The impact of biodegradable plastics in the properties of recycled polyethylene terephthalate

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ABSTRACT

Since biodegradable materials are unwittingly mixed with synthetic materials, this work aimed to study the feasibility of reliably identifying some biopolymers, treated as contaminants, in the recycling process of polyethylene terephthalate (PET). The results showed that the miscibility between PET-PLA and PET-PHB is good. However, PHB is degraded in the recycling of PET due to the high processing temperatures used; meanwhile, PET and TPS are poorly miscible, characteristics also reflected in the microstructure. The contaminants decrease the mechanical properties of the recycled PET. Both, FTIR and DSC, do not allow to identify these contaminants. FESEM resulted in the most successful technique to detect the biodegradable polymers in the PET matrix. No significant degradation of PET under composting conditions was obtained due to the presence of biodegradable polymers, and the effects of the biodegradable contaminants continue to reduce the mechanical performance of the recycled PET after one year of storage.

Keywords: recycling; polyethylene terephthalate (PET); biodegradable materials; contaminants, miscibility.

1. INTRODUCTION

Polyethylene terephthalate (PET) is one of the most produced and consumed plastics in the world [1]. The PET, together with polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinylchloride (PVC), is part of the so-called commodity plastics [2, 3]. Particularly, the use of PET is almost restricted to packaging because of its good mechanical properties and barrier properties for carbon dioxide. Consequently, PET has become essential in the food industry [4]. In the beginning, the PET was used as a replacement for glass in the carbonated beverage containers. Subsequently, its uses overcame and displaced the PVC in all types of beverages, such as mineral water [5, 6]. At present, it has also displaced other materials in the production of thermoformed trays specially used for the food industry.

Since PET primarily uses is packaging, this polymer has a short shelf life, which has motivated many studies regarding its recycling process [6, 7]. The recycling of PET allows the revalorization of this plastic waste, which is also a sustainable solution. Several revalorization routes have been proposed such as recovery as textile fibres [7] or as reinforcement in other thermoplastics [8]. However, mechanical recovery is the most used and effective recycling process. Due to the specificity of its applications, the PET presents neither contamination nor degradation during its use. For this reason, the residue of the PET is homogeneous and clean. These characteristics allow recycled PET to be reintroduced in the manufacturing process, along with virgin material [9]. Besides the recycling option, the environmental pollution of all plastics and polymers linked to the microplastics phenomena in the sea, which in the case of PET tends to go to the bottom of the seabed [10], have promoted the search for more sustainable materials. One example is the PET coming from renewable sources [11]. As well, poly (ethylene furanoate) (PEF) has been also considered as a substitute for PET. This polymer is obtained from biomass but is still far from being a real alternative [12]

In this regard, recycling is currently the most viable option to recover the PET from plastic waste. Nevertheless, its recycling process can be hindered by the

presence of biodegradable materials, which are also used in the bottles and packaging sectors [13, 14]. Materials such as poly(lactic acid) (PLA) [15] and thermoplastic starch (TPS) [16, 17] are already common, but many others are soon to be introduced such as polyhydroxyalkanoates (PHAs) [18]. Biodegradable materials are compostable and difficult to recover and revalue. Therefore, they must be treated as organic waste, not as recyclable plastics. However, biodegradable plastics are often mixed with recyclable plastics, especially in the urban trash containers, which can lead to interferences in the PET recycling process, as occurred with other commodity plastics as PS o PP [19, 20], or as seen when PET and PVC coexisted in the use of bottles, where the presence of PET hindered the recovery of PVC [21–23]. This situation is aggravated because the PET transformation process is very sensitive to phenomena such as crystallization, incompatibility with other materials, and hydrolysis, especially at the high temperatures where PET is processed.

In this study, the influence of biodegradable plastics on the recovery of polyethylene terephthalate (PET) has been studied. Different weight percentages of poly(lactic acid) (PLA), thermoplastic starch (TPS) and polyhydroxybutyrate (PHB) have been added to the PET destinated to be recycled. The blending process has been carried out by extrusion of the different mixes at high temperatures, since the recycled PET must be processed between 260 °C and 270 °C, being a very high processing temperature for biodegradable materials [24]. After extrusion, the different samples have been characterized by the mechanical, microstructural, thermal, and composting properties to verify the influence of small amounts of biodegradable polymers on the quality of the recycled PET [25].

2. EXPERIMENTAL PART

2.1. Materials

2.1.1. Materials and samples preparation

Recycled PET pellets were supplied by Extremadura Torrepet S.L. (Badajoz, Spain), was used as a matrix. Poly(lactic acid) (PLA), thermoplastic starch (TPS), and polyhydroxybutyrate (PHB) were used to emulate biodegradable contaminant materials in the recycling process of PET. PLA 4032D was kindly supplied by NatureWorks LLC (Minnetonka, MN, USA), PHB P226 was kindly provided by Biomer (Krailling, Germany) and TPS Mater-Bi NF866 was kindly supplied by Novamont (Novara, Italy). The biodegradable polymers were blended with PET in concentrations of 0, 2.5, 5 10, and 15 wt.%.

The formulated materials were melt blended in a twin-screw extruder (Dupra S.L., Castalla, Spain) with a temperature profile of 200/220/240/260/270 ° C from hopper to die and a screw speed of 50 rpm. To obtain standard samples for mechanical characterization according to ISO-527-2 [26], the formulations were injection moulded in a Sprinter 11 t injection machine from Erinca S. L. (Barcelona, Spain) with a temperature profile of 240/260/270 °C (from hopper to die). Before processing the samples, they were dried at 60 °C for 24 hours in an air circulation oven.

2.2. Methods

2.2.1. Miscibility between the components

Solubility is an approximate value to determine the affinity between plastic. However, it is an objective method developed as an alternative to the experimental results in the study of polymer mixtures [27, 28]. To assess the relative affinity of PET with the selected biodegradable polymers, the relative solubility (δ) was determined using the group contribution method, also known as the Small method [29]. The Small method considers that mixtures components are compatible if their solubility parameters are similar. Small made a list of molar attraction constants (F) (Table 1) for several molecules. Thus, δ can be obtained by adding the molar attraction constants, considering the contribution that each group makes in the overall structure of the molecule (Equation (1).

$$\delta = \frac{\rho \sum F_j}{M_n} \quad (1)$$

Where ρ is the polymer density, Mn is the molar mass of the repetitive unit, and $\sum F_j$ is the summation of the contributions of all groups of the polymer [19].

Table 1. Small attraction constants for some functional groups at 25 °C [30]

Group	F^* ($cal^{1/2} \cdot cm^{3/2}/mol$)
$-CH_3$	214
$-CH_2-$	133
-CH<	28
>C<	-93
-OH	83
-O-	70
-H	80-100
>C=O	275
Phenyl group	735

2.2.2. Microstructural and mechanical characterization

The microstructure of cryofractured surfaces of PET and PET blends were analysed by a field emission microscope FESEM ZEISS ULTRA 55 from Oxford Instruments (Oxfordshire, United Kingdom) operated at 2 kV. Before the observation, the sample surfaces were coated with a gold-palladium alloy, on a Sputter Coater Emitech SC7620, Quorum Technologies (East Sussex, UK), to facilitate their conductivity. The mechanical characterization was carried out by using an Ibertest universal testing machine ELIB 30 (S.A.E Ibertest, Madrid, Spain) following the ISO-527 standard [31]. All the tests were carried out at room temperature, at a speed of 10 mm/min, and with a load cell of 5 kN. Five specimens of each formulation were tested. The mean values and the standard deviation of Young's modulus, tensile strength, and elongation at break are reported.

2.2.3. Quality control assessment through Fourier transform infrared spectroscopy and differential scanning calorimetry

Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) analyses were carried out as quality control analyses. The tests were done to determine the presence of biodegradable polymers as contaminants into the recycled PET matrix after the recycling process. FTIR was conducted using a Perkin Elmer SpectrumBX spectrometer (PerkinElmer Spain S.L., Madrid, Spain) coupled with an ATR MIRacle ™ Pike Technologies (Madison, WI, USA). The samples were examined between 4000 and 600 cm^{-1}, with 20 scans and a resolution of 32 cm^{-1}. The DSC was performed in a Mettler Toledo 821 equipment (Mettler Toledo, Schwerzenbach, Switzerland) using samples of 4–6 mg. The DSC program consisted of a first heating scan from 25 °C to 280 °C, followed by cooling from 280 °C to 25 °C and second heating from 25 °C to 300 °C. The heating and cooling programs were performed at a rate of 10 °C/min in a nitrogen atmosphere (30 mL/min). The melting temperature (T_m) and the melting enthalpy (ΔH_m) were obtained directly from the second heating in the DSC curves. The crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) is also reported.

2.2.4. Disintegration under composting conditions

The disintegration degree under composting conditions was performed according to the ISO 20200 standard [32]. The compost had the following basic properties: organic solids 45%, vegetable solids 40%, 30% humidity, and pH between 6 and 7. As samples, dog bone shape specimens of PET with 15 wt.% of biodegradable polymers were used. The samples were recovered at 8, 21, and 30 days to evaluate their visual appearance and to determine their degree of disintegration by gravimetry after been subjected to composting conditions. All samples were inserted in a textile mesh to facilitate their removal from the compost, and to allow the moisture and microorganisms access. Besides, the samples subjected to 30 days under composting conditions were then analysed by thermogravimetric analysis (TGA), using a Linseis TGA PT1000 (Selb, Germany). The samples (10 mg) were heated from 30 to 800 °C at 10 °C/min under air atmosphere.

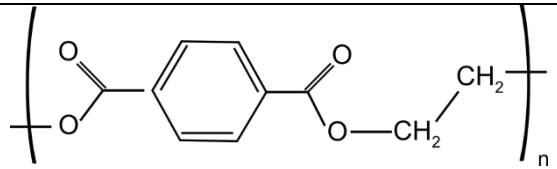
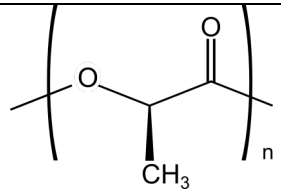
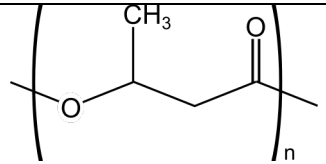
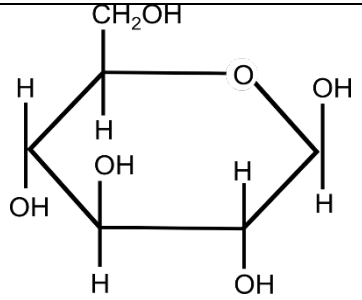
Finally, to determine the stability of the recycled pellets in time, an injection process (under the same conditions described above) was carried out after one year of storage of the prepared formulations, to obtain standards testing specimens. Subsequently, the specimens were mechanically characterized by a tensile test (under the same conditions described in the mechanical characterization section). PET-PLA was the only characterized blend as PET-PHB and PET-TPS blends were extremely brittle to be successfully unmoulded from the injection machine, after processing the pellets stored one year.

3. RESULTS AND DISCUSSION

3.1. Miscibility between PET and the studied biodegradable polymers

The calculated solubility (δ) and the thermal properties of PET, PLA, PHB, and TPS are shown in Table 2. Among the biodegradable polymers, the PHB solubility (19.9 $MPa^{1/2}$) is the closest to the PET solubility (24.3 $MPa^{1/2}$), followed by PLA (19.2 $MPa^{1/2}$). Therefore, the miscibility of the PET-PHB and the PET-PLA blends will be good. However, for PET-PHB blends, it should be considered that the processing temperature of PET (around 270 °C) is higher than the degradation temperature of PHB (above 220 °C [18]) and much higher than the melting temperature of the PHB (around 180 °C [15]). Consequently, during the processing of the PET-PHB blends, PHB degradation phenomena will occur, leading to a possible loss of properties of the final material. Regarding the PLA, the solubility factor is also closer than the one for PET which indicates that the resulting blend will consist of two partially compatible phases, with good interfacial adhesion, that will result in a blend with good mechanical properties. For TPS, the solubility factor (8.8 $MPa^{1/2}$) is 15 points less than the PET value, which predicts that both materials will exhibit immiscibility phenomena and the final blend will contain two phases with low affinity for each other, a disperse phase of the biodegradable polymer (TPS) and the PET as matrix phase. As a result, it will result in a blend with low mechanical properties [19, 20, 27, 33].

241 **Table 2.** Calculated solubility parameter, density, and thermal properties of PET, PLA, PHB, and TPS

Polymer	Structure of the repeating unit	Calculated solubility parameter δ ($MPa^{1/2}$)	Density (g/cm^3)	Processing temperatures (°C)	Onset degradation temperature (°C)
PET		24.3	1,35	270	410 [34]
PLA		19.2	1.24 [35]	180 [36]	320 [37]
PHB		19.9	1.25 [38]	170 [15]	220-250 [18, 39]
TPS		8.8	1.27 [40]	160 [16]	285 [16]

3.2. Microstructural characterization

FESEM images of the cryofracture surfaces from the studied materials are presented in Fig. 1. Recycled PET shows a uniform surface, without visible flaws or cracks in the surface (Fig. 1-a and Fig. 1-a'). Meanwhile, all the blends of PET-biodegradables polymers show irregularities in their microstructures. This confirms that the recycled PET does not possess any contamination. In the formulated blends, when PET was contaminated with biodegradable polymers, porosities in the microstructure were observed due to the incompatibility between PET and the respective biodegradable polymer. These porosities are more evident when the contaminants are PLA (Fig. 1-b and Fig. 1b') and TPS (Fig. 1-d and Fig. 1-d').

The PET-15PLA micrographs (Fig. 1-b and Fig. 1-b') show partial miscibility between the phases PET-PLA since some parts of the micrograph show a uniform surface with no noticeable defects (see the red circles in Fig. 1-b). This agrees with the behaviour of the solubility parameter already discussed. The fractured surface of the samples presents a characteristic roughness of partially miscible blends [34, 41]. Nevertheless, due to the high amount of the contaminant (15 % of PLA), it is possible to detect the beginning of the saturation of the PLA phase, which can lead to complete phase separation, if the amount of the contaminant increases. This means that PLA is observed as a disperse phase in a spherical shape, with an approximate size of 1 μm, embedded in a matrix phase formed by PET (red arrow in Fig. 1-b). It is also noted that, at the moment of the cryofracture, the material fails through these spheres, so the gaps left in the matrix by the spheres of the PLA phase are evident, as shown in Fig. 1-b'.

For PET-15PHB (Fig. 1-c and Fig. 1-c'), it is difficult to identify the different phases in the FESEM micrographs. This can confirm the good miscibility between the phases, predicted by the solubility parameter. However, in Fig. 1-c' it is possible to observe the presence of small holes in the microstructure (red arrows). These holes are related to the degradation and disintegration of PHB,

caused by the high processing temperature during the material extrusion and injection. [42]. It is known that the onset degradation temperature of PHB is around 220 °C [39], while PET melting temperature (T_m) is around 255 °C, as evidenced in Table 3. Finally, PET-15TPS (Fig. 1-d and Fig. 1-d') present a phase separation between the components, easily observed at higher magnification (Fig. 1-d'). Again, this agrees with the miscibility parameter prediction. The biodegradable polymer (TPS) form a disperse phase in spherical shape distributes in the PET matrix phase (red arrow in Fig. 1-d'). The holes left in the structure after the cryofracture are also visible, and in some cases, it is possible to see that the spheres of TPS are still embedded in the matrix. The size of the holes is lower than 1 μm which could indicate low saturation of the dispersed phase (TPS).

3.3. Mechanical characterization

Fig. 2 shows the mechanical properties comparison between the studied materials, where it is possible to confirm that the tensile behaviour of recycled PET is modified with the presence of the biodegradable materials as contaminants [43]. This result was expected since the recycling process of PET is complex [44]. As well, the blends with biodegradable polymers have changed the properties of other polymer matrices (i.e. PS, PP) previously studied [19, 20]. In Fig. 2 -a, it is seen that the tensile strength in all PET-biodegradable polymers blends decreases concerning the value observed for the recycled PET (0 % of the content of biodegradable polymers). It is seen that each biodegradable polymer, when blended between 2.5 to 15 wt.%, have different effects on the PET tensile strength, which confirms that the PET tensile strength is dependent on the type and content of the contaminant (in this case, the PLA, PBAT or TPS as a biodegradable polymer)

The presence of PLA in PET produced the lowest decrease (10 %) in the PET tensile strength, compared to the other contaminants. Moreover, the tensile strength of PET-PLA remains constant in the studied range (up to 15 wt. %). TPS reduced by 33 % the tensile strength of recycled PET. As well, PET-TPS

tensile strength tends to stay constant in contents between 5 to 15 wt.%. In contrast, PHB produced a completely different effect on PET. PET-PHB tensile strength behaviour is decreasingly linear and inversely proportional to the biodegradable polymer content, achieving a decrease of 44 % in the recycled blend with 15 wt. % of PHB. This behaviour agrees with the miscibility results previously discuss. TPS would generate problems in the recycled PET related to the incompatibility between the components. However, despite the good compatibility between PET-PHB, the problems could be associated with the degradation of PHB within the PET matrix. On the other hand, the compatibility between PLA and PET helps to have blends with stable mechanical properties. The obtained results are in good agreement with the microstructural characterization observed by FESEM.

On the other hand, the presence of contaminants in the recycling process of PET has a determining effect in the elongation at break of the blends. As shown in Fig. 2-b, the elongation at break values drops sharply with the introduction of a biodegradable polymer in the recycled PET matrix. The PET-biodegradable polymer blends recorded a loss in the elongation at break between 80 and 95 %. Additionally, the decrease in the elongation at break values are also dependent on the content of the contaminants. Conversely, small amounts of PLA are tolerated in a PET matrix, since a blend of PET with 2.5% of PLA, tends to increase PET elongation at break by 10 %. This is attributed to the stability of PLA against recycling processes [45, 46].

The Young's modulus of PET with different contents of biodegradable polymer contaminants (Fig. 2-c) is always lower than the recycled PET Young's modulus. In the PET-TPS blends, the values of Young's modulus suffer a linear drop with the increase of the contaminant due to the incompatibility between both materials. Nevertheless, in the case of PET-PHB and PET-PLA mixtures, Young's modulus tends to stabilize to values between 1400 and 1600 MPa, with the increase in the contaminant. In both blends, the trend of variation of the module is similar. However, in any case, Young's moduli of the blended materials are lower than the recycled PET modulus (1700 MPa). This behaviour demonstrates the miscibility between the components of the material, previously

discussed. The behaviour of Young's modulus values is expected since the microstructure of the material is altered by the presence of biodegradable material contaminants.

3.4. Quality control assessment through Fourier transform infrared spectroscopy and Differential scanning calorimetry

The Fourier transform infrared spectra (FTIR) of recycled PET and PET-biodegradable polymers blends are shown in Fig. 3. In the infrared spectrum of recycled PET, its characteristic absorption bands can be found at 1714 cm^{-1} (high-intensity peak) which corresponds to the symmetric stretching of the C=O group [47, 48]; 1370 and 1172 cm^{-1} (shoulder peaks) indicating the flexion of the CH_2 groups; 1244 cm^{-1} (high-intensity peak) and 972 cm^{-1} (shoulder peak) given by the stretching of the C–O group of the amorphous and crystalline part of the PET, respectively [49]; 1406, 1020 and 872 cm^{-1} (medium intensity peaks) due to the vibration of aromatic rings; 796 cm^{-1} (low-intensity peak), 846 cm^{-1} (shoulder peak) and 724 cm^{-1} (high-intensity peak) corresponding to flexions of the aromatic ring outside the plane [48]. The mentioned absorption bands are observed in the spectra of all the blends and no differences can be determined in the PET spectrum due to the presence of PLA, PHB, and TPS in a 15 wt. %. Thus, the FTIR technique is not suitable for identifying the presence of biodegradable polymers in recycled PET, unlike other recycled matrices contaminated with biodegradable polymers, such as polystyrene [19] or polypropylene [20].

According to literature, PLA and PHB have carbonyl groups (–C=O) as characteristic groups. Therefore, an overlap of these bands by the C=O group band of the PET is presumed. PLA presents its absorption bands between 1745 cm^{-1} and 1755 cm^{-1}, while PHB present them at approximately 1720 cm^{-1} [15, 50, 51]. In the case of PET-TPS, the characteristic bands of TPS are not found in the blend spectrum. In neat TPS, these bands are located at 1010, 1148 and 926 cm^{-1}(pyranosic ring) to 2924 cm^{-1} and 2884 cm^{-1} (C-H group), 1648 cm^{-1} (bound water) and 3284 cm^{-1} (OH) [17, 52, 53]. The impossibility of identifying

biodegradable polymers in a PET matrix can be due to two effects: (1) due to the C=O bonds of PET [54], as mention above, which can hinder the process of identifying PLA and PHB C=O bonds, and (2), due to the molecular groups of PET, which are very active in the infrared [55, 56] causing that PET bands overlap the bands of other polymers.

Table 3 shows the thermal characterization parameters of the blends obtained by the differential scanning calorimetry analysis (DSC) along with the thermal properties of the virgin polymers, taken from literature. Generally, in a blend of miscible polymers, the thermal properties tend to an intermediate point between the components. This is verified in PET-15PLA where the T_m and T_c are diminished concerning the virgin PET and the temperature values are between PET and PLA melting and crystallization temperatures. However, despite the good miscibility between PHB and PET, in the PET-15PHB blend, the displacement of T_m is imperceptible. As mention in the discussion of FESEM results, PHB is degraded due to the high processing temperatures, therefore, the effect of the blend properties is unnoticed. On the contrary, according to the miscibility analysis, TPS and PET have low miscibility. Thus, two or more melting temperatures (peaks) should be distinguished, each one related to PET and TPS, respectively. Nonetheless, no differences were found either in the T_m or in the T_c of the PET-15TPS and recycled PET. These results suggest that the phenomena associated with the PET thermal transitions are very energetic and mask the presence of the biodegradable polymers even at the content of 15 wt.% of the polymer.

The reported behaviour of the blends is confirmed when analysing the melting and crystallization enthalpies (ΔH_m and ΔH_c), where PET-15PHB and PET-15TPS show enthalpies values closer to recycled PET. Meanwhile, the blend PET-15PLA present lower melting and crystallization enthalpies than those for recycled PET. This suggests that PLA produces a dilution effect in the thermal transitions of the recycled PET in approximately 15 %, which is the content of the biodegradable polymer in the studied formulation. However, PHB is partially degraded and TPS is lowlily miscible with PET. Thus, the dilution effect in the thermal transitions of these two blends is unnoticeable compared to the

transitions of recycled PET. These results show that the identification of biodegradable contaminants in PET could not be assessed by a simple technique as FTIR or DSC, which could represent a problem at an industrial level in the quality control process.

Table 3. Thermal properties of virgin PET, PLA, PHB, and TPS; and thermal properties obtained by DSC of recycled PET and PET-biodegradable polymers blends

Sample	T_c (ºC)	ΔH_c (J/g)	T_m (ºC)	ΔH_m (J/g)
PET[57]	204.6	42.4	250.2	40.6
PLA[58]	151.5	5.3	168.1	32.6
PHB[59]	56.5	13.8	169	57.2
*TPS[16]	92.5	9.2	150.3	2.5
Recycled PET	203.2	43.6	252.1	37.3
PET-15PLA	190.5	31.4	242.1	29.3
PET-15PHB	213.6	44.7	248.1	38.7
PET-15TPS	205.7	38.2	250.8	37.4

*Commercial TPS (Mater-Bi NF 866)

3.5. Disintegration under composting conditions

Fig. 4-a shows the comparative images of the PET-biodegradable polymer blends, before and after being subject to composting conditions for different days. After 30 days of incubation, the visual analysis reveals that PET-15PLA surface undergoes a modification, evidenced by the appearance of clefts in the places where the sample had contact with the textile mesh, attributed to the beginning of the disintegration of the PLA [60, 61]. Furthermore, PET-15PLA sample adopts a slightly yellowish coloration, which indicates a change in the refractive index, attributed to the hydrolytic degradation of PLA [62, 63]. At the same time, PET-15PHB presents subtle signs of cracking after 21 days of incubations (see red circle), attributed to the failure of the material due to the

premature degradation of the PHB because of the processing temperatures. PET-15TPS does not show significant changes in its surface after 30 days of composting, possibly due to the stability of the TPS under composting conditions [64, 65].

Fig. 4-b shows the disintegration degree of each sample with respect to the incubation time. It is seen that until day 21 of incubation, the disintegrations grade in all the samples is less than 1%. On day 30, PET-15PHB and PET-15PLA tend to increase their disintegration degree to 0.8 and 1.5%, respectively. In the PET-15PLA, the degradation is exclusively attributed to the PLA portion in the blend. This is in agreement with the degradation percentage of PLA obtained in other studies at the same time [60, 61]. In the PET-15PHB and PET-15TPS blends, it was expected higher disintegration of the biodegradable portion of the blend [66, 67]. However, the PHB portion only loses 5% of its initial amount in the blend, while in TPS no weight change was detected during this incubation time. This evidence that PET interferes with the degradation mechanisms of PHB and TPS. Moreover, the results expose the low degradability of PET under composting conditions, even when it is blended with biodegradable polymers. The results agree with literature, where PET has been blended with biodegradable polymers and with certain additives to improve its biodegradability. Chiellini et al. (1996) work with PET and 15 wt.% of polycaprolactone (PCL). After 60 days of incubation under composting conditions, they found a decrease of 0.8% of the initial weight [68]. Meanwhile, Gómez et al. (2013) incorporated 1% EcoPure and found no significant change in PET weight after 115 days of incubation [69].

To determine any difference in the thermal degradation of the blends after composting conditions, the comparative curves of the thermogravimetric analysis for the different PET samples, before and after 30 days of disintegration under composting conditions are shown in Fig. 5. It is seen that the thermogravimetric behaviour of the PET blends with the different biodegradable polymers does not show significant changes after the disintegration test, as shown in Fig. 5-a, Fig. 5-c, and Fig. 5-e. It is also observed that the thermal degradation of PET-15PLA and PET-15TPS occurs in

a single step. Meanwhile, PET-PHB thermal degradation occurs in two steps, being the first step (at about 310 °C) attributed to the PHB degradation [19, 20]. A decrease in the maximum degradation rate (T_d) of PET-15PLA, PET-15PHB, and PET-15TPS can be seen in Fig. 5-b, Fig. 5-d, and Fig. 5-f, respectively. In PET-15PLA, T_d decreases 8 °C after undergoing the composting disintegration process. In PET-PHB, it is observed that in the first step the degradation temperature decreases 11 °C and in the second step, the temperature of maximum degradation rate drops 6 °C. Finally, in PET-15TPS the temperature of maximum degradation rate decreases 1 °C. These results show that most of the biodegradable polymers in the samples have not been completely disintegrated after 30 days of the test. Thus, it is presumed that PET generates an interference by interacting with biodegradable polymers in a way that limits their degradation capacity [20], which is in good accordance with that previously discussed in the disintegration analysis under composting conditions.

Finally, for a deeper understanding of the PET blends behaviour over time, the pellets of each blend were stored for one year and later processed by injection moulding to obtain standard testing specimens. It is worth to mention that due to the high brittleness of PET-PHB and PET-TPS blends, it was not even possible to obtain injected specimens since they were broken when removed from the mould. The tensile strength of the PET-PLA blends, determined by mechanical characterization, is shown in Fig. 6-a. The results reflect a decrease of more than 20 % of the tensile strength in the samples with more than 5 % of PLA in their content. Besides, an increase in the dispersion of the results is observed. The results reveal that contaminant interference did not only occurs immediately after the PET recycling process, but the reduction of mechanical properties continues over time. As well, a comparison of Young's modulus of the PET-PLA before and after aging (Fig. 6-b), shows that the tensile modulus of PET is negatively influenced by aging, causing a reduction in this value even in low contents of PLA (2.5 wt.%). Young's moduli of the stored materials tend to a stable value of about 800 MPa, half of the values of the initial material. On the other hand, the mechanical properties of recycled PET (the tensile strength and Young's modulus) remain invariable during the storage time.

4. CONCLUSIONS

Blends of polyethylene terephthalate (PET) with biodegradable polymer were successfully characterized to study the possible interferences of the biodegradable materials in the recycling process of PET coming from packaging waste. The characterization showed that poly(lactic acid) (PLA), polyhydroxybutyrate (PHB), and thermoplastic starch (TPS) do interfere in the mechanical properties of recycled PET. Through the study of miscibility by the relative solubility using the Small method and by the microstructural characterization using FESEM, it was found that PLA is partially miscible with recycled PET, while TPS presents low miscibility with the PET matrix. On the other hand, despite the good miscibility predicted for the PET-PHB blends, the morphology of the blend exhibited small holes, which suggest that the high temperatures of recycling processing (temperature profile around 270 °C) cause thermal degradation of PHB. In the mechanical characterization, the elongation at break of recycled PET drastically drops with the addition of PLA, PHB, and TPS. As well, a decrease in the tensile strength and Young's modulus was registered. These prove that the contamination of PET with the studied biodegradable polymers directly affects the mechanical performance of the recycled material. The disintegration under composting conditions showed that PET interferes with the degradation of the biodegradable polymers (PLA, PHB, or TPS) since the blends did not show a considerable weight loss after 30 days of being subjected to composting conditions. The characterization of PET-biodegradable polymer blends after one year of storage reveals that the biodegradable polymers continue affecting the mechanical performance of recycled PET. Finally, it was concluded that FTIR and DSC are not the most suitable technics for identifying the presence of biodegradable polymers (PLA, PHB, and TPS) in a PET matrix since PET mask the energetic transition and the FTIR signal of the contaminants due to its intrinsic high energetic characteristics which difficult a clear identification of the contaminants. Thus, the feasibility of reliably identifying the mentioned biodegradable materials in the recycled PET matrix by the simple quality control methods is not possible. Microscopical techniques (SEM or FESEM) are the more accurate methods to detect contaminants in the recycled PET, even though these techniques are not

always easily accessible in the industrial environment. The negative influence of the biodegradable materials in the recycled PET and the difficulty of identifying their presence as contaminants motivate extreme precautions in the design and implementations of the collecting, selection, separation, and cleaning processes of the residues to be recovered and recycled

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