Using the Small Punch Test to analyse the influence of UV radiation on the mechanical behaviour of recycled PET

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ABSTRACT

The aim of this work is to study the influence of ultraviolet (UV) radiation exposure on the properties of recycled polyethylene terephthalate (rPET). Four types of masterbatches were used which contained red pigments, antioxidants and UV absorbers. Flat plates were injection moulded and some samples were used as-moulded, some were subjected to UV radiation for 900 h and some samples received a thermal treatment in order to post-crystallize the bottle-grade rPET. The three sets of samples were analyzed by means of tensile tests, DSC and intrinsic viscosity. However, the irradiated samples could not be tested with these methods due to their small size. The aim was to evaluate the feasibility of small punch tests (SPT) in order to accurately characterize these small samples. It was found that the two parameters governing the rPET degradation and hence the mechanical properties were a proper drying and a sufficiently low level of contamination of the raw material before processing. Tensile test results showed that the four types of masterbatch did not alter the mechanical properties of the rPET, whereas the thermal treatment increased stiffness and strength while the failure strain decreased drastically. Analogous to these results, SPTs on UV-aged samples showed no significant differences between irradiated and not irradiated samples. SPT was capable of detecting small differences for the irradiated samples due to the different types of masterbatches.

Keywords: Small Punch Test, recycled polyethylene terephthalate, UV-ageing, post-crystallization.

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1. Introduction

The recycling of 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 natural decomposition because it is a non-degradable plastic in normal conditions. No known organism can consume its relatively large molecules and therefore complicated and expensive procedures are needed in order for PET to degrade biologically [1]. 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 [2]. 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 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 [1-2].

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 [3]. In the current work rPET was selected as base material for urban outdoor furniture in the frame of an industrial project. For outdoor applications, PET needs to be stabilized with additives such as antioxidants and 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 ºC) the degree of crystallinity is not affected by photoageing [4-6].

Due to these reasons the rPET used in this study was stabilized with different additives (see section 2.1) and subjected to accelerated ageing in a laboratory weathering chamber at ambient temperature and humidity (see section 2.2). The UV-ageing was carried out on small plates (see figure 2a) in order to optimize the available space in the weathering chamber of this time-consuming and costly procedure. During UV-ageing one half of each plate was exposed to UV radiation whereas the other half was protected from 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 is studied in order to accurately characterize these small samples.

The small punch test has been a revolutionary procedure for the mechanical characterisation 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 0.5mm 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 [7].

The SPT has also been used in the mechanical characterization of different types of materials other than steel [ref. ceramics] and its applicability in the estimation of the tensile mechanical properties of different types of polymers has been proved [8-11].

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 1a shows a sketch of the SPT and figure 1b shows the location of a specimen in the lower die. As a result of this test a load-punch displacement curve is obtained (figure 1c) and its analysis provides a series of parameters related to conventional tensile properties.

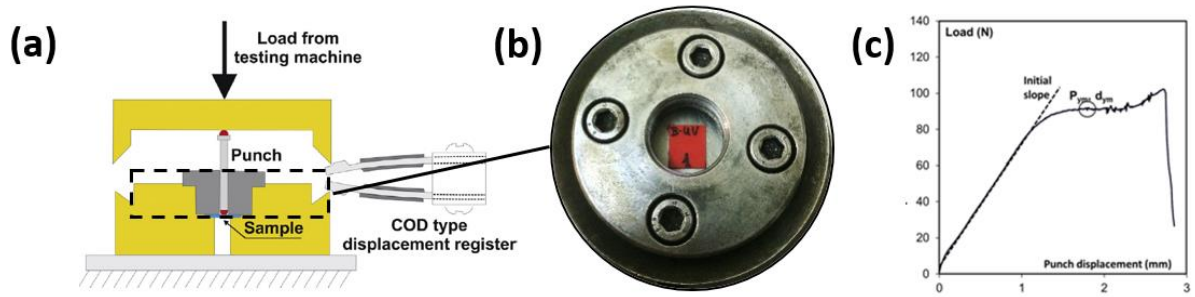

Figure 1. (a) Small punch test device [5]; (b) Detail of the sample in the lower die; (c) Main points in a typical polymeric SPT curve [11].

Figure 1c 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, eq. 1), the yield stress σ_y (related to the first maximum of the load, P_m, eq. 2), and the yield strain ε_y (related to the displacement at the first maximum of the load, d_m, eq. 3). Some of the typical relationships between the aforementioned SPT parameters and the tensile properties are:

$$E = \alpha_1 \frac{Slope_{ini}}{t} + \alpha_2 \quad (1)$$

$$\sigma_y = \beta \frac{P_m}{t^2} \quad (2)$$

$$\varepsilon_y = \delta \frac{d_m}{t} \quad (3)$$

being *t* the initial specimen thickness and α_1, α_2, β and δ the characteristic material coefficients.

The aim of this work is to study the influence of UV radiation and of a thermal treatment on the properties of recycled PET modified with different types of masterbatches which contained red pigments, antioxidants and UV absorbers. The three sets of samples (pristine, UV-aged and recrystallized) were analysed by means of tensile tests, DSC and intrinsic viscosity. However, the UV-aged samples could not be tested with these methods due to their small size. Therefore, the feasibility of small punch tests in order to accurately characterize these small samples was studied.

2. MATERIALS AND METHODS

2.1. 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 GPa, tensile strength: 54 MPa, failure strain: 240%, measured at a degree of crystallinity of 9%. 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).

2.2. Sample preparation

The rPET was dried at 120ºC for 4 h in a DSN560HE dehumidifier (Piovan, Santa Maria di Sala, Italy) with a dew point of -40ºC prior to injection moulding. Plates for accelerated ageing with dimensions of 100x75 mm^2 and with graduated thicknesses of 1 mm, 1.8 mm and 2.5 mm (see figure 2a) were injection moulded using a Victory 110 injection moulding machine (Engel Austria GmbH, Schwertberg, Austria) with a clamping force of 1100 kN. A constant melt temperature profile from hopper to nozzle of 275–270–265–260–40ºC was employed, the mould temperature was kept at 25ºC and the selected injection speed was 75 cm^3/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 2b–c). The exposed samples were referred to “UV”.
Some of the injection moulded plates were recrystallized at 120ºC for 4 h in a convection oven (J. P. Selecta, S. A., Barcelona, Spain). These samples were referred to “RC”.

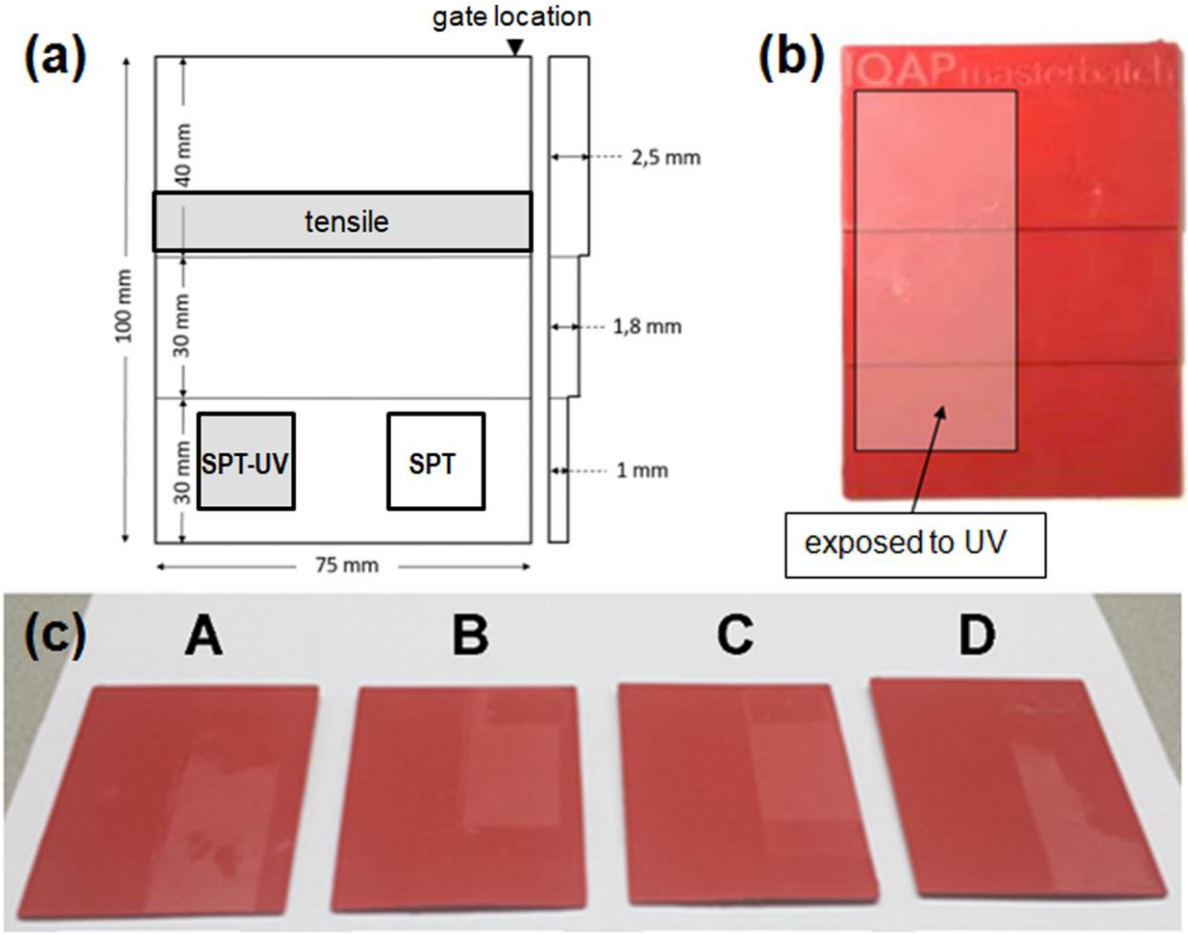

Figure 2. Plate dimensions and position of extracted tensile and SPT specimens (a). Photography of a plate with the indicated UV-aged zone on the back side (b). Injection moulded plates after exposure to UV radiation for 900 h (c).

2.3. 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 (T_{cc}, T_m) and corresponding enthalpies (ΔH_{cc}, ΔH_m) were determined from the first heating run. The degree of crystallinity (X_c) of PET was evaluated from the first heating run according to Equation 4.

$$\chi_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \cdot 100 \quad (4)$$

where ΔH_m (in J/g) is the measured melting enthalpy, ΔH_{cc} (in J/g) is the measured cold crystallization enthalpy, and ΔH_m^0 is the melting enthalpy for a fully perfect crystalline PET which is found in literature to be 140 J/g [12]).

The intrinsic viscosities of rPET pellets as well as of injection moulded rPET plates containing masterbatch were measured according to ISO 1628 [13] using a Cannon-Ubbelhode viscosimeter in a thermostated bath of 30 ºC. 50 mg of polymer was dissolved in a mix of phenol and 1,1,2,2-Tetrachloroethane (60/40 wt./wt.) at a temperature of 80 ºC. Four different polymer concentrations were used, namely 0.5, 0.9, 0.3 and 0.2 g/dL. The intrinsic viscosity 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 527 [14] 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 11 kN load cell and a contact extensometer to measure strain. A minimum of five specimens were tested at a constant crosshead speed of 10 mm·min^{-1} whereas the tensile modulus (E) was determined at 1 mm·min^{-1}. Prismatic specimens with dimensions of 75x10x2.5 mm^3 were cut from the injection moulded plates which were not subjected to UV-ageing (see figure 2a). 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 10x10 mm^2 cut from the 1 mm thick section of the injection moulded plates, in both areas: exposed and not exposed to UV-ageing (see figure 2a). These tests were carried out using an experimental device as shown in figure 1a, 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 6mm gage-length COD extensometer attached between the upper and lower dies, as can be seen in figure 1a). The thickness of the specimens was obtained as the average of six measurements by means of a precision micrometer and a minimum of six samples was used to characterise each material. Obtained curves were analysed with a Matlab subroutine specially developed for these material tests that provides the values of the characteristic parameters.

3. RESULTS AND DISCUSSION

In a first step, plates for accelerated ageing were injection moulded from rPET and 3 wt%. of masterbatches A, B, C and D, respectively. Some of these plates were subjected to accelerated ageing by means of UV radiation for 900 h; Images of these samples are shown in figure 2c. Recall that the four types of masterbatch contained: red pigments (masterbatch A), red pigments and antioxidants (B), red pigments and UV absorbers (C) and red pigments, antioxidants and UV absorbers (D). As can be seen in figure 2c, although all the samples suffer a slight discoloration due to the radiation, the sample containing masterbatch C retained its colour better than the others. This result was verified by IQAP via colorimetry tests.

The influence of the four different masterbatches on the mechanical properties was evaluated by tensile tests on prismatic specimens extracted from the pristine plates. Moreover, some specimens containing masterbatch C were recrystallized and also tensile tested. Results are shown in table 1 and figure 3. 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 small punch test was employed in order to mechanically characterize the UV-aged plates as will be shown later.

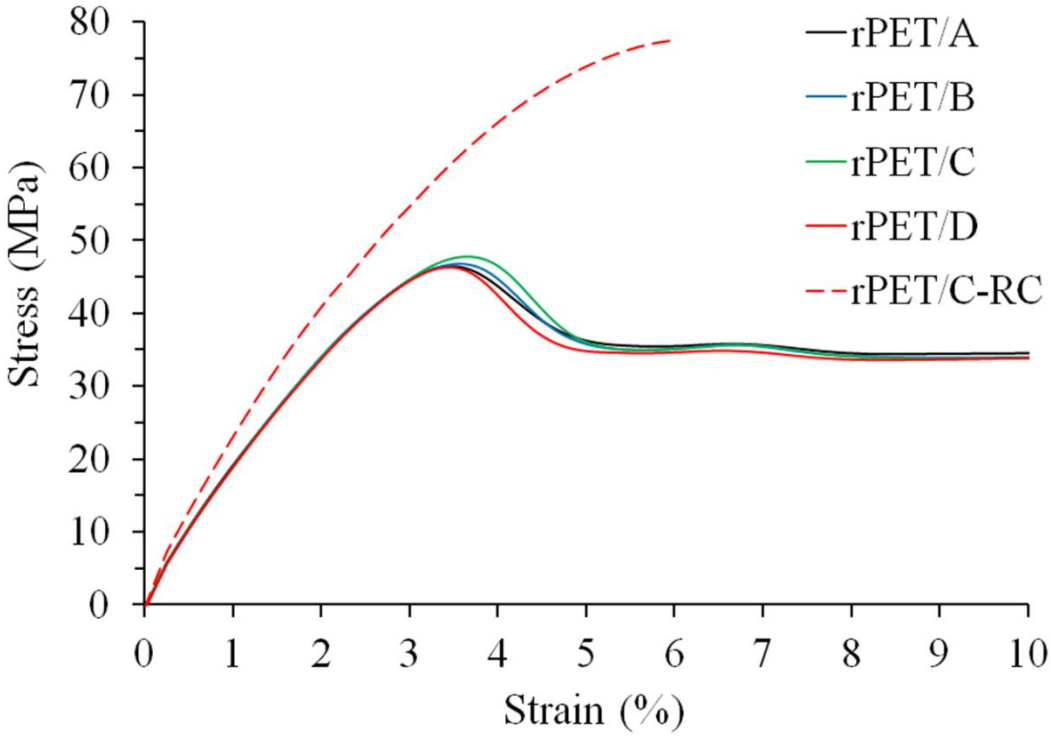

Figure 3. Engineering stress vs. strain curves of prismatic specimens cut from 2.5 mm thick plates.

Table 1. Tensile properties and degree of crystallinity of prismatic specimens cut from 2.5 mm thick plates.

Sample	E [GPa]	σ_M [MPa]	ε_B [%]	X_C [%]
rPET/A	2.5 ± 0.1	47 ± 1	61 ± 10	14.6
rPET/B	2.5 ± 0.1	45 ± 3	67 ± 28	7.7
rPET/C	2.5 ± 0.1	46 ± 7	42 ± 11	8.2
rPET/D	2.5 ± 0.1	45 ± 4	45 ± 15	9.4
rPET/D-RC	3.1 ± 0.2	77 ± 2	5 ± 1	29.5

Regarding the pristine plates containing masterbatch, no significant difference in stiffness and strength was found between the four different compositions (figure 3). The moduli were virtually equal and similar tensile strengths were observed, whereas small differences were found in the failure strains. 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. Comparing the tensile data from table 1 to the properties of rPET given by the material supplier (E = 2.4 GPa, σ_m = 54 MPa, ε_b = 240%, 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-aging was too small to be able to extract tensile specimens. So it was decided to characterize the UV-aging effect using the small punch test. It should be noted that the specimens were placed in the testing device in such a way that the UV-aged surface faced downward (see figure 1a and 1b). In other words, making sure that the aged surface was submitted to tensile stresses. In addition, and in order to compare the results, the SPT tests were also performed on specimens extracted from the areas that had not been subjected to UV radiation.

All the SPT specimens were extracted from the 1 mm thick section of the injection moulded plates (see figure 2c) and DSC analysis performed on that zone showed a degree of crystallinity of 9.7% and 11.7% for the unaged and UV-aged samples, respectively. This means that the crystal fraction of the UV-aged samples slightly increased by 2% due to chemi-crystallization.

Figures 4 and 5 show some SPT load-displacement curves representatives of the different materials tested both in their original state (Figure 4) and subjected to UV-aging (Figure 5). Figure 4 also includes a representative curve of the recrystallized sample rPET/C-RC. In addition, and based on a series of interrupted test, figure 5 shows the evolution of the tensile strained surface of a specimen as the test develops.

As can be seen, the SPT curves of the materials not subjected to UV-aging (Figure 4), show a similar trend than the tensile test ones. All the curves show similar values of initial slope and maximum load. A parallel behaviour was found in the UV-aged specimens (Figure 5). In contrast, the recrystallized sample, rPET/C-RC, showed a considerably higher slope and P_m values, as shown in Figure 4.

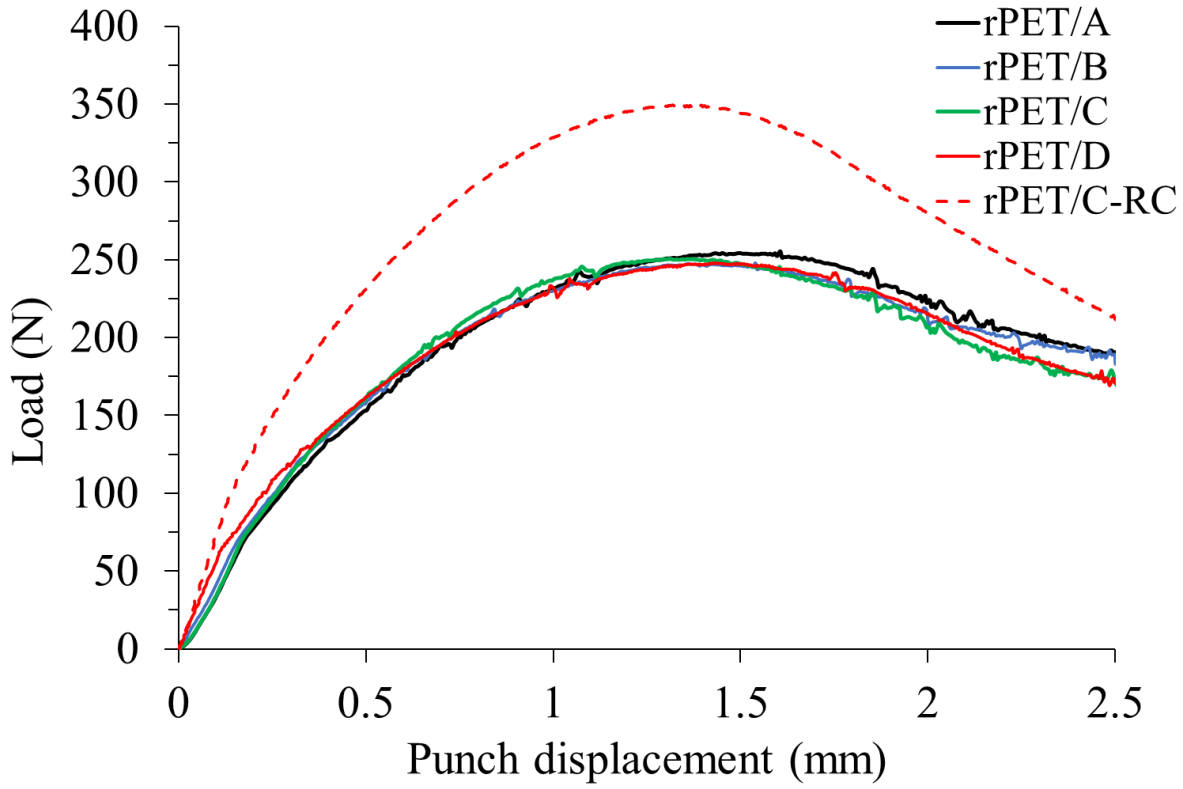

Figure 4. Representative load vs. punch displacement curves of specimens cut from 1 mm thick pristine and recrystallized rPET/C plates.

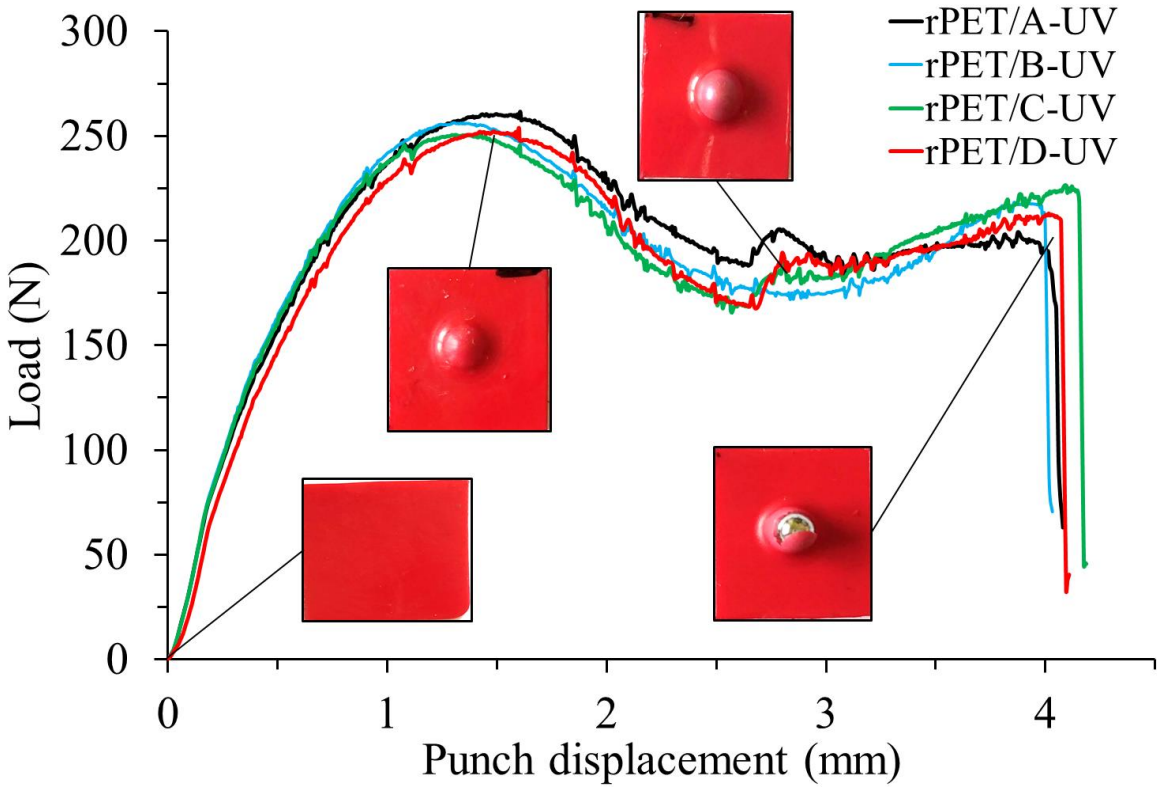

Figure 5. Representative load vs. punch displacement curves of specimens cut from 1 mm thick UV-aged plates.

The values of the SPT characteristic parameters extracted from the tests are shown in table 2. Comparing pristine, UV-aged and recrystallized rPET/C, no significant difference between pristine and UV-aged samples were seen, whereas the recrystallized sample showed a stiffer ($Slope_{ini}/t$) and stronger (P_m/t^2) behaviour due to its considerably higher degree of crystallinity.

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

Sample	$Slope_{ini}/t$ [MPa]	P_m/t^2 [MPa]	d_m/t [mm/mm]
rPET/A	239 ± 20	249 ± 20	1.40 ±0.26
rPET/A-UV	244 ± 13	240 ± 9	1.22 ± 0.23
rPET/B	248± 6	247 ± 9	1.38 ± 0.12
rPET/B-UV	249 ± 8	257 ± 12	1.38 ± 0.13
rPET/C	247 ± 11	259 ±7	1.39 ±0.12
rPET/C-UV	245 ± 6	257 ± 2	1.33 ± 0.06
rPET/D	248±9	259 ±12	1.47±0.10
rPET/D-UV	253 ± 4	267 ± 4	1.48 ± 0.09
rPET/C-RC	319 ± 15	339 ± 12	1.33 ± 0.07

These results suggest that although the UV-ageing 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.

4. CONCLUSIONS

The aim of this work was to study the influence of UV radiation and of a thermal treatment on the properties of recycled PET modified with different types of masterbatches which contained red pigments, antioxidants and UV absorbers. However, the UV-aged samples could not be tested with conventional tensile tests due to their small size and the feasibility of small punch tests in order to accurately characterize these small samples was studied.

Tensile tests carried out on the unaged materials showed that the different types of masterbatches had no direct reinforcing effect on the rPET matrix and thermal analysis confirmed that the masterbatches did not act as a nucleation agent. In contrast, the recrystallization thermal treatment considerably increased the degree of crystallinity, which led to a higher stiffness and strength but also a lower failure strain. The same conclusions were extracted when the small punch test was used as mechanical characterization method of these materials.

When injected plates were subjected to an industrial UV-aging treatment, the irradiated area size was too small to extract tensile specimens; it was only possible to obtain miniature samples such as SPT specimens. The SPT characterization of the UV-aging samples showed no significant differences between the radiated and unradiated plates regardless of the type of masterbatch used in its manufacture.

According to its aim, this work shows the feasibility of using the miniature small punch test to analyse the effect of UV radiation in the mechanical behaviour of recycled PET, especially if that characterization is not possible by conventional tensile tests.

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