter. Several barrel temperature sets and residence times were studied. The initial average molar mass values are the following $M_n = 36.0 \text{ kg mol}^{-1}$ and $M_w = 79.6 \text{ kg mol}^{-1}$.

Macromolecular and morphological testing: Morphological changes were followed with a Q1000 by TA instrument.

The crystallinity ratio χ_c (%) was measured from the melting peak enthalpy ΔH_f using $\Delta H_f^\circ = 140 \text{ J g}^{-1}$ for a 100% crystalline PBT sample^[14] according to the following equation

$$\chi_c = 100 \left(\frac{\Delta H_f}{\Delta H_f^\circ} \right) \quad (1)$$

Results were exploited using TA Analysis software.

Gel permeation chromatography: GPC were performed by PeakExpert Laboratory (Tours, France) based on a detailed experiment given in Laun et al.^[15] Molar masses were given as PMMA equivalent.

Mechanical testing: Before any mechanical testing, both dumb-bell were placed at least 24 h in a desiccator at 50%RH at 23°C following the norm ISO 291.

Uniaxial tensile testing on dumb-bell was performed at room temperature using an INSTRON 5581 machine with a 10 kN cell. Three solicitation rates were tested: 10, 50, and 100 mm min^{-1} . No extensometer was used during tests hence only the crosshead displacement was recorded.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

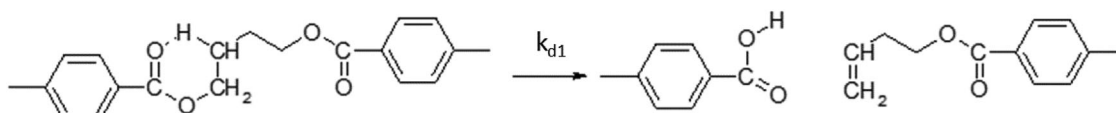


Figure 4. Degradation path proposed by Samperi et al.,^[2] Montaudou et al.,^[13] and Passalacqua et al.^[2] completed with present results

Keywords

chain scissions, injection molding, mechanical properties, Poly(butylene terephthalate)

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