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Using the small punch test to analyse the influence of ultraviolet radiation on the mechanical behaviour of recycled polyethylene terephthalate

Tobias Abt, Guillermo Álvarez, Cristina Rodríguez and Maria Lluisa Maspoch

Abstract
The aim of this work is to evaluate the feasibility of small punch test as a tool for analysing the mechanical response of small plastic parts or specimens. Here, the small punch test was used to study the possible influence of ultraviolet radiation exposure on the mechanical properties of outdoor furniture made from recycled polyethylene terephthalate in the frame of an industrial project with participants from both industry and academia. The industrial project partners prepared four types of masterbatches in order to stabilize the recycled polyethylene terephthalate and to minimize photodegradation as well as colour change in the final product. The masterbatches contained red pigments, antioxidants and ultraviolet absorbers. Flat sample plates were injection moulded from recycled polyethylene terephthalate and these masterbatches. Some sample plates were used as-moulded, some samples received a thermal treatment in order to post-crystallize the bottle-grade recycled polyethylene terephthalate and some other samples were subjected to ultraviolet radiation for 900 h. In the frame of an industrial project, the ultraviolet ageing was performed superficially only on one side of the plates in order to evaluate the colour change. The three sets of samples were analysed by means of tensile tests, differential scanning calorimetry and intrinsic viscosity. However, the irradiated samples could not be tested with tensile tests due to their small size. Therefore, small punch test was used to accurately characterize these small samples. The feasibility of the small punch test as a valid mechanical characterization method of this type of materials was demonstrated by comparing the small punch test results from the unirradiated samples with the tensile test ones. The mechanical parameters obtained from both type of tests showed the same results. Although the used industrial ultraviolet ageing process produced a colour change in the studied recycled polyethylene terephthalate samples, it was possible to verify via small punch tests that the mechanical properties were not affected.

Keywords
Small punch test, recycled polyethylene terephthalate, mechanical characterization

Introduction
The recycling of polyethylene terephthalate (PET) at the end of its life cycle has become a major task in recent years for both industry and academia. This is because virgin PET is one of the most important engineering plastics due to its increasing use in the past two decades for many applications, especially for bottles and fibres. Recycling is the best option to economically reduce PET waste. The other driving force for PET recycling is that PET has a slow rate of decomposition in composting conditions. On the other hand, the price of virgin PET remains relatively stable. Therefore, new and cheaper PET recycling technologies provide the industry with relatively cheaper PET. The major factor affecting the suitability of post-consumer PET flakes for recycling is the level and nature of contaminants present in the flakes. Contamination of post-consumer PET is the main cause of deterioration of its physical and chemical properties during re-processing, which leads to a molecular weight reduction or intrinsic

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viscosity (IV), respectively. Commercial PET has a wide range of IV that varies from 0.45 to 1.2 dL/g; standard bottle-grade PET has an IV of 0.8 dL/g. Recycled post-consumer bottle-grade PET can be reused in various applications such as textile fibres, straps, sheets, containers and even for PET bottle-to-bottle recycling. However, the latter requires super-clean recyclates which are costly. In search for a low-cost application of recycled polyethylene terephthalate (rPET), in the current work, rPET was selected as base material for urban outdoor furniture in the frame of an industrial project with partners from both industry and academia. For outdoor applications, PET needs to be stabilized with additives such as antioxidants and ultraviolet (UV) stabilizers. Unstabilized PET is susceptible to photodegradation which causes a molecular weight reduction and the formation of chemical groups such as carbonyls, carboxyls and hydroperoxides, which in turn lead to brittleness, surface cracks, surface deterioration, loss of transparency, yellowing or colour change. If the photodegradation takes place above the glass transition temperature, then the so-called chemi-crystallization occurs and broken molecules in the amorphous phase may further rearrange. Otherwise, below T_g (i.e. 65–70°C), the degree of crystallinity is not affected by photoageing.

In this way, one of the industrial project partners (namely IQAP Masterbatch S.L., Les Masies de Roda, Spain) prepared four types of masterbatches to stabilize the rPET used in this work. These masterbatches contained red pigments, antioxidants and UV absorbers. Flat sample plates were injection moulded from rPET and these masterbatches in the company installations. Some of these sample plates were further analysed as-moulded, some samples received a thermal treatment in order to post-crystallize the bottle-grade rPET and some other samples were subjected to an industrial process of UV radiation. This type of UV ageing process aims to simulate the solar radiation exposure of outdoor furniture. Therefore, during UV ageing, one half of each plate was exposed to UV radiation whereas the other half was covered with a metal sheet and was therefore protected from UV exposure. These sample plates were the starting material for the work at hand, which aim was to mechanically and thermally characterize as-moulded, UV-aged or recrystallized sample plates in order to see whether colour fastness and mechanical property retention can be ensured in the final product after prolonged UV exposure. However, the UV-aged area of the plates was too small to extract tensile specimens and hence conventional mechanical testing was not possible. For this reason, in the present work, the feasibility of small punch tests (SPTs) is studied in order to accurately characterize these small samples.

The SPT has been a revolutionary procedure for the mechanical characterization of metal alloys since its implementation to determine the evolution of the mechanical properties of these materials during their service life in nuclear reactors. The advantage of the SPT with respect to other tests is the small dimensions of its specimens (usually in form of small discs of 10 mm diameter and 0.5 mm thickness) and, therefore, the low volume of material required for the mechanical characterization. Thus, this test allows to obtain the mechanical properties in case that only a small amount of material is available. The SPT has also been used in the mechanical characterization of different types of materials other than steel and its applicability in the estimation of the tensile properties of different types of polymers has been proved.

During the test, the specimens are firmly clamped between two circular dies and are punched into a circular hole by a hemispherical punch until failure. Figure 1(a) shows a sketch of the SPT and the location of the specimen in the device. As a result of this test, a load–punch displacement curve is obtained (Figure 1(b)) and its analysis provides a series of parameters related to conventional tensile properties. Figure 1(b) shows a typical load–punch displacement plot obtained from the test of a thermoplastic.
polymer, identifying the useful values of load and displacement related to different tensile or fracture test parameters of these types of materials: elastic modulus $E$ (related to the initial slope of the SPT curve, equation (1)), the yield stress $\sigma_y$ (related to the first maximum of the load, $P_m$, equation (2)) and the yield strain $\varepsilon_y$ (related to the displacement at the first maximum of the load, $d_m$, equation (3)). Some of the typical relationships between the aforementioned SPT parameters and the tensile properties are

$$E = \frac{\text{Slope}_{\text{init}}}{t} + \alpha_2$$

(1)

$$\sigma_y = \frac{P_m}{t}$$

(2)

$$\varepsilon_y = \frac{d_m}{t}$$

(3)

being $t$ the initial specimen thickness and $\alpha_1$, $\alpha_2$, $\beta$ and $\delta$ the characteristic material coefficients.

As a summary, and in the frame of an industrial project whose aim was to develop urban outdoor furniture made from recycled PET, this work analyses the possible influence of UV radiation exposure on the mechanical properties of these materials using the SPT. In this way, the UV-aged samples whose small size did not permit the extraction of other types of samples were not only evaluated from an aesthetic point of view by means of colour fastness but also the mechanical property retention. The SPT results are compared to the ones obtained from tensile tests of uniradiated samples in order to ensure the applicability of the SPT for the characterization of these materials.

**Materials and methods**

**Materials**

Recycled post-consumer PET pellets were supplied by Marketing Mix 2011, S.L. (Llagostera, Spain). According to the supplier, the total content of contaminations (PVC, polyolefins, paper, metal, etc.) in the rPET was less than 260 ppm and the tensile properties were as follows: tensile modulus: $2.4 \pm 0.1$ GPa, tensile strength: $54 \pm 1$ MPa, failure strain: $240\% \pm 70\%$, measured at a degree of crystallinity of $9\%$. Tensile properties were determined according to ISO 527 at room temperature and a crosshead speed of 10 mm/min, whereas the tensile modulus ($E$) was measured at 1 mm/min. Four types of PET-based masterbatches were used, namely one containing red pigments (referred to as ‘A’), one containing red pigments and antioxidants (‘B’), one containing red pigments and UV absorbers (‘C’) and one containing red pigments, antioxidants and UV absorbers (‘D’). They were provided by IQAP Masterbatch S.L. (Les Masies de Roda, Spain). Unfortunately, the exact composition of the masterbatches is confidential. Nevertheless, it can be said that the additives were chosen according to the project objectives which were mainly the colour fastness of the urban outdoor furniture when exposed to UV radiation, guaranteeing, in addition, the retention of the mechanical properties of rPET.

**Sample preparation**

Sample preparation was done in the installations of IQAP Masterbatch S.L. Four types of plates, referred to as ‘rPET/A’, ‘rPET/B’, ‘rPET/C’ and ‘rPET/D’, were injection moulded from rPET and 3 wt% of the corresponding masterbatch. All materials were dried at 120°C for 4 h in a DSN560HE dehumidifier (Piovan, Santa Maria di Sala, Italy) with a dew point of $-40^\circ$C prior to injection moulding. Plates with dimensions of $100 \times 75$ mm² and with graduated thicknesses of 1, 1.8 and 2.5 mm (see Figure 2(a)) were injection moulded for accelerated ageing and subsequent industrial colour control using a Victory 110 injection moulding machine (Engel Austria GmbH, Schwertberg, Austria) with a
clamping force of 1100 kN. The mould for these plates was especially designed by IQAP Masterbatch S.L. for colour tests. The mould comprised different thicknesses and surface roughnesses since the colour of plastic parts depends on these features. A melt temperature profile from hopper to nozzle of 275 °C–270 °C–265 °C–260 °C–40 °C was employed for all materials, the mould temperature was kept at 25 °C, and the selected injection speed was 75 cm³/s.

Accelerated ageing was carried out on the above described plates in a Xenon arc test chamber at ambient temperature and humidity. The injection moulded plates were exposed to UV radiation for 900 h. Specifically, one half of each plate was exposed to UV light whereas the other half was protected from exposure (see Figures 2 and 3). The exposed samples were referred to ‘UV’.

Some of the injection moulded plates were recrystallized at 120 °C for 4 h in a convension oven (J. P. Selecta, S. A., Barcelona, Spain). These samples were referred to ‘RC’.

Characterization techniques

Differential scanning calorimetry (DSC) was performed on a Q2000 TA Instruments device calibrated with indium according to the following cycle: heating from 30 °C to 290 °C at 10 °C/min, 3 min isothermal step at 290 °C, cooling to 30 °C at –10 °C/min, 3 min isothermal step at 30 °C, final heating from 30 °C to 290 °C at 10 °C/min. The sample weight placed in the DSC aluminium crucibles was around 8 mg. The cold crystallization and melting temperatures (Tcc, Tm) and corresponding enthalpies (ΔHcc, ΔHm) were determined from the first heating run. The degree of crystallinity (χc) of PET was evaluated from the first heating run according to equation (4)

\[ \chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \cdot 100 \]  

(4)

where ΔHm (J/g) is the measured melting enthalpy, ΔHcc (J/g) is the measured cold crystallization enthalpy and ΔHm⁰ is the melting enthalpy for a fully perfect crystalline PET which is found in the literature to be 140 J/g.¹⁵

The IVs of rPET pellets as well as of injection moulded rPET plates containing masterbatch were measured according to ISO 1628¹⁶ using a Cannon-Ubbelhode viscosimeter in a thermostated bath of 30 °C. Fifty milligram of polymer was dissolved in a mix of phenol and 1,1,2,2-tetrachloroethane (60/40 wt/wt) at a temperature of 80 °C. Four different polymer concentrations were used, namely 0.5, 0.9, 0.3 and 0.2 g/dL. The IV was found to be 0.6 dL/g for the rPET pellets and it decreased to around 0.5 dL/g for the injection moulded specimens. This small degradation was due to the injection moulding process.

The mechanical properties were determined by tensile tests according to ISO 527¹⁷ at room temperature and at a crosshead speed of 10 mm/min on a Zwick Z010 universal testing machine (Zwick/Röll, Ulm, Germany), equipped with a load cell of 11 kN and a contact extensometer to measure strain. A minimum of five specimens were tested at a constant crosshead speed of 10 mm/min whereas the tensile modulus (E) was determined at 1 mm/min. Prismatic specimens with dimensions of 75 × 10 × 2.5 mm³ were cut from the injection moulded plates which were not subjected to UV ageing (see Figure 2(a)). They were tested using a distance between grips of 50 mm and an extensometer reference length of 30 mm.

SPTs were carried out on squared samples of 10 × 10 mm² cut from the 1-mm-thick section of the injection moulded plates, in both areas: exposed and not exposed to UV ageing (see Figure 2(a)). These tests were carried out using an experimental device as shown in Figure 1(a), designed and manufactured by the SIMUMECAMAT research group and mounted on a universal Instron testing machine equipped with a load cell of 5 kN. A punch diameter of 2.5 mm, a hole in the lower die with a diameter of 4 mm (with 0.2 mm corner radius) and a displacement rate of 0.2 mm/min were employed in all these tests. The punch displacement was measured using a 6 mm gage-length COD extensometer attached between the upper and lower dies, as can be seen in Figure 1(a).⁻¹⁴ The thickness of the specimens was obtained as the average of six measurements by means of a precision micrometre and a minimum of six samples was used to characterize each material. Obtained curves were analysed with a MATLAB subroutine specially developed for these material tests that provides the values of the characteristic parameters.

Results and discussion

Images of the four types of sample plates after the accelerated ageing process are shown in Figure 3. As can be seen in this figure, the UV-exposed zone of all the samples showed a slight discoloration due to the radiation. Nevertheless, and as it was verified by IQAP via colorimetry tests, the sample containing masterbatch C retained its colour better than the others.¹⁵

The influence of the four different masterbatches on the rPET mechanical properties was evaluated by
tensile tests and is shown in Figure 4. This figure also shows a representative stress–strain curve of the recrystallized sample containing masterbatch C. Table 1 compiles the tensile properties and the degrees of crystallinity measured in the same zone were the tensile specimens were extracted. Unfortunately, no specimens could be extracted from the UV-aged plates due to the small size of the aged area since only one half of the plates were exposed to UV radiation. For this reason, the SPT was employed in order to mechanically characterize the UV-aged plates as will be shown later.

Regarding the pristine plates containing masterbatch, no significant difference in stiffness and strength was found between the four different compositions (Figure 4). The tensile modulus values were virtually equal and similar tensile strengths were observed. The degrees of crystallinity in the 2.5-mm-thick samples were around 8%–9% for masterbatches B, C and D whereas the one of masterbatch A was somewhat higher. According to IQAP, masterbatch ‘A’ contained a relatively higher amount of inorganic fillers as the other masterbatches. This higher amount of inorganics could have a nucleating effect on rPET, accounting for a higher crystal fraction on rPET/A. Comparing the tensile data from Table 1 to the properties of rPET given by the material supplier (E = 2.4 ± 0.1 GPa, σ_m = 54 ± 1 MPa, ε_B = 240% ± 70%, measured at a degree of crystallinity of 9%), it can be seen that the masterbatch did not affect the crystallinity and hence the mechanical properties. However, the plates exhibited a lower tensile strength and failure strain as compared to rPET, which was ascribed to the prismatic specimen shape and not to the presence of the masterbatch. In contrast, the recrystallized sample rPET/C-RC showed a considerably higher stiffness and strength as compared to the pristine samples. However, the fracture type changed from ductile to brittle and the failure strain decreased to 5%. This was due to the remarkably higher degree of crystallinity induced by the post-crystallization which increased the crystal fraction from around 9% to 30%.

As mentioned earlier, the volume of material subjected to UV ageing was too small to be able to extract tensile specimens. Therefore, it was thought to use the SPT to characterize the UV ageing effect on the mechanical properties of rPET. However, and in order to verify its applicability in this kind of materials, the SPT was also used in the mechanical characterization of all samples that had been characterized by tensile tests, namely pristine rPET/A-B-C-D and recrystallized rPET/C-RC.

Figure 5 shows representative SPT curves of pristine and recrystallized samples and the mean values and standard deviations of the SPT parameters are shown in Table 2. As can be seen, the SPT curves of the pristine materials showed a similar trend as the tensile tested samples. The SPT results demonstrate that the type of masterbatch did not affect the mechanical response of rPET. The four materials exhibited virtually identical SPT curves and therefore similar values of Slope_{ini}, P_{tm} and d_m. In contrast, the recrystallized sample rPET/C-RC showed a stiffer (Slope_{ini}/t) and stronger (P_{tm}/t^2) behaviour due to its considerably higher degree of crystallinity.
These results demonstrate again the direct relationship between the SPT and the tensile test parameters (expressions 1 to 3) as already indicated by other authors, and consolidate the SPT as a valuable mechanical characterization method for polymeric materials, especially in cases where the amount of available material is small, as it was the case of this industrially UV-irradiated material.

It should be noted that all the SPT specimens were extracted from the 1-mm-thick section. Regarding the UV-irradiated specimens, they were placed in the testing device in such a way that the surface directly exposed to the UV radiation (coloured face) faced downwards, that is, making sure that the UV-aged surface was submitted to tensile stresses. In other words, the indenter penetrated the unirradiated sample surface.

Figure 6 shows some SPT curves obtained from the UV-aged samples. In addition, and based on a series of interrupted test, the evolution of the tensile strained surface of a specimen as the test develops is also shown. All the curves exhibited similar values of initial slope, maximum load and displacement at maximum load (see Table 2), and therefore, the effect of UV radiation, if any, was the same for all masterbatches.

Comparing the values of the SPT characteristic parameters shown in Table 2, no significant differences between pristine and UV-aged samples were seen. All the SPT specimens were extracted from the 1-mm-thick section of the injection moulded plates (see Figure 2(a)) and DSC analysis performed on that zone showed a degree of crystallinity of around 10% and 12% for the unaged and UV-aged samples, respectively. In contrast to the crystal fractions of the 2.5-mm-thick samples reported in Table 1, the 1-mm-thick sections of the plates did not exhibit significant differences in crystallinity due to the very fast cooling of thin parts during injection moulding. This means that the crystal fraction of the UV-aged samples slightly increased by 2% due to chemi-crystallization. This crystallinity increase was not sufficient to cause a change in the mechanical properties of the plates due to the UV ageing.

Table 2. Small punch test parameters of specimens cut from 1-mm-thick pristine, recrystallized and UV-aged plates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope ( \text{SPT} / \text{N/mm} )</th>
<th>( P_m / \text{MPa} )</th>
<th>( d_m / \text{mm/mm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>rPET/A</td>
<td>239 ± 20</td>
<td>249 ± 20</td>
<td>1.40 ± 0.26</td>
</tr>
<tr>
<td>rPET/A-UV</td>
<td>244 ± 13</td>
<td>240 ± 9</td>
<td>1.22 ± 0.23</td>
</tr>
<tr>
<td>rPET/B</td>
<td>248 ± 6</td>
<td>247 ± 9</td>
<td>1.38 ± 0.12</td>
</tr>
<tr>
<td>rPET/B-UV</td>
<td>249 ± 8</td>
<td>257 ± 12</td>
<td>1.38 ± 0.13</td>
</tr>
<tr>
<td>rPET/C</td>
<td>247 ± 11</td>
<td>259 ± 7</td>
<td>1.39 ± 0.12</td>
</tr>
<tr>
<td>rPET/C-UV</td>
<td>245 ± 6</td>
<td>257 ± 2</td>
<td>1.33 ± 0.06</td>
</tr>
<tr>
<td>rPET/D</td>
<td>248 ± 9</td>
<td>259 ± 12</td>
<td>1.47 ± 0.10</td>
</tr>
<tr>
<td>rPET/D-UV</td>
<td>253 ± 4</td>
<td>267 ± 4</td>
<td>1.48 ± 0.09</td>
</tr>
<tr>
<td>rPET/C-RC</td>
<td>319 ± 15</td>
<td>339 ± 12</td>
<td>1.33 ± 0.07</td>
</tr>
</tbody>
</table>

These results suggest that although the industrial UV ageing used in this project did affect the colour, it did not lead to a severe photodegradation or chemi-crystallization, and, therefore, the degree of crystallinity and the mechanical properties were not significantly altered.

**Conclusion**

This work is part of an industrial project which aim was to develop outdoor furniture made from recycled PET. With this purpose, injected moulded plates made from rPET stabilized with four different types of masterbatches were subjected to an industrial UV ageing and the effect of this ageing treatment, both in its superficial appearance and in its mechanical properties was analysed. Because the applied industrial UV ageing only affected a small superficial zone of the plates, the SPT was used as an alternative characterization technique in order to compare the mechanical properties of both unaged and aged materials.

The feasibility of the SPT as a valid mechanical characterization method of this type of materials was demonstrated by comparing the SPT results from the unaged samples with the tensile test ones. The mechanical parameters obtained from both tests showed the same results. While the type of used masterbatch did not affect the mechanical behaviour of the plates, the use of a recrystallization treatment increased the values of the stiffness and strength of these materials.

Although the used industrial UV ageing process produced a colour change in the studied rPET samples, it was possible to verify via SPTs that the mechanical properties were not affected. Consequently, the structural integrity was guaranteed although the rPET suffered a slight discoloration in conditions of simulated solar radiation.

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