THERMAL PROPERTIES OF POST-CONSUMER PET PROCESSED IN PRESENCE OF PHOSPHITES

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Abstract

Thermal properties of recycled triphenylphosphite (TPP) chain extended poly(ethylene terephthalate) (PET) was investigated. As the TPP concentration increases, both reaction residues and molecular mass increase affecting significantly the thermal properties and crystallization behavior of the material. The presence of TPP residues did not affect the crystalline melt temperature (T_m), but modified the glass transition temperature (T_g), the crystallization temperature on heating (T_{hc}) and the crystallization temperature on cooling (T_{cc}). In the samples submitted to extraction with acetone, the properties were influenced by molecular mass changes, probably due to the presence of some insoluble reaction residue. The thermal stability of the sample purified by extraction after chain extension was comparable to that of the non-extended sample when heating was carried out under nitrogen atmosphere.

Keywords: chain extender, poly(ethylene terephthalate), recycling, thermal properties

Introduction

Mechanically recycled poly(ethylene terephthalate) (PET) is usually submitted to thermal and hydrolytic degradation when in the melt state during reprocessing [1–3]. These processes provoke the drop of molecular mass decreasing some properties of the recycled material. In order to reduce the effects of these degradation processes, some additives acting as chain extenders can be used during the melting of post-consumer PET [4–7]. These additives can compensate the loss of viscosity as they link chains while degradation processes cause the breaking of molecules. Moreover, some chain extenders like phosphites can also act as antioxidant agent [8, 9].

In a previous work [10], we report the chain extension of post-consumer PET with several phosphite chain extenders. Monitoring of torque during processing in the presence of triphenylphosphite (TPP) showed that the viscosity of molten PET reached a maximum value after which it started to decrease due to the predominance

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of degradation process. As TPP concentration increased, both the rate of molecular mass enhancement and the rate of degradation, after the maximum viscosity point, increased.

In the mechanism suggested for chain extension reaction of PET induced by triphenylphosphite (TPP), the formation of small molecules as by products [5, 11] is foreseeable. These residues may modify the crystallization characteristics and other important properties of PET.

In this paper the results of the investigation about the influence of TPP on the thermal properties of PET mechanically recycled are reported. The flakes of post-consumer PET bottles were processed in an internal mixer connected at a torque rheometer. Addition of TPP at several concentrations was carried out 1.5 min of processing. One part of each sample was extracted with acetone to remove possible reaction residues and both purified and non-purified samples were analyzed by differential scanning calorimetry. The values of glass transition temperature (T_g), crystalline melt temperature (T_m), crystallization temperature on heating (T_{hc}), crystallization temperature on cooling (T_{cc}), melt enthalpy (ΔH_m) and crystallization enthalpies (ΔH_{hc} and ΔH_{cc}) were determined.

Some authors [5, 12] suggested that phosphorous atoms could be incorporated in the polymer chains, affecting their stability at high temperatures. On that account, differences on thermal stability of a TPP chain extended sample, previously extracted with acetone to avoid the residue influence, and a non-additivated sample were also studied by thermal gravimetric analysis (TG).

Experimental

Materials

Flakes of PET were obtained by grinding the post-consumer PET bottles without caps and labels. The flakes with 3 mm average diameter were washed with plenty of water and pre-dried by room exposure. The drying procedure consisted in heating the flakes for 16 h in an oven at 160°C under dry nitrogen flow. The flakes were maintained inside a dessicator until processing. Triphenylphosphite – 97% (Merck), analytical grade phenol (Vetec) and 1,2,4-trichloro-benzene (Baker) were used as received.

PET processing

A Haake 9000 torque rheometer, equipped with internal mixer and counter rotors was used to process the flakes. Addition of the liquid organic phosphite was carried out by using a syringe. The additive was injected after melting of the flakes (90 s), which was confirmed by the drop of torque. The influence of TPP concentration (1, 1.5, 2, 2.5 and 5%) was studied by the torque monitoring.

Viscometry

Melt processed samples were dissolved in phenol/trichloro-benzene (50:50 *v/v*). Determination of intrinsic viscosity [η] of each sample were carried out in an Ubbelohde viscometer at 30°C and the viscosity molecular mass $\overline{M}_v$ was calculated using by the Mark–Houwink–Sakurada equation with *K* and a constant being $1.48 \cdot 10^{-4}$ and 0.81, respectively [13]. In some cases, small amounts of insoluble fraction was observed. It was removed by filtrationin a 5 μm Millipore membrane. In all cases, concentration was corrected by mass the solid residue after solvent evaporation.

Thermal analysis

The thermal behavior of the samples were investigated using a differential scanning calorimeter Perkin Elmer, model DSC 7, under nitrogen atmosphere, in the following sequence: (1) Fast heating of the sample (25–280°C, 200°C min^{-1}) followed by fast cooling (280–25°C, 200°C min^{-1}); (2) second heating run at 10°C min^{-1} until 280°C, when T_g, T_{hc}, T_m, ΔH_{hc} and ΔH_m were determined; (3) second cooling run at 10°C min^{-1} until 25°C, for the determination, T_{cc} and ΔH_{cc}. The crystallinity (X_c) was calculated by the equation:

$$X_c = (\Delta H_m - \Delta H_c)/\Delta H^o \text{, where } \Delta H^o = 32.5 \text{ cal g}^{-1} \text{ [14]}$$

Thermal gravimetric analysis (TG) was performed in a Perkin Elmer TGA-7, using a temperature range of 30–700°C (10°C min^{-1}) and N_2 atmosphere. A sample processed with 1.5 mass% of TPP, previously extracted with acetone, and a sample processed without the phosphite were used.

Impurities of purified samples for thermal analysis were extracted with acetone in a soxhlet for 24 h.

Results and discussion

Effect of TPP concentration on torque curves

The effect of TPP concentration on the torque curves obtained from the torque rheometer is presented in Fig. 1. It was reported [15] that the maximum torque value observed when PET is processed in the presence of TPP decreases as the phosphite concentration increases. However, in this work the opposite was found. The curves indicate that the enhancement of melt viscosity at the beginning of the processing run increases with TPP concentration. For higher concentrations, a maximum torque value followed by a torque decrease that was more evident as TPP concentration increased. The significant rise of torque indicates that, in addition to linear extended chains, formation of branches or crosslinks is also probable in the case of phosphorous(III) incorporation into the backbone of the extended-chain. Scheme 1 shows a possible structure for a branched polymer. The decrease of torque after 7 min of processing, observed for samples processed with 2 and 2.5 mass% in Fig. 1, can be due to the break of these less stable linkages, although acid by-products formed, as phenol,
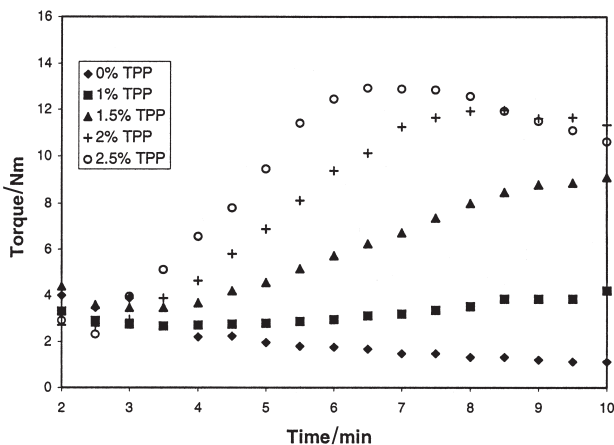
Fig. 1 Torque curves of recycled PET processed in the internal mixer at 260°C and 60 rpm with different TPP concentrations

can also contribute to degradation of ester bonds in the polymer chains. Intrinsic viscosities ([η]) measurements, carried out on samples processed for 10 min (Table 1) showed the same tendency of the torque value, i.e. the final torque was proportional to [η]. Value of K and a for the Mark-Houwink-Sakurada equation, these values are related to linear polymers. Intrinsic viscosity is related to hydrodynamic volume of polymer molecules in solution and branching reduces it; in view of the fact that for many samples there must be a certain amount of branched polymers in solution, there is the probability of underestimation of $\overline{M}_v$. Nevertheless, the results are consistent, since even if we consider this point an increase of the molecular mass is undoubtedly.

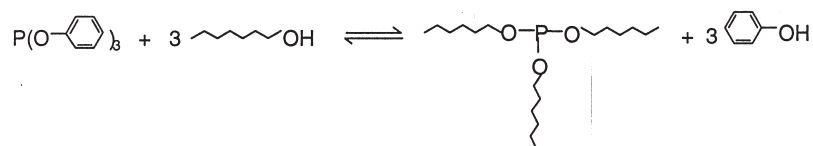**Table 1** The final torque [a] (τ_f) of TPP additivated samples and their viscosity molecular mass ($\overline{M}_V$)

C^b/%	τ_f/Nm	$\overline{M}_V$
0	1.13	17.800
1.0	4.19	25.000
1.5	9.10	29.000
2.0	11.35	48.900
2.5	10.63	32.600

[a] After 10 minutes of processing; [b] C: TPP concentration
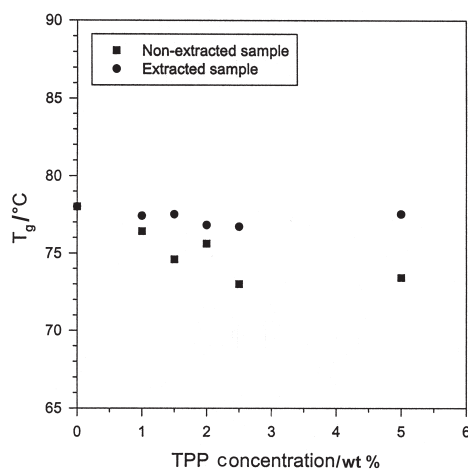
Fig. 2 Influence of TPP concentration (C) on the glass transition temperature (T_g) of extracted and non-extracted samples
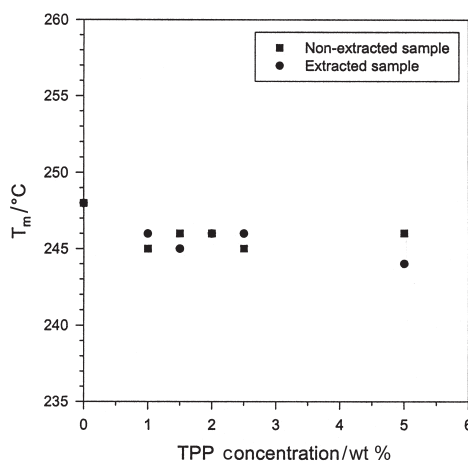

Fig. 3 Influence of TPP concentration (C) on the crystalline melt temperature (T_m) of extracted and non-extracted samples

Thermal behavior

As shown in Fig. 2, T_g of purified samples (acetone extract PET) did not change in samples processed with different amounts of TPP. Nevertheless, for the samples containing reaction residues, a drop of T_g was observed. This behavior suggests that the reaction residues act as a plasticizer in the range of concentration studied, modifying the overall mobility of chains.

Figure 3 shows that T_m did not change either, when TPP concentration was increased. This fact indicates that the presence of reaction residues did not modify the crystal perfection.
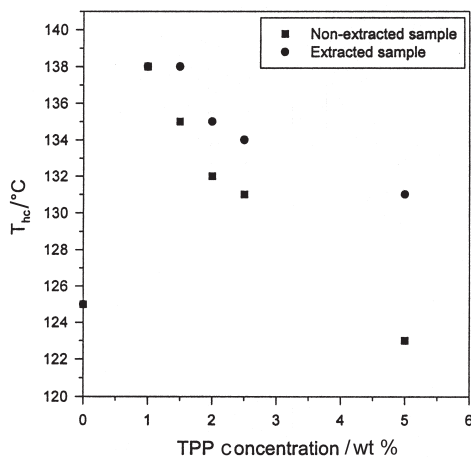
Fig. 4 Influence of TPP concentration (*C*) on the crystallization temperature (T_{hc}) on heating of extracted and non-extracted samples
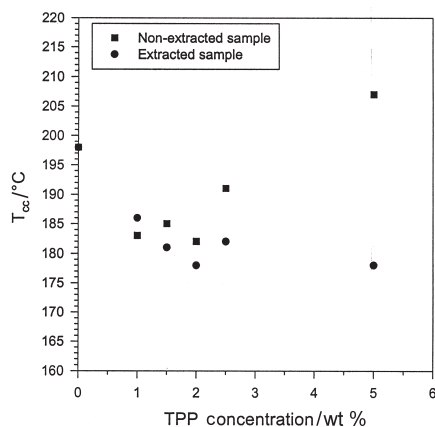

Fig. 5 Influence of TPP concentration (*C*) on the crystallization temperature (T_{cc}) on cooling of extracted and non-extracted samples

The crystallization temperature on heating T_{hc}, changed significantly as a function of TPP concentration (Fig. 4). In the non-extracted samples, the polymer molecules have more mobility due to the plasticizing effect caused by the reaction residues, that promote an easier crystallization. Thus, crystallization on heating occurs in lower temperatures, as the amount of residues is increased. It was expected that, in the purified samples, only the molecular mass would influence T_{hc}. Samples with higher molecular masses, resultant from the addition of higher amounts of TPP, would have lower segmental mobility and, therefore, would crystallize at higher temperatures on heating. However, this behavior was not observed. Samples with higher molecular masses, which correspond to the samples processed in presence of higher

TPP amounts, showed lower T_{hc} values. This fact suggests the presence of some compound acting as nucleating agent, which was not extracted by acetone.

The crystallization temperature on cooling, T_{cc}, also changed as a function of TPP concentration as shown in Fig. 5. For the non-extracted samples, there was an overlap of two effects when TPP concentration increases: 1) the increase of the molecular mass that can lead to reduction of T_{cc} and 2) the increase of reaction residues that can promote the crystallization contributing to rise T_{cc}. It seems that the second effect was predominant from 1% TPP. In the case of extracted samples, only the effect of molecular mass was observed. Therefore, the T_{cc} values became lower as TPP concentration added during the process increased.

The enthalpies of melting (ΔH_m) and crystallization (ΔH_c and ΔH_{cc}) represent the energy necessary for each transition, which were also affected by TPP concentration as shown in Table 2. The ΔH_m increased when the amount of TPP was raised in the bulk PET as a consequence of the increase of crystalline content.

Table 2 Crystallization and melt enthalpies of TPP additivated samples

C/%	ΔH_c/J g^{-1}		ΔH_m/J g^{-1}		ΔH_{cc}/J g^{-1}	
	Ne	E	Ne	E	Ne	E
0	2.7	2.7	36.6	36.6	37.7	37.7
1.0	22.5	17.4	34.4	35.0	31.4	30.99
1.5	20.8	21.1	36.0	31.97	34.6	31.1
2.0	20.0	21.3	37.3	32.8	31.4	30.7
2.5	17.3	20.0	39.6	33.5	37.6	32.1
5.0	1.6	19.0	44.4	30.3	45.6	30.4

C: TPP concentration, Ne: non-extracted sample, E: extracted sample
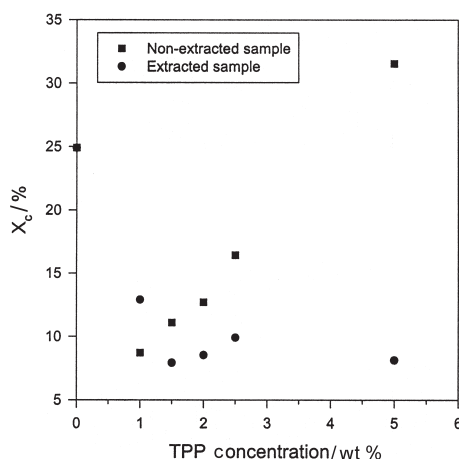

Fig. 6 Influence of TPP concentration (C) on the crystallinity (X_c) of extracted and non-extracted samples
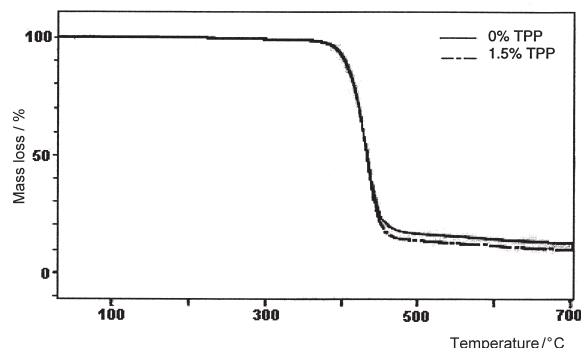
Fig. 7 Mass loss (*M*) in the thermal degradation of recycled PET processed by 10 minutes with 0 and 1.5% of TPP

Figure 6 presents the degree of crystallinity as a function of TPP concentration. The melt and fast cooling seem to be ineffective in avoiding the crystallization of the samples particularly the one with the lowest molecular mass (0% TPP) and the one with the highest amount of reaction residue (5% TPP, non-extracted). In the first case, it is known that the rate of crystallization is higher for chains with lower molecular mass. Therefore, the cooling procedure employed seems not fast enough to avoid the crystallization at this step of the analysis. The non-extracted samples showed a tendency of increasing crystallinity as additive concentration was raised, probably due to the plasticizing effect discussed previously.

TG curves obtained for two samples are presented in Fig. 7. In spite of the fact that phosphorous linkages could be formed, they did not modify considerably the one tendency to degradation during heating in the case of the sample processed with 1.5 mass% of TPP for 10 min and extracted with acetone. The sample processed at the same conditions without any additive showed practically the same degradative behavior. Although it is probable that the break of phosphorous linkages occur on heating, there was not any increase in the rate of volatile substances formation.

Conclusions

Excepting the crystalline melt temperature, the other thermal properties of post-consumer PET investigated changed when it was processed with TPP. The molecular mass and reaction residues content increase when the concentration of chain extender was raised, changing drastically the molecular mobility of the samples submitted to DSC analysis. In the range of TPP concentration studied (1–5 mass%), the plasticizing effect of reaction residues could decrease both T_g (about 5°C) and T_{hc} (about 15°C) while the increase of T_{cc} was about 25°C. The crystallinity was raised from 8 to 32%.

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