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CHARACTERIZATION OF RECYCLED THERMOPLASTICS CONTAMINATED WITH BIODEGRADABLE POLYMERS

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ABSTRACT:

In this work, the presence of biodegradable polymers in recycled plastic materials was characterized using readily available techniques. Recycled polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) were studied. Contamination of these with polylactic acid (PLA), polyhydroxybutyrate (PHB) and thermoplastic starch (TPS) was simulated using 10% by weight of the contaminant. Fourier transform infrared spectrometry (FTIR) and differential scanning calorimetry (DSC) were used as characterization techniques. In addition, the effect of aging on recycled products from PET blends contaminated with TPS and PHB is studied. The results show changes in the intensity of the bands of the FTIR spectra in the PS and PP blends contaminated with biodegradable polymers. By DSC, changes in the cold crystallization peak of recycled PET are observed when mixed with TPS and PHB, while when the contaminant is PLA, the changes are masked due to the thermal characteristics of both materials. In PS, changes in the calorimetric curves are identified by the presence of PLA and PHB. Contamination with PLA, PHB and TPS hinders the processing of recycled PET after one year of storage due to the aging of the material.

Keywords: recycling, biodegradable plastics, polypropylene, polystyrene, polyethylene terephthalate, polypropylene, polyethylene terephthalate

RESUMEN:

En este trabajo se caracteriza la presencia de polímeros biodegradables en materiales plásticos reciclados mediante técnicas de fácil acceso. Se estudiaron polipropileno (PP), poliestireno (PS) y tereftalato de polietileno (PET) reciclados. Se simuló la contaminación de estos con ácido poliláctico (PLA), polihidroxi butirato (PHB) y almidón termoplástico (TPS), usando un 10% en peso del contaminante. Como técnicas de caracterización se usaron espectrometría infrarroja de transformada de Fourier (FTIR) y calorimetría diferencial de barrido (DSC). Además, se estudia el efecto del envejecimiento en los productos reciclados a partir de mezclas PET contaminadas con TPS y PHB. Los resultados muestran cambios en la intensidad de las bandas de los espectros FTIR en las mezclas de PS y PP contaminadas con polímeros biodegradables. Mediante DSC se aprecian cambios en el pico de cristalización en frío del PET reciclado cuando se mezcla con TPS y PHB, mientras que cuando el contaminante es PLA, los cambios se enmascaran debido a las características térmicas de ambos materiales. En el PS se identifican cambios en las curvas calorimétricas por la presencia de PLA y PHB. La contaminación con PLA, PHB y TPS dificulta el procesamiento del PET reciclado después de un año de estar almacenado debido al envejecimiento del material.

Palabras clave: Reciclaje, plásticos biodegradables, polipropileno, poliestireno, tereftalato de polietileno

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Institutions or organizations that finance the research and code that identifies it

1. - INTRODUCTION

The increasing demand for plastic materials has resulted in a considerable increase in the production of these materials from 1.5 million tons in 1950 to 359 million tons in 2018 [1,2]. As a consequence, there has been an increase in plastic waste in landfills and in the environment [3] and worldwide concern about the post-consumer handling of these materials [4].

One of the most favorable strategies for the management of plastic waste is the circular economy. This strategy consists of both the extension of the useful life of the material and the recovery and revaluation of waste. In this way, waste is minimized and the value of the product is maintained for a longer time [1,5]. In plastics, the way to revalue waste and increase its useful life is through reuse and recycling [6].

Mechanical recycling is an effective and economical method for the treatment of thermoplastic waste [7]. The quality of recycled plastic is highly dependent on the origin and history of the initial plastics and the processing method used, which can lead to deterioration of its properties [8,9]. In addition, the rise of biodegradable polymers has caused a new concern for recyclers since biopolymers have not been integrated into the waste treatment system at present [10].

Biodegradable polymers are plastics that can be metabolized and degraded to lower molecular weight compounds by microorganisms, macroorganisms and/or enzymes [11, 12]. Biodegradable polymers fall into three categories: (1) synthetic polymers such as poly lactic

acid (PLA) [13, 14], (2) polyesters produced by microorganisms such as polyhydroxybutyrate (PHB) [15] and, (3) natural polymers such as polysaccharides in which thermoplastic starch (TPS) is found [16, 17]. In recent years, their use has increased, so that in 2020, 2.11 million tons of biodegradable plastics have been produced worldwide and it is expected that in 2025 a production of 2.87 million tons will be reached [18].

Despite the biodegradable nature of biodegradable polymers, if the right conditions are not provided, these plastics will remain in the environment longer than expected. As a consequence of poor waste management, biodegradable polymers can easily enter the recycling chain of conventional thermoplastics [19]. In this way, biodegradable polymers could compromise the quality of the final product in plastic recycling processes [20, 21], which represents a problem due to incompatibility with synthetic plastics and processing temperatures (generally low for biodegradable polymers and high for synthetics) that could thermally degrade these materials and generate interferences in the structure of the recycled plastic [22, 23].

In terms of plastics recycling, polyethylene terephthalate (PET) is one of the dominant materials due to its wide use for single-use products, especially beverage bottles. It yields a high-quality recycled material that can sustain a profitable recycling business. However, the quality of recycled PET can be affected by contamination in the recycling stream, which means losses for the industry [22] that not only implies more costs and time for sorting the material, but also an impact on PET processing and the quality of the final product [20, 24].

In 2014, Samper et al. conducted a study on the influence of biodegradable materials on the properties of recycled polystyrene (PS) and found that even at low percentages biodegradable polymers produce a significant loss in the thermal and mechanical properties of recycled PS [25]. When the study was conducted with recycled polypropylene (PP), it was found that biodegradable polymers in percentages higher than 2.5 wt% affect the flowability index of recycled PP. Whereas, percentages equal to or greater than 5 wt% affect the mechanical properties of the material [26]. In 2021, Aldas et al. presented the results of the study of the impact of biodegradable materials on the properties of recycled polyethylene terephthalate (PET), where it was found that PHB shows the thermal degradation after PET processing, while TPS does not have good miscibility and PLA is partially miscible with PET. These effects caused a decrease in the mechanical properties of recycled PET [24].

The present study seeks to characterize blends of conventional thermoplastics contaminated with biodegradable polymers by using Fourier transform infrared spectrometry (FTIR) and differential scanning calorimetry (DSC). Both techniques are easily accessible to quality control departments and can be applied directly to the finished product without the need for extensive sample preparation. The study was performed on thermoplastics of industrial interest, polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET) [24, 27]. The biodegradable polymers of greatest commercial interest, polylactic acid (PLA), polyhydroxybutyrate (PHB) and thermoplastic starch (TPS), were evaluated as contaminants. The blends were prepared using 10% by weight of the contaminant in the synthetic plastic. Finally, the effect of aging on recycled products from PET contaminated with PLA, PHB and TPS was studied, since PET tends to have longer storage time.

2. - MATERIAL & METHODS

2.1.- MATERIALS

The recycled synthetic polymers used were: polyethylene terephthalate (PET), polystyrene (PS) and polypropylene (PP). The recycled PET, with a density of 1.35 g/mL and a melting temperature of 252 °C, was supplied by Extremadura Torrepet S.L. (Badajoz, Spain). Recycled PS with MFI 7.5 g/10 min (200 °C, 5 kg) and recycled PP with MFI 12.00 g/10 min (230 °C, 2.16 kg) were supplied by ACTECOS.A. (Ibi, Spain), Ref. 10805 and REF. 10251C respectively. As biodegradable polymers: polylactic acid (PLA), polyhydroxybutyrate (PHB) and thermoplastic starch (TPS) were used. PLA 4032D (density 1.24 g/mL and MFI 7 g/10 min (210 °C, 2.16 kg)) was provided by NatureWorks LLC (Minnetonka, USA), PHB P226 (density 1.25 g/mL and MFI 10 g/10 min (180 °C, 5 kg)) was supplied by Biomer (Krailling, Germany) and TPS type Mater-Bi@NF 866 (density 1.27 g/mL and MFI 3.5 g/10 min (150 °C, 2.16 kg)) was supplied by Novamont (Novara, Italy).

Recycled polymer blends were prepared with 10 wt% of each biodegradable polymer as contaminant. The materials were processed by extrusion and subsequent injection molding to emulate methods used on an industrial scale. A twin-screw extruder (Dupra S.L., Castalla, Spain) with a L/D 25 ratio at a screw speed of 20 rpm and an Erınca S. L. injection molding machine (Barcelona, Spain) were used, with injection times of 20 rpm. (Barcelona, Spain), with filling and cooling times of 2 and 30 s respectively. The temperature profiles used (increasing from the feeding zone towards the nozzle) both in extrusion and the injector were as follows: for PET it was 200/220/240/260/270 °C, for PS 180/185/190/195/200 °C and for PP 200/205/210/215/220 °C.

The blends of the obtained materials were identified with the acronym of the recycled thermoplastic polymer followed by the acronym of the biodegradable polymer. i. e. PET, for recycled PET; PET-PLA, for the PET blend with 10 wt% PLA; PET-PHB, for the PET blend with 10 wt% PHB.

2.2.- METHODOLOGY

Attenuated total reflectance mode Fourier transform infrared spectrometry (FTIR-ATR) analysis was performed to characterize the material mixtures. The analysis was performed on a Perkin Elmer BX spectrometer coupled with a Pike MIRacle™ ATR (Beaconsfield, UK) using the injected specimens. All materials were analyzed in the 4000 to 600 cm⁻¹ range with a resolution of 16 cm⁻¹ and 20 scans.

The differential scanning calorimetry (DSC) assay was performed in a Mettler DSC821e calorimeter (Toledo, Spain). About 5 mg of sample was placed in standard 40 µL aluminum crucibles. The samples were analyzed in thermal cycles consisting of heating, followed by cooling and then a second heating. A heating rate of 10 °C/min and a nitrogen atmosphere with a flow rate of 30 mL/min were used for all cycles. The thermal cycles of the PET-containing blends were: heating from 40 to 300 °C, cooling from 300 to 40 °C and second heating from 40 to 330 °C. The PS-containing materials were tested as follows: heating from 25 to 200 °C, cooling from 200 to 25 °C and second heating from 25 to 250 °C. Finally, for PP-containing blends, the cycles were: heating from 40 to 200 °C, cooling from 200 to 40 °C and second heating from 40 to 240 °C.

For the study of the aging of recycled PET blends contaminated with biodegradable polymers, PET blends containing 10 wt % of each biodegradable polymer (PLA, TPS PHB, separately) were prepared by extrusion. This material was stored as pellets in a rack at 25 °C and 50 % RH for one year. Then, the pellets of the different blends were injected at the same conditions mentioned above. DSC tests were performed on the stored and injected material to analyze the consequences of degradation and aging that can occur in synthetic plastics contaminated with biodegradable materials when stored for long periods of time.

3. - RESULTS

3.1.- FOURIER TRANSFORM INFRARED SPECTROMETRY (FT IR)

The study with Fourier Transform Infrared Spectrometry in Attenuated Total Reflectance (FTIR-ATR) mode was carried out in order to verify the possibility of identifying biodegradable polymers in the studied synthetic materials PET, PS and recycled PP. The biodegradable polymers analyzed (PLA, PHB and TPS) present characteristic bands between 1790 and 1750 cm⁻¹, corresponding to the carbonyl group present in the structure of PLA and PHB and to the plasticizers present in TPS [25,26].

The infrared spectrum of recycled PET and PET-PLA, PET-PHB and PET-TPS blends is shown in *Fig. 1-a*. In the spectrum of recycled PET, the bands corresponding to its characteristic groups are observed: i) carbonyl group (C=O) at 1718 cm⁻¹, ii) aromatic rings at 1402, 1014 and 872 cm⁻¹, iii) methylene group (-CH₂) at 1370 and 1172 cm⁻¹, iv) C-O bonds at 1240 and 970 cm⁻¹ [28,29]. The carbonyl band overlaps with the band characteristic of biodegradable polymers, for all the blends studied. No changes are observed in the characteristic bands of PET by the addition of biodegradable polymers.

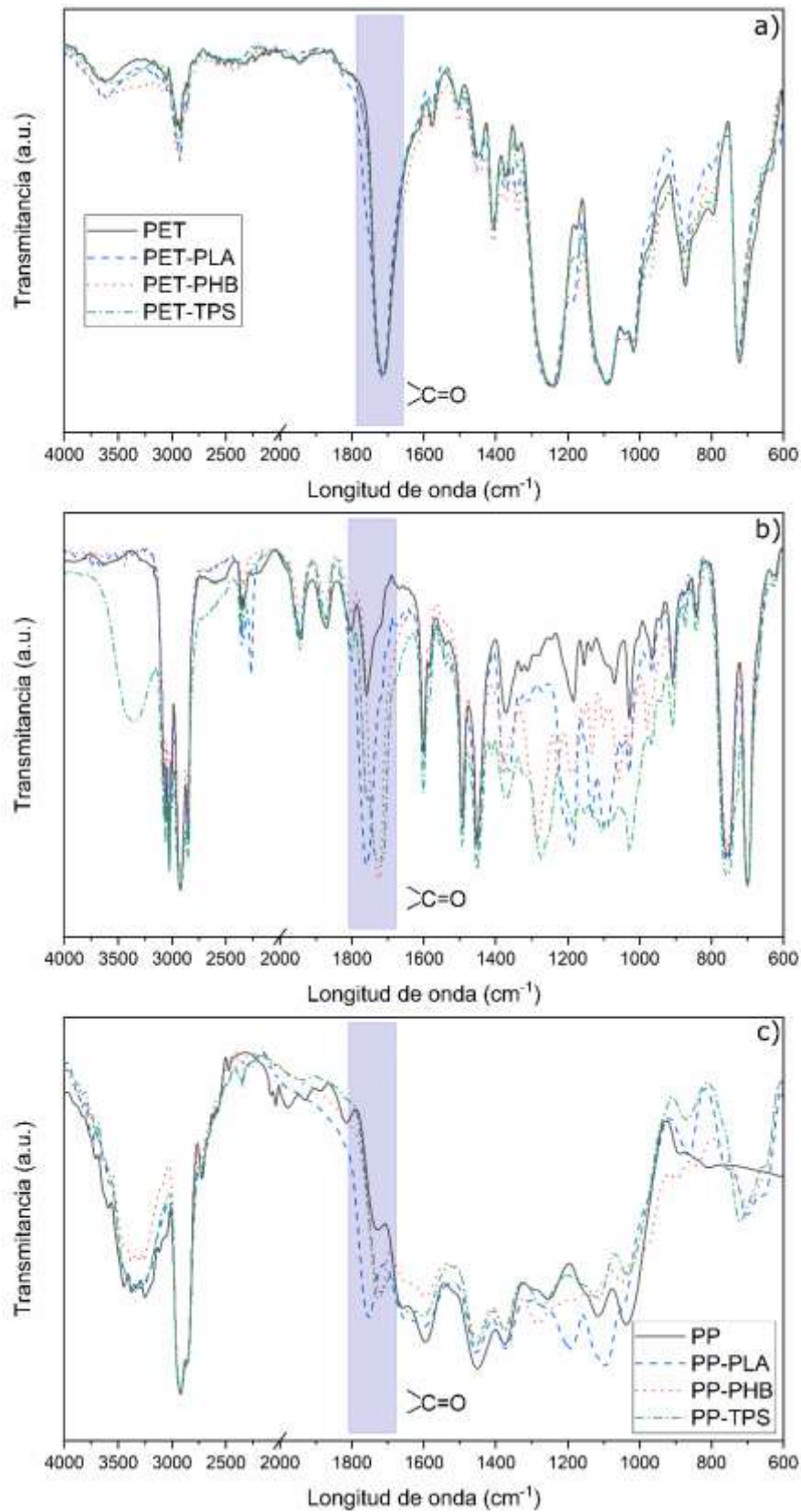


Fig. 1. FTIR spectrum of (a) recycled PET, (b) PS and (c) PP contaminated with 10% by weight of PLA, PHB and TPS

The infrared spectra obtained for the PS samples and the PS-PLA, PS-PHB and PS-TPS blends are shown in Fig. 1-b. The bands corresponding to the characteristic groups of PS are found in: i) stretching vibrations of C-H bonds in aromatics at 3064 and 3024

cm⁻¹, ii) C=C stretching vibrations in aromatics at 1600, 1496 and 1450 cm⁻¹, iii) monosubstitution of a C-H of the benzene ring 762 and 696 cm⁻¹ [27,30].

The only relevant change observed is that in the samples containing biodegradable polymer, an increase in the intensity of the carbonyl band (C=O) is generated, located between 1796 and 1730 cm⁻¹. The increase in the intensity of the band is justified by the contribution of carbonyl groups from PLA [31] and PHB [32], and in the case of TPS, the carbonyl band is attributed to the plasticizer used in the manufacture of TPS [33,34].

Fig. 1-c shows the spectra of recycled PP and its blends PP-PLA, PP-PHB and PP-TPS. The bands corresponding to the characteristic groups of PP are: i) CH₃ group motions located at 1028, 1164, 1456 and 2854 cm⁻¹, ii) CH₂ group deformation located at 2926 cm⁻¹, iii) C-H group motions at 880 and 1164 cm⁻¹ and iv) C-C group vibrations at 808 cm⁻¹ [35]. The most noticeable difference between the spectra of PP and blends of PP with biodegradable polymers is the band corresponding to the carbonyl group (1700 cm⁻¹ and 1800 cm⁻¹) present in these materials, as discussed in the previous paragraph.

3.2.- THERMAL CHARACTERIZATION BY DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The calorimetric curve of recycled PET is shown in *Fig. 2-a*. It can be seen that, in the first heating, the glass transition temperature (T_g) is at 73.5 °C followed by a cold crystallization peak located at 125.7 °C and then the melting of the material occurs at a temperature of 255.8 °C. When the material goes through the cooling cycle, a crystallization peak at 203.2 °C is observed. In the second heating cycle, the characteristic peak of cold crystallization does not appear because the cooling is performed in a controlled manner. It can be seen that the melting peak is formed by two peaks, one at 252.5 °C and the other around 240 °C, which may be due to a decrease in the size of the PET chains. This behavior can be attributed to the entry of PET of different molecular weight in the recycling process [36].

The thermal properties of recycled PET are affected with the presence of biodegradable polymers, as shown in *Fig. 2-b*. The incorporation of PLA in recycled PET causes a decrease in the melting temperature and enthalpy of fusion in both the first and second heating. It is observed that the presence of 10% PLA in recycled PET decreases the melting temperature from 252.5 °C to 237.2 °C and also decreases the enthalpy of fusion to -27.6 J/g. This indicates that the crystallization of PET decreases due to the presence of this biopolymer. In addition, the crystallization temperature is also negatively affected and decreases from 203.2 °C to 193.1 °C. The above changes indicate that PLA enters into the PET chains and exerts a plasticizing effect, decreasing the crystalline zones of PET.

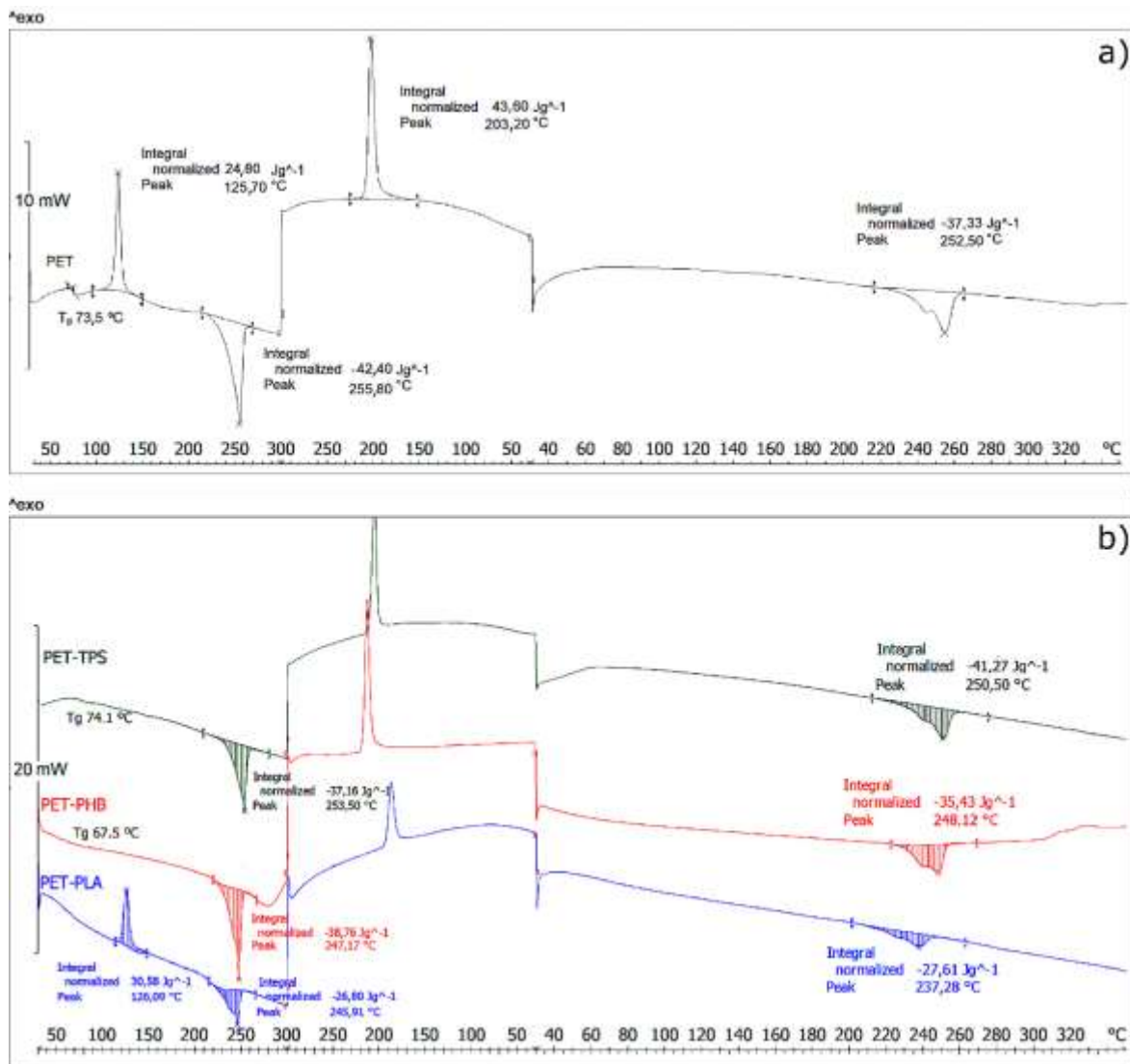


Fig. 2. DSC calorimetric curve of a) recycled PET and b) recycled PET with 10 wt.% PLA, PHB and TPS

It is observed that the addition of PHB in the recycled PET causes a decrease in Tg from 73.5 °C of the recycled PET to 67.5 °C in the PET-PHB blend. The melting temperature of the recycled PET is also affected with the addition of PHB as it decreases in both the first and second heating from 255.8 to 247.2 °C and from 252.5 to 248.1 °C, respectively. The crystallization temperature on cooling is delayed by more than 10 °C with the addition of PHB. These results indicate that the PHB chains are introduced into the PET chains, so that their mobility increases [37]. It can be seen that the addition of TPS does not change the Tg of PET, while the melting temperature (Tm) varied slightly with a decrease of 2 °C in the second heating in the PET-TPS blend. As with the PET-PHB blend, no cold crystallization occurs and the Tg is only noticeable at the first heating.

In Fig. 3 it can be seen that PS has the typical behavior of an amorphous material and that its glass transition temperature is at 85.5 °C. It is observed that with only 10 % PLA new thermal transitions appear in PS. These transitions correspond to Tg of PLA, which is located at 64.6 °C, the Tg of PS at 88.0 °C and a melting peak corresponding to PLA at 166.2 °C with a melting enthalpy of -3.3 J/g [38]. It can be seen that the calorimetric curve of the PS-PHB mixture has a Tg at 86.8 °C, which corresponds to the Tg of PS and a melting peak at 168.8 °C with a melting enthalpy of -4.5 J/g, which corresponds to the melting process of PHB. The Tg of PHB cannot be observed in the DSC because it is below room temperature. No significant changes are observed in the calorimetric curve of PS-TPS due to the addition of TPS. Only a glass transition temperature corresponding to that of PS can be distinguished, which is 88.6 °C. The Tg of TPS is not visible in the DSC because it is below room temperature. The absence of the melting peak is due to the amorphous nature of the PS used in this study, and to the low amount of TPS in the sample. TPS has a low crystallinity, so its enthalpy of fusion is low and, coupled with the low amount of TPS present in the sample, the melting of the TPS crystals is unnoticed by the equipment.

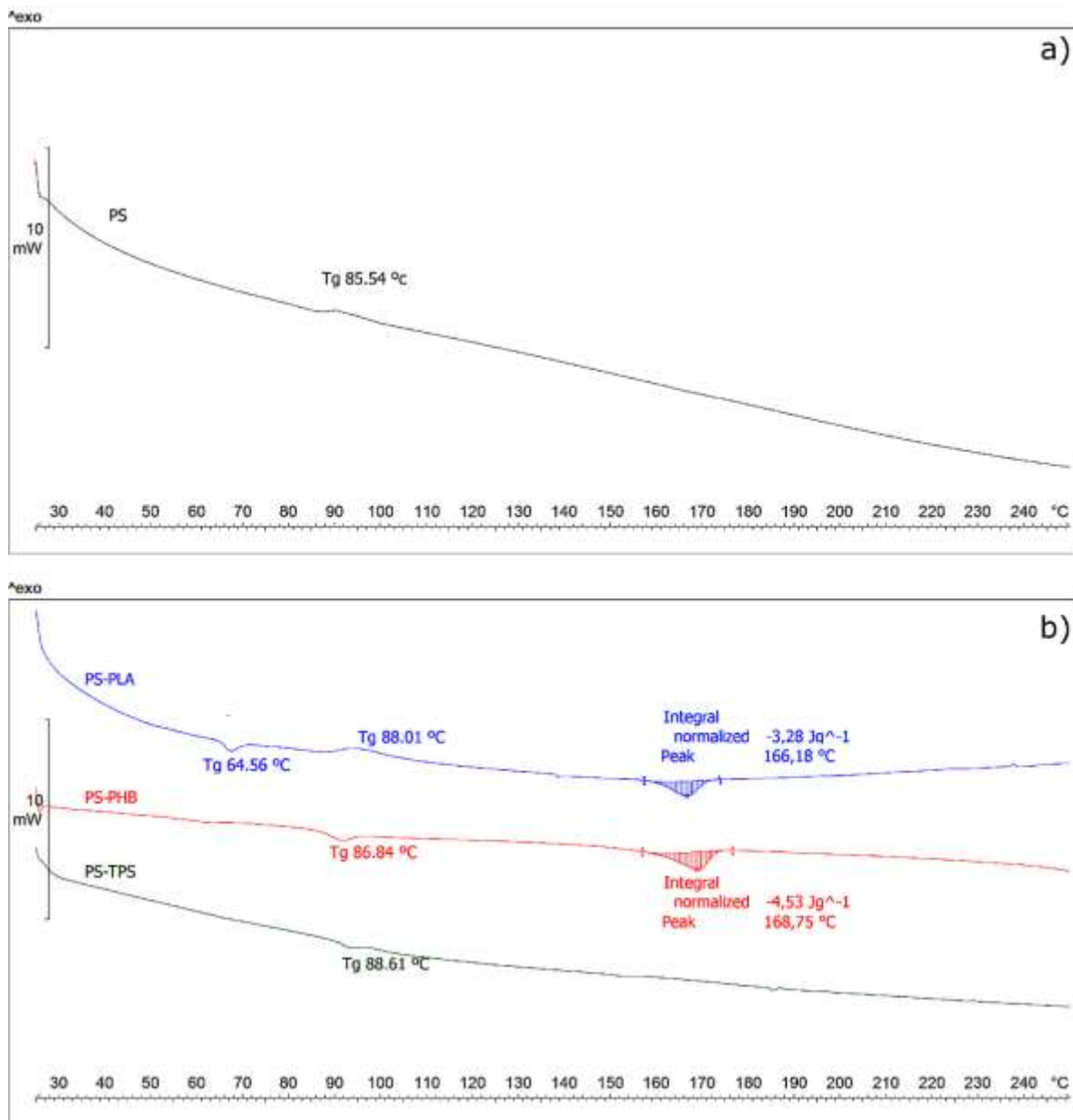


Fig. 3. DSC calorimetric curve of a) recycled PS and b) recycled PS with 10 wt.% PLA, PHB and TPS

Regarding the recycled PP, the calorimetric curve (Fig. 4-a) shows that its melting temperature is 166.9 °C and its crystallization temperature (T_c) is located at 125.4 °C. In addition, another melting peak can be observed at 128.5 °C, which indicates that the recycled PP presents polyethylene (PE) contamination. It can be seen that the incorporation of biodegradable polymers does not produce a significant variation in T_m, which varies between 162.5 and 166.2 °C (Fig. 4-b); but it does cause a decrease in T_c, reaching values between 121.5 and 123.6 °C. Finally, it was determined that the crystallization and melting enthalpies show a decrease with the addition of biodegradable polymers [37]. The presence of contaminants interferes in the chain ordering and therefore the amount of crystalline zones of the polymer decreases.

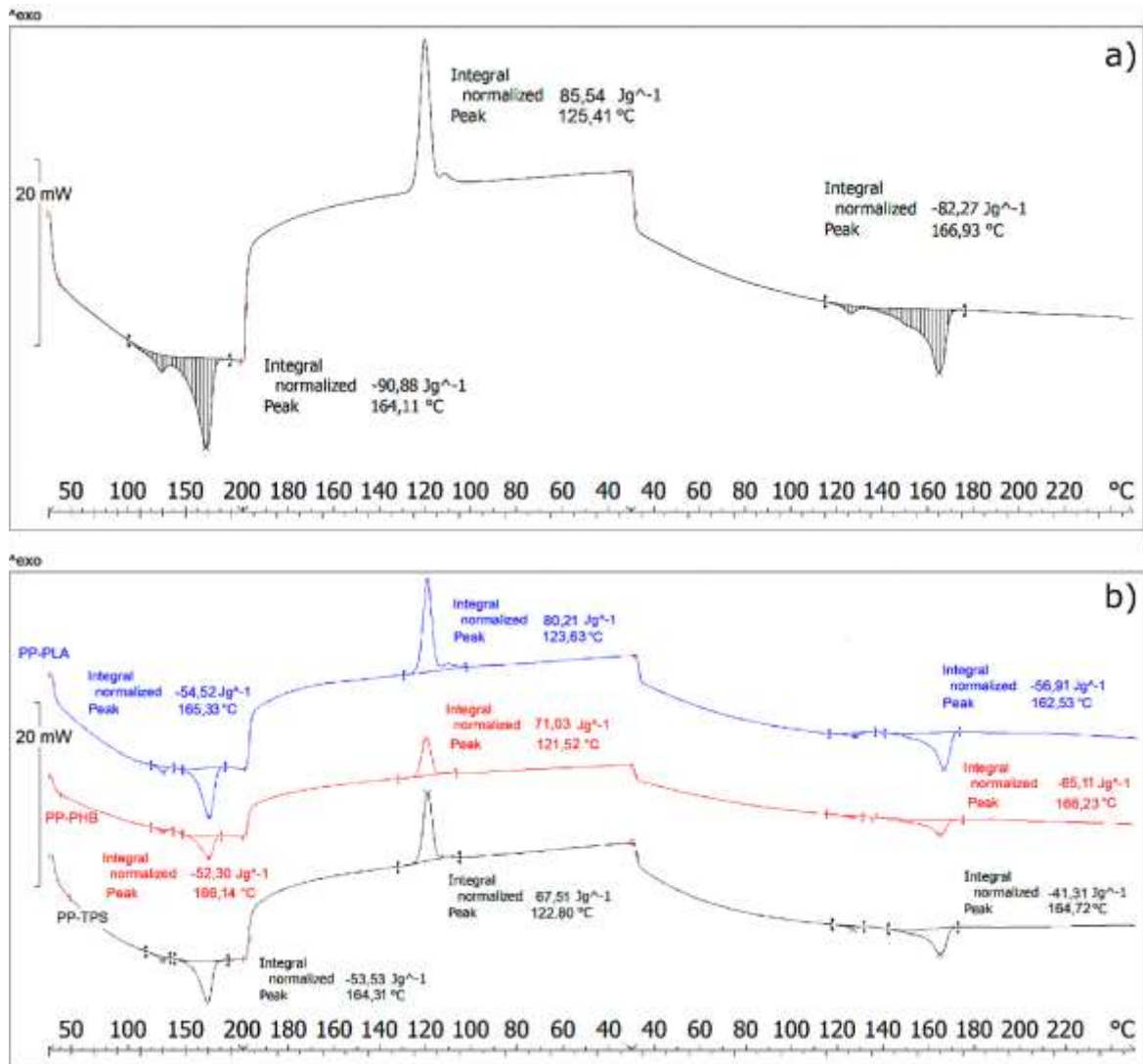


Fig. 4. DSC calorimetric curve of a) recycled PP and b) recycled PP with 10 wt.% PLA, PHB and TPS

3.2.- NATURAL AGING STUDY OF RECYCLED PET BLENDS CONTAMINATED WITH BIODEGRADABLE POLYMERS

The specimens prepared with aged blends of recycled PET and PET contaminated with 10% by weight of PLA, PHB and TPS are shown in Fig. 5. It can be seen that the recycled PET has a greenish-yellow color, while the blends with PLA and PHB have a whitish-yellow color. It can be seen that the specimen of the PET-PHB mixture is fractured due to the deterioration of properties suffered by the material. The specimens with TPS present a dark coloration, which indicates thermal degradation of the material [8], due to the TPS component.

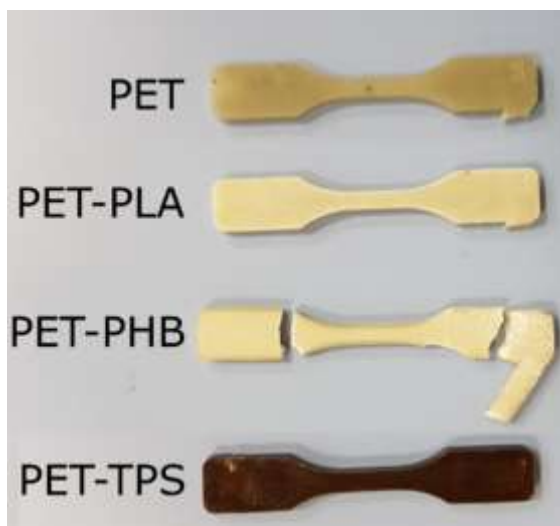


Fig. 5. Aged specimens obtained by injection molding of recycled PET and the blend of recycled PET with 10 wt.% of biodegradable polymers

The processing of PET-PHB and PET-TPS blends was negatively affected by two factors: 1) aging of the samples and 2) high processing temperature of PET (between 260-270 °C). This temperature is higher than the degradation temperature of TPS (whose initial degradation temperature is around 109.3 °C [39]) and PHB (initial degradation temperature around 220 °C [40]). The PET-PLA blend did not present any major problems during processing among the three blends analyzed.

The results of the DSC tests performed on the aged PET materials and the PET blend with 10% by weight of biodegradable polymers (PLA, PHB and TPS) are summarized in Table 1. In the aged PET it is observed that the glass transition temperature (T_g) increases with respect to the unaged PET, which translates into a decrease in the mobility of the PET chains due to the passage of time by storage of the material. The degradation temperature decreases, which confirms the loss of thermal properties linked to aging. In PET blends with PLA, TPS and PHB, a decrease in T_g is observed. It was previously determined that the chains of biodegradable polymers exert a plasticizing effect and break the ordered zones (crystalline zones) of the material, so that upon aging, the PLA, PHB and TPS chains also shorten and therefore their plasticizing power in the PET structure increases, which leads to a decrease in T_g .

Sample	Vitreous Transition	Crystallization		Fusion		Degradation
	T_g °C	T_{cc} °C	ΔH_{cc} J-g-1	T_m °C	ΔH_m J-g-1	T_{deg} °C
PET	73.5	125.7	24.8	252.5	-37.3	> 330.0
PET injected-aged	77.7	125.2	19.8	252.3	-33.4	307.7
PET-PLA	66.7	-	-	237.2	-27.6	> 330.0
Injected PET-PLA - aged	61.7	119.9	29.5	244.3	-40.5	338.5
PET-TPS	74.1	-	-	250.5	-41.27	> 330.0
PET-TPS injected - aged	51.4	98.6	27.9	253.3	-40.0	285.3
PET-PHB	67.5	-	-	248.1	-35.43	319.8
Extruded PET-PHB - aged	55.4	109.0	11.2	248.5	-39.6	278.1

Table 1. Calorimetric data of recycled PET and recycled PET with 10 wt.% PLA, TPS, and PHB, after 1 year of storage

The results of the DSC test performed on the aged PET materials and the PET-PLA, PET-TPS and PET-PHB blends are shown in Fig. 6. It can be observed that the contamination of PET with PLA, added to the aging effect, causes a decrease of 16 °C in the T_g , 6 °C in the cold crystallization temperature (T_{cc}) and 8 °C in the T_m of the material. However, the degradation temperature (T_{deg}) increases considerably due to the contaminating effect of PLA on PET.

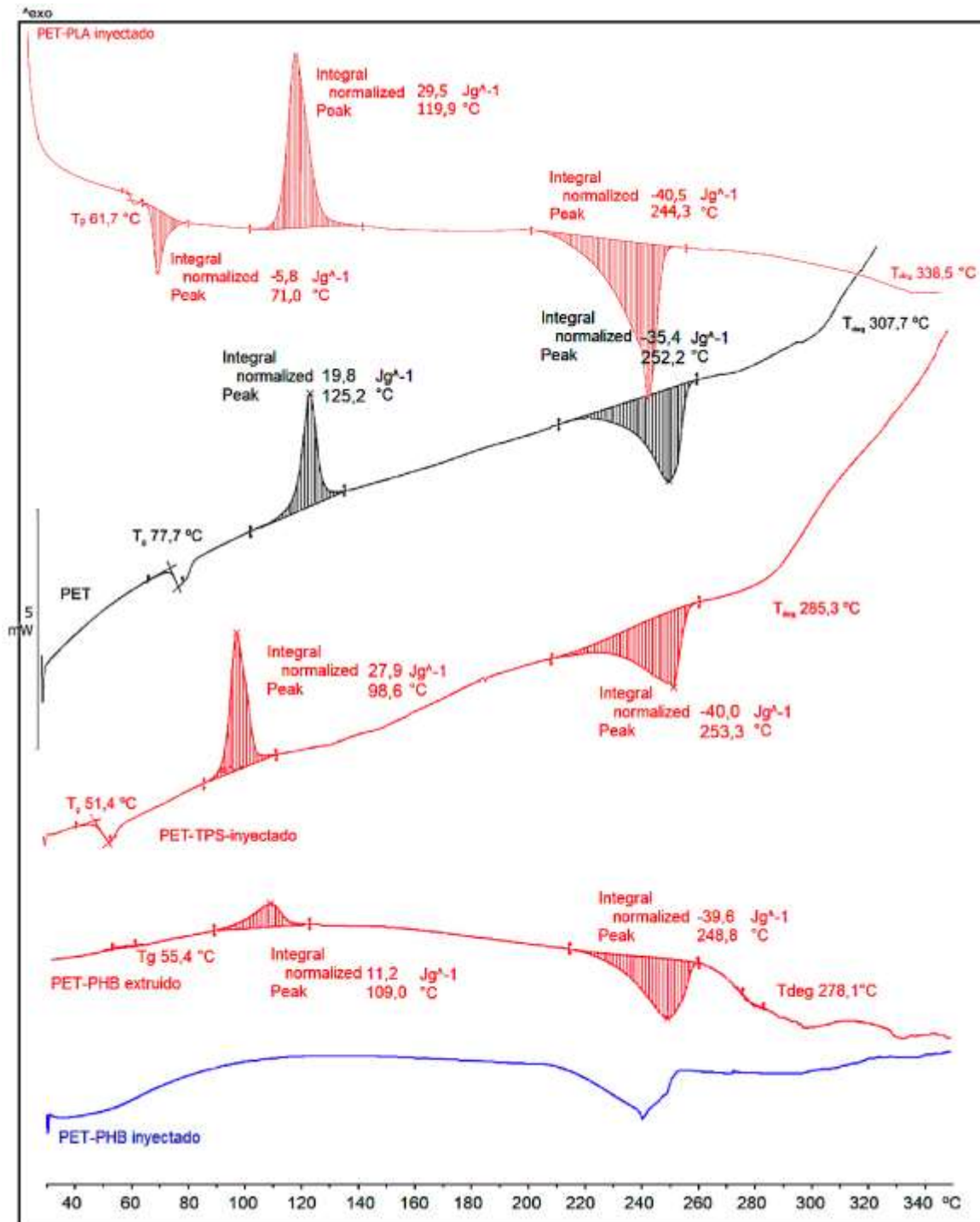


Fig. 6. DSC calorimetric curves of PET and PET with 10% by weight of PLA, TPS and PHB after 1 year of aging

The calorimetric curves of the materials show that the aged PET contaminated with 10% TPS presents a decrease of more than 20 °C of the T_g and T_{cc} of the aged PET. The T_{deg} decreases more than 30 °C, from 307.7 °C of the recycled PET to 285.3 °C in the aged PET-TPS blend (Table 1 and Fig. 6).

The PET-PHB mixture aged for one year showed good fluidity in the injection process but the test tubes obtained broke very easily in the ejection process after injection as can be seen in Fig. 7. This behavior is attributed to the degradation of the PHB during processing and to the natural aging that this material undergoes during prolonged storage.

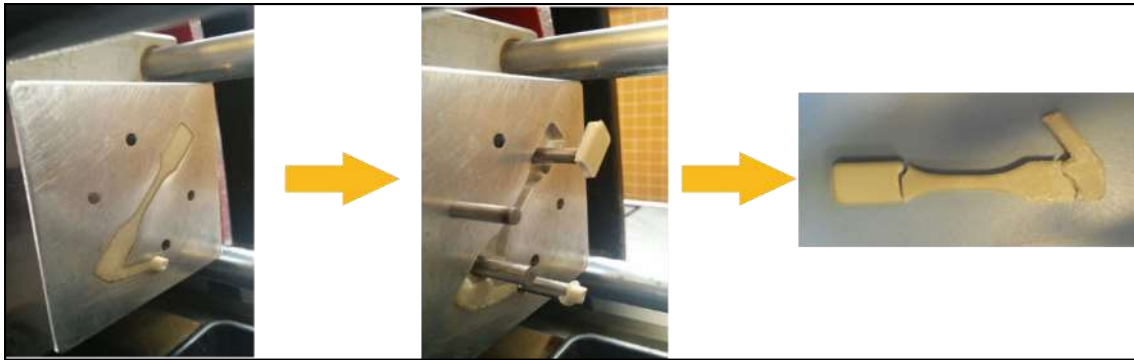


Fig. 7. Injection process of the PET mixture with PHB after one year of aging

The DSC of the PET-PHB blend, extruded and stored for 1 year, and this same blend after injection is shown in Fig. 6. It is observed that there is a decrease in the crystallization temperature of 20 °C, from 125.2 °C for PET to 109.0 °C for PET-PHB. The same occurs with the glass transition temperature. The results indicate that the one-year extrusion and aging process causes a decrease of more than 20 °C in T_g and 15 °C in T_{cc} compared to recycled PET. The melting temperature remains constant, although an increase in crystallinity is seen as the melting enthalpy increases from 35.4 J/g of the recycled PET sample to 39.6 J/g of the extruded and aged PET-PHB sample. Finally, in Table 1 it can be seen that the degradation temperature of the recycled and aged PET decreases more than 30 °C from 307.7 °C to 278.1 °C in the PET-PHB sample.

4. - CONCLUSIONS

The use of identification techniques easily accessible to quality control departments was studied to characterize blends of recycled thermoplastics contaminated with biodegradable polymers. Using Fourier transform infrared spectrometry (FTIR), it was determined that in both recycled polypropylene (PP) and polystyrene (PS) blended with biodegradable polymers, there was an increase in the intensity of the band of the carbonyl group (C=O), between 1700-1800 cm⁻¹. While in the blends of polyethylene terephthalate (PET) with biodegradable polymers, no changes in their infrared spectra were distinguished. Differential scanning calorimetry (DSC) allowed detecting that the peak of cold crystallization, in the first heating of PET contaminated with thermoplastic starch (TPS) or polyhydroxybutyrate (PHB), disappears due to the presence of these contaminants. The calorimetric curve of PET with polylactic acid (PLA) did not show significant differences with respect to that of recycled PET. In the calorimetric curves of the mixtures of recycled PS with PLA and PHB, the appearance of a melting peak due to the presence of these contaminants was evidenced. In the PS-TPS mixture, the melting peak linked to TPS was not detected, due to its low crystallinity. No significant changes were found in the calorimetric curves due to the addition of biodegradable polymers in PP, but a decrease in the melting and crystallization enthalpy was detected when these contaminants were added. Finally, it was determined that biodegradable polymers have an important influence on the aging of PET, producing problems both in its processing and in the properties of the final product.

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