Influence of Biodegradable Materials in the Recycled Polystyrene

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ABSTRACT: Polystyrene (PS) is one of the commonly used polymer in food packaging, that is why it generates a large amount of residual PS: because of the need of reduce environmental damage that occurs, it is common to recycle this polymer. Recycling of PS may be affected by the introduction of biodegradable polymer in industrial food. For this reason we have studied the influence that generates small amounts of biodegradable polymer (PLA, PHB, and TPS) in the recycled PS properties. The recycled PS and biodegradable polymers blends were evaluated by measuring the Vicat softening temperature, melt flow index, Fourier transformed infrared spectroscopy, and mechanical properties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41161.

INTRODUCTION

Polystyrene (PS) is one of the most produced and consumed polymers in the world. It is a thermoplastic with good processing properties that is utilized for many plastics commodities because of their large availability at low cost. Therefore, PS is known as one of "packaging plastics" since it is widely used in different short-term applications. Despite the increasing attention for biodegradable polymers for food packaging sector, PS and others polyolefins are still the most common polymers used for this purpose. As a result, enormous PS consumption from food packaging has led to a generation of huge amount of plastic waste. The treatment of this sort of waste has captured researchers' and industries attention during the last two decades,[1–4] due to the need to reduce the environmental damage. In order to reduce the accumulation of plastics waste, one commonly being used practice is to recycle them.

On the other hand, the increasing proactive attitude toward a reduction on the environmental impact promotes the use of biodegradable polymers for food industry as a replacement of petrochemical plastics.[5–7] In this sense, there are some biodegradable polymers that are gaining place in food packaging industries such as poly(lactic acid) (PLA),[8,9] poly(hydroxybutyrate) (PHB),[10] and thermoplastic starch (TPS)[11] since they could be disintegrated under composting conditions in just about one month.[8,10,11]

Adding biodegradable materials into the packaging market chain imply another nature of plastic disposal that have to be managed. Due to the low knowledge of consumers about where they have to throw away these new biodegradable materials after their use, they are commonly disposed with traditional packaging plastics. Although biodegradable plastic products can also be recycled after their uses by traditional recycling ways.[12]

To obtain productive recycling process from mixtures of different polymeric materials derived from plastic waste, it is necessary to first separate them according to their types.[13] However, the separation processes of the different plastics during recycling can be very complex and expensive; therefore, the presence of some impurities from other different plastics is common in the polymeric recycled materials.[14] The presence of others polymeric fractions in recycled plastics influences the structure and mechanical properties of the recycled products.[15] Assuming continuous high growth of biodegradable plastic market, it will be more and more common to find low amount of biodegradable materials in recycled plastics. It is known that mixtures of different types of polymers often result in a loss of the mechanical properties[16] and causes a diminution in the thermal stability.[1]

In this work, recycled PS and biodegradable polymers blends were studied in order to simulate a recycled PS contaminated with low amount of biodegradable materials. Three different biodegradable materials were used at different percentage. The influence of each biodegradable material in PS thermal properties was evaluated at five different concentrations of biodegradable materials by using Vicat softening temperature (VST) and melt flow index (MFI). Extruded blends followed by an injection molding process were prepared in dog-bone bars. The

thermal stability requirements were evaluated by measuring the VST. In order to know the influence of different amount of biodegradable samples on the mechanical properties of PS, tensile test was carried out. While Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to evaluate the structural and surface properties. The disintegration under composting conditions was monitored to obtain a prospective approach on the degradation of blends system based on biodegradable materials incorporated into PS matrix.

EXPERIMENTAL

Materials and Sample Preparation
PS scrap were provided by ACTECO S.A. (Ibi, Spain) coming from food packaging.

PLA 4032D was supplied by NatureWorks LLC (USA), PHB P226 was provided by Biomer (Krailling, Germany), and TPS Mater Bi was supplied by Novamont (Novara, Italy).

Blending of PS with biodegradable polymers was carried out using a screw extruder (Dupra S.L., Castalla, Spain) at 30 rpm rotor speed with a temperature of 180–200°C. The blending were prepared by varying the biodegradable polymers contents, from 0 to 15% (0, 2.5, 5, 7.5, 10, and 15%) (wt %). Later, samples for different mechanical tests were prepared by an injection molding process on a Babyplast standard 6/6 (Cronoplanst S.L., Abrera, Spain). We used a mold with normalized sample dimensions for tensile test according to ISO-527.

Mechanical Properties
The mechanical characterization was carried out using tensile and hardness tests.

The tensile tests were carried out using a universal ELIB 30 (S.A.E Ibertest, Madrid, Spain) following ISO-527. All the tests were carried out at room temperature at a speed of 10 mm min^{-1} and with a load cell of 5 kN. At least five test pieces of each sample were used.

The hardness tests were carried out using a Shore D Durometer, as indicated in the norm UNE-EN ISO 868. The equipment used was a mod. 673-D Durometer (Instrumentos J. Bot S.A., Barcelona, Spain) using samples of 4 mm thickness. A minimum of five measurements were taken and the average values were calculated.

Infrared Spectroscopy Analysis
FTIR measurements were carried out using Perkin–Elmer Spectrum BX infrared spectrometer (Perkin-Elmer España S.L., Madrid, Spain). For its completion, films with sufficient transparency were obtained through dissolution with trichloroethylene and subsequently dried to remove all solvent traces. Hundred scans at a resolution of 4 cm^{-1} were carried out for each sample.

Scanning Electron Microscopy Analysis
The images obtained by SEM microscopy were performed with a Phenom (FEI company, Eindhoven, the Netherlands), using voltage 5 kV. The samples were previously covered with a layer of gold.
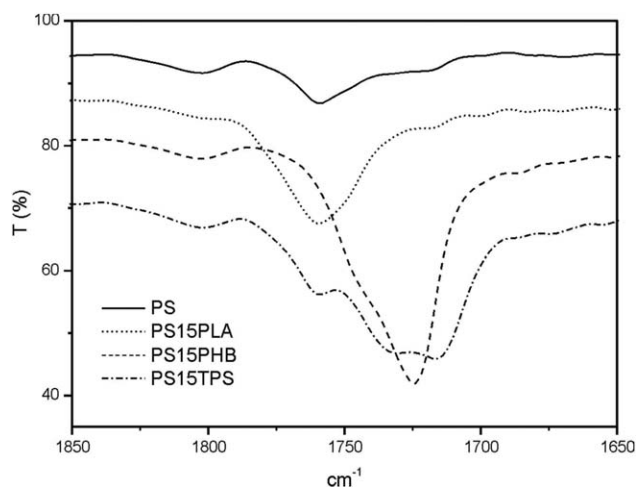

Figure 1. FTIR spectra: PS and PS/biodegradable materials blends.

Disintegration Under Composting Conditions
The mature compost was obtained from Mantillo. The compost had the following basic properties: organic solids 45%, vegetable solids 40%, 30% of humidity, and pH between 6 and 7. Test dog-bone of the highest amount of biodegradable material (15%) was buried into a compost reactor (28 cm × 19 cm × 12 cm) containing compost medium with water content of around 50%. Samples were recovered at 8, 21, and 30 days.

After each extraction, a visual check and SEM images of the samples were carried out to study the degree of physical degradation in compost as a function of time. Thermogravimetric analysis (TGA) tests were also done by using a TGA/SDTA 851 Mettler Toledo thermal analyzer (Schwarzenbach, Switzerland). Samples were weighted around 10 mg and heated from 30 to 600°C at 10 °C/min under air conditions.

Other Techniques
MFI measurements were obtained with an extrusion plastometer (AtsFaarS.p.A, Vignate, Italy) according to the guidelines of ISO-1133, the temperature and load used were 200°C and 5 kg, respectively. And VST measurements were made on a standard Vicat/HDT station DEFLEX 687-A2 (Metrotec S.A., San Sebastian, Spain) following ISO-306.

RESULTS AND DISCUSSION

Detection of Biodegradable Materials in Recycled PS by FTIR
The FTIR technique provides a simple method for the detection of biodegradable materials in PS because the infrared spectra of the PLA, PHB, and TPS have different characteristic bands of PS. As shown in Figure 1 between 1790 and 1750 cm^{-1}, the blends PS/biodegradable materials (with 15% wt biodegradable material) exhibit a strong band that has no pure PS, this band is due to C=O carbonyl stretching of PLA[17] and PHB[18] and plasticizers used to obtain the TPS.[19–21].

Miscibility of PS/Biodegradable Polymers
According to the chemical nature of the polymers, these may be more or less miscible with each other. In general, semicrystalline and amorphous polymers show incompatibility in the final mixture.[16,22] These incompatibilities may generate a

Table I. Small's Molar Attraction Constants for Several Functional Groups

Group	$F^{\star}$ (cal$^{1/2}$ c.c.$^{1/2}$)	Group	$F^{\star}$ (cal$^{1/2}$ c.c.$^{1/2}$)
—CH$_3$	214	—C$_6$H$_5$	735
—CH$_2$—	133	—O—	70
—CH<	28	—H (variable)	80-00
>C<	−93	—OH	83
>C=O	275		

Table II. Values of the Solubility Parameters Calculated from the Constants in Table I

Polymer	Structure	$\delta_{(cal)}$ (MPa$^{1/2}$)
Polystyrene		18.5
PLA		19.1–20.1
PHB		21.4
TPS		8.4

lamination of material and loss of mechanical properties. Furthermore, the incompatibility also depends on the percentage of impurities present, the percentage of each polymer in the mixture, the percentage of crystallinity, or the polarity of the components.

The relative affinity of two polymers can be estimated using the solubility parameters (δ).[23] Thus, the proximity of both polymer parameters is used to evaluate the miscibility between them. To consider the components of the mixture compatible, the solubility parameters of the polymers should be of the same order.

Several methods have been developed for the determination of the solubility parameter, however, it is generally calculated from the structural formula, due to its simplicity and the validity of the results obtained. Considering various types of simple molecules, Small made a list of molar attraction constants (F) for several molecules,[24] which are additive. Thus, δ can be calculated by adding the molar attraction constants, considering the contribution that each group makes the overall structure of the molecule [eq. (1)].
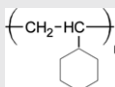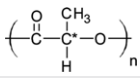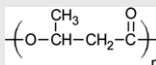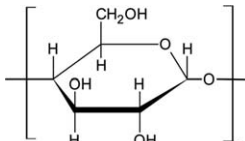
$$\delta = \frac{\rho \sum_j F_j}{M_n} \qquad (1)$$

where ρ is the density of the polymer, M_n is the molar mass of the repeating unit, and $\sum_j F_j$ is the sum of the group contributions to the cohesive energy density.

The values of molar attraction constants (F) of functional groups at 25° C are shown in Table I. Small used it to calculate the solubility parameter.

The results of calculation of δ according to the method by Small, using eq. (1) and Table I, can be seen in Table II.

The results of δ, according Small's method, using eq. (1) and Table I, can be seen in Table II. It can be seen that δ of PS is 18.5 MPa$^{1/2}$ and that none of the biodegradable materials presents similar δ, although the PLA is the biodegradable material having the nearest δ of 19.4–20.1 MPa$^{1/2}$ to PS and the TPS is the material with the least close to δ of PS (8.4 MPa$^{1/2}$); therefore, biodegradable materials studied are not miscible with the PS and small amounts of biodegradable materials produced a decrease in the mechanical properties of the recycled material. Also as can be seen in the SEM images taken with PS15PLA [Figure 2(a)], PS15PHB [Figure 2(b)], and PS15TPS samples [Figure 2(c)] clearly show phase separation of the blends, indicating immiscibility of the components of the blends. When two polymers that form a blend are immiscible, a biphasic system is formed. One of them acts like matrix phase and the other acts like dispersed phase. In general, these materials have poor mechanical properties, because the adhesion between the phases is not good and stress concentrations areas are generated.[25–27]

Mechanical Characterization

The analysis of the mechanical properties of the blends includes different parameters, such as tensile strength, elongation at break, and the energy under stress–strain curve (toughness modulus).
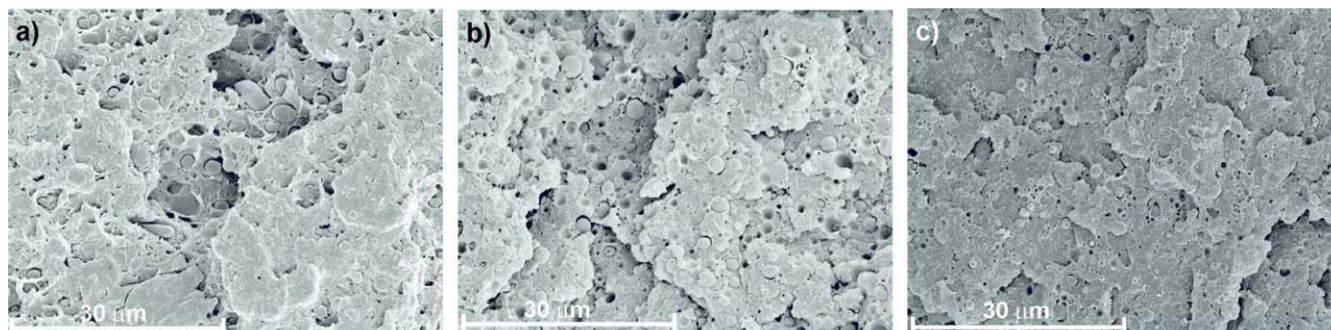

Figure 2. SEM image at 2000× magnification of the samples, (a) PS15PLA; (b) PS15PHB; and (c) PS15TPS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
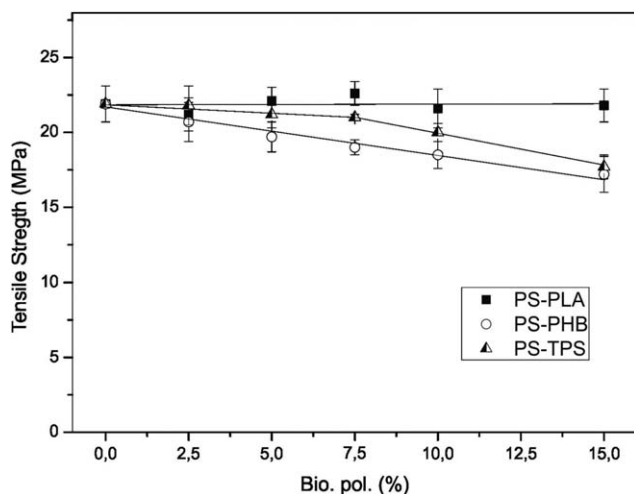
Figure 3. Variation of tensile strength versus biodegradable polymers wt % incorporated to PS.

Figure 5. Variation of toughness modulus versus biodegradable polymers wt % incorporated to PS.

Compatibility between the two polymers of the blend is a major factor that affects the performance of the material; if the polymers are incompatible, a general alteration in the mechanical properties of the blend can be observed. Incompatibility causes important negative effects on the properties of the material.[28]

Figure 3 shows the evolution of the tensile strength considering the composition of all blends. It can be seen that the addition of PLA does not vary significantly this property because tensile strength practically remains constant in all formulations. However it can be seen that the incorporation of PHB and TPS in the PS causes a decrease of the tensile strength, more pronounced in the case of the PHB. This decrease is due to the lack of interaction between the interfaces of the components of the blend as discussed above.

The graphical representation of the elongation at break also shows decreased property with increasing content of biodegradable material. The elongation at break of the samples with low content of biodegradable material (2.5–7.5 wt %) decreases
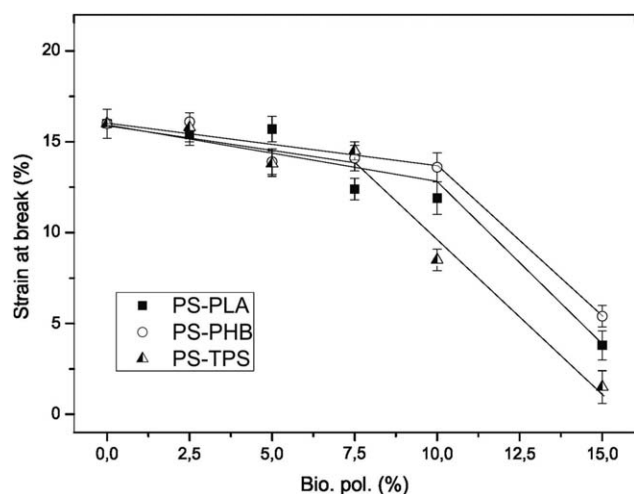
slightly, but high concentrations of biodegradable material content (10, 15 wt %) result in a sharp decrease in elongation, sharper in the case of PS-TPS samples with a decrease of the elongation at break of 90% (Figure 4).

As expected, also the toughness modulus decreases as the content of biodegradable polymer increases. Figure 5 shows a comparison of the blends and it can be appreciated that the incorporation of PLA in PS causes less decrease of toughness modulus than PHB and TPS.

As we have seen the mechanical properties of the blends decrease with increasing the percentage of biodegradable material. It is one of the indications of the immiscibility of the components. It was also detected that the PLA is the biodegradable material that decreases the mechanical properties of PS, this phenomenon can be explained by the proximity of δ of PLA and PS.

Thermal Properties

In the previous sections, we have described the changes in mechanical properties caused by the presence of biodegradable polymers, but it is not the only important property that may
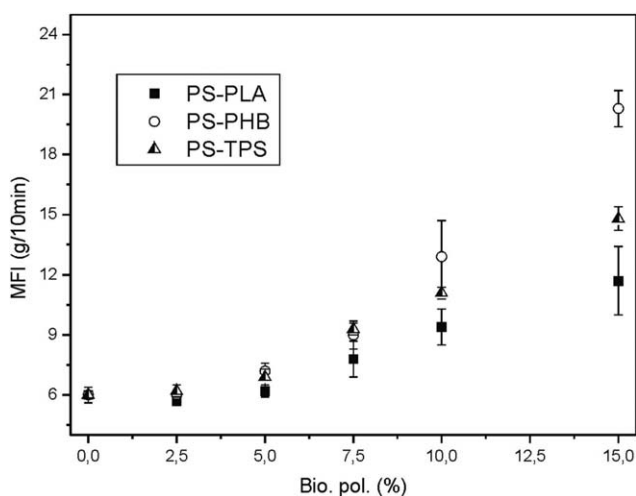

Figure 4. Variation of strain at break versus biodegradable polymers wt % incorporated to PS.

Figure 6. Plot of MFI index versus different biodegradable polymers wt %.
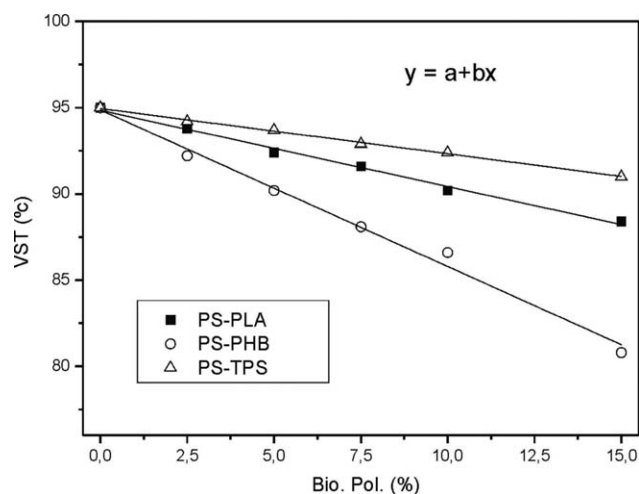
Figure 7. Plot of VST temperature versus different biodegradable polymers wt %.

affect the recycling of materials. Another important effect is the possible alteration of the MFI of the blends, since this property is very important for processing of the material.[29]

The graphical representation of the results (Figure 6) shows that the MFI increases as the biodegradable polymer content increases. It can also be seen that PHB is the biodegradable polymer more increases MFI than the PS. This result could be related with some levels of PHB degradation. PHB has a small processing window for melt extrusion by reason of its melting point is approximately at 180°C while the degradation temperature is typically around 270°C.[30] Thus, at the processing temperature used for PS processing, in the range of 180–200°C, somewhat PHB thermal degradation takes place. Meanwhile, the

PLA is less than change the MFI of PS. This behavior is very similar to the mechanical properties of the blends.

The thermal stability of blends of PS with biodegradable polymers was determined by the VST. The results for all blends tested (Figure 7) show a linear correspondence between the VST and blend composition. Systems PS/biodegradable polymers reduce the VST with increasing concentration of biodegradable polymer. This behavior can be attributed to the strong macroscopic nature with respect to temperature VST and other qualities like mechanical properties, in which the levels of interaction between the interface of the integral components of the blend plays a decisive role.

Disintegration Under Composting Conditions

Macroscopic observations of the recovered samples after 8, 21, and 30 days of exposure to composting conditions are shown in Figure 8. All samples suffered physical changes after 21 days because of the physical disintegration of biodegradable materials. All samples presented a surface deformation after 30 days. Also SEM images showed some changes in the samples surfaces (Figure 8).

Macroscopic observations were confirmed with TGA tests. TGA results showed that in PS samples added with PLA and PHB, the decomposition steps have been resolved into different components which the first one can be assigned to the loss of the biodegradable material, PLA and PHB, and the second step is the degradation of PS itself. In the case of TPS the degradation occurred in only one step. It was clear noticeable that the initial degradation temperature was shifted toward lower temperatures [Figure 9(a,c,d)] as degradation time increased for all studied formulations. PS-TPS15% samples also showed that the maximum degradation temperature was shifted to higher temperatures after the compost exposition due to the lesser amount of
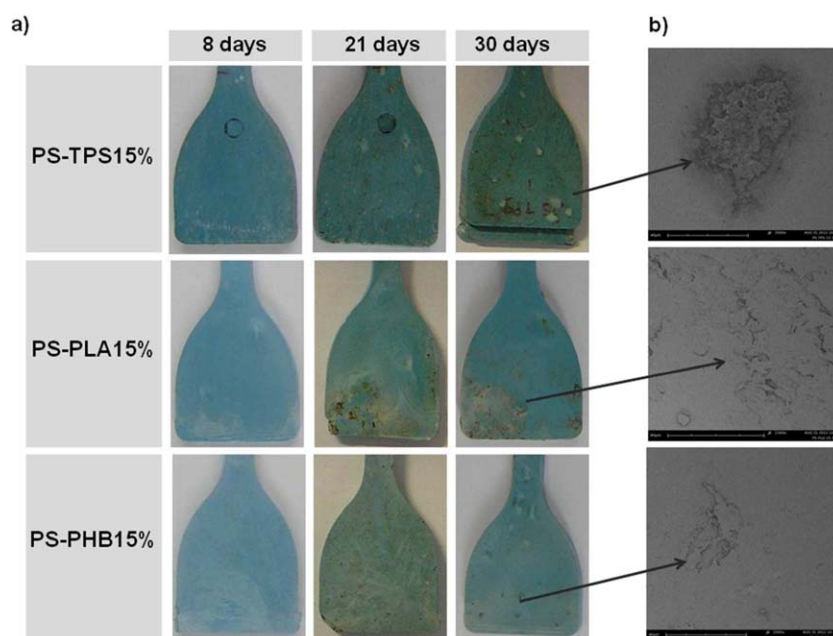

Figure 8. PS-TPS15%, PS-PLA15%, and PS-PHB15% composites after 8, 21, and 30 days exposed to a composting conditions at 58°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
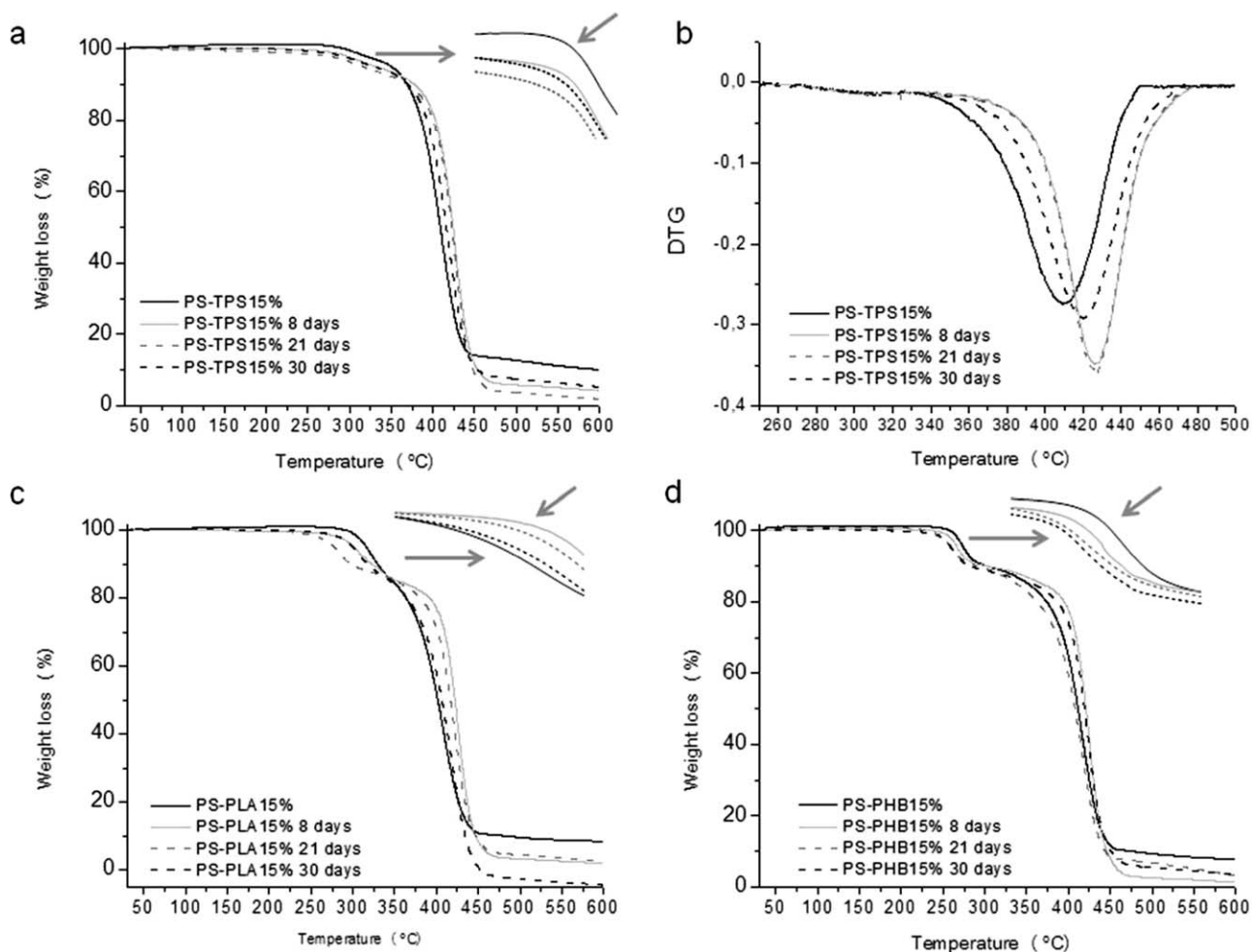
Figure 9. TGA graphs of blends composites after 8, 21, and 30 days exposed to a composting conditions ($T = 58°C$), (a) TGA curves of PS-TPS composites, (b) DTG curves of PS-TPS composites, (c) TGA curves of PS-PLA composites, and (d) TGA curves of PS-PHB.

TPS in the formulation leading to less contaminated PS with higher thermal stability. These results showed that all biodegradable material content decreased after their exposure to compost. It has been reported that neat PLA and TPS are disintegrated under composting conditions in 25–30 days.[8,10] Meanwhile, PHB need more time to be disintegrated in compost (~45 days)[10] However, in the present work, there remained biodegradable material in each sample after 30 days in compost, showing that PS presence delay de-disintegration of biodegradable materials. It is known that polymers disintegration in composting material starts by a hydrolysis reaction.[31] In this case the molecular interactions between biodegradable materials and PS could prevent biodegradable materials from water; therefore the action of microorganisms is delayed.

CONCLUSION

In this work, we have evaluated mechanical and thermal properties of blends made with recycled PS and different biodegradable polymers (PLA, PHB, and TPS).

The presence of low percentages of the biodegradable polymers in the recycling of PS causes significant losses in mechanical properties and thermal properties (Vicat, MFI). The decrease of

these properties is a clear indication of immiscibility between the components, this effect is also visible in the SEM images of fractured specimens. Incorporating biodegradable polymers in the recycled PS can cause partial biodegradation of the material if given the right conditions.

Therefore it is essential to detect the biodegradable materials recycling PS for possible elimination of the production chain. The detection of these materials is relatively simple when using FTIR equipment because biodegradable polymers exhibit a strong band between 1790 and 1750 cm^{-1}.

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