The Effect of Glass Fibre and a Phosphorus-Containing Flame Retardant on the Flammability of Recycled PET

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Summary: The availability of scrap poly(ethylene terephthalate) (PET) from post-consumer bottles is increasing as the post-consumer collecting systems are becoming more usual in daily life. PET is well known as a high-performance engineering thermoplastic because of its good thermal stability, chemical resistance, and excellent mechanical properties. Many efforts have been carried out to use this material in housings of electronic applications. However, the flammability of PET is a shortcoming in some of these applications.
In this study, our attempt is to incorporate a non-halogenated flame retardant, in form of a phosphorus-containing compound, together with a commercial glass fibre grade to achieve UL94 test V-0 rating for PET. An investigation of thermal stability and flammability (HDT, UL94 V-test) and mechanical (tensile, flexural and impact tests) properties of glass fibre filled PET samples is reported as a function of fraction of flame retardant.
This work shows the influence of the filler content and the interfacial filler/matrix adhesion on the flame retardant and the mechanical properties.

Keywords: fibres; flame retardance; mechanical properties; phosphorus; recycling

Introduction

Recycling of polymeric materials is of fundamental importance because of environmental, economic and social factors, and in recent years has grown in a very impressive way. Concerning mechanical recycling of thermoplastics, studies are focused on the thermo-mechanical degradation processes appearing during recycling processes resulting in a poor secondary material, with regard to its properties [1].

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The availability of scrap poly(ethylene terephthalate) (PET) from post-consumer bottles is increasing as the post-consumer collecting systems are becoming more usual in daily life. PET is well known as a high-performance engineering thermoplastic because of its good thermal stability, chemical resistance and excellent mechanical properties. Since recycled PET is becoming more competitive in some sectors, replacing more common polymers, many efforts have been carried out to use this material in applications considered in this study (TV components) [2-3].

In this study, the flammability of PET is a shortcoming in some of these applications. Requirements about burning behaviour and the need of using an halogen-free flame retardant, for environmental and public health reasons, have led to the study of the addition of a phosphorus-based flame retardant in recycled PET [4-5].

The aims of this study are to: investigate the synergistic effect of a phosphorus-containing flame retardant and glass fibre on the flammability of PET; optimise additive contents of the mixtures to obtain UL94 V-0 rating; and study the influence of the additives on the mechanical properties.

Experimental

Materials

The recycled material of this study is a mixture of PET flakes of different colours, coming from post-consumer sorted plastic bottles (PET-B). A commercial PET, provided by DuPont, RYNITE R 530L NC 010, filled with 30% glass fibre (PET-A), has been used as a reference to investigate the role of glass fibre interfacial adhesion on the flame retardant behaviour.

The filler fraction consists of two types of glass fibre (GF), one type, class E, without a surface treatment, and a second type FV Chopped Strand 3540 from PPG Industries, provided by QUIMIDROGA, with a surface treatment adapted for PET (no details of the coupling agent are provided).

The flame retardant (FR) is a viscous liquid phosphorus compound FYROFLEX BDP Bisphenol A bis-(diphenylphosphate), provided by AKZO NOBEL, with a phosphorus-content of 9%.

Processing

PET materials were dried at 140°C for 4 hours prior to and during extrusion and injection moulding processing in a dehumidifying drier. Masterbatches of 35% weight GF with PET-B and masterbatches of 15%GF + 53%FR with PET-B were made by twin-screw extrusion (COLLIN ZK-25, L/D=36). The processing temperatures were 250-270°C depending on the compositions. Both masterbaches were physically blended in different proportions with PET-B flakes to prepare the materials of the study (table 1). All materials were injection moulded in a mould cooled at 20°C to obtain standard specimens (figure 4 of the ASTM D-647 standard). The specimens produced were dumbbell for tensile tests and prismatic (3.2*12.7*127 mm) for impact, HDT and flammability tests.

Characterisation

Flammability tests were performed according to UL94 norm at room temperature. A sample was exposed vertically to a Bunsen burner flame for 10 seconds. If the flame extinguished, another 10 seconds application was made. Total burning time of the two ignitions for five samples are shown in table 1. Charpy impact tests were carried out according to ASTM D-256 using a CEAST pendulum impact tester with 2 J capacity providing an impact speed of 2.9 m/s on specimens with a 1.25 mm notch. Determination of HDT temperature was performed according to ISO 75 in a CEAST 6510, each material 5 times. Tensile tests were performed according to ASTM D-638M-91a in a Galdabini 1890 Sun 2500 universal testing machine with a load cell of 25 kN and a video extensometer, at a crosshead speed of 10 mm/min at room temperature.

Results and Discussion

Due to confidential reasons, phosphorus and glass fibre contents are shown relative to values of PET-C5 phosphorus content. The selection of this material as a reference is because it shows the best flame retardance behaviour with the minimal phosphorus content.

Preliminary study of the upward-burning characteristics

Firstly, the study has investigated the flammability of different starting materials.

Flammability of PET-B is V-2 rating. It shows considerable dripping and ignites the surgical cotton. Previous studies concluded that addition of a phosphorus-containing flame retardant alone, even in high concentrations, did not lead to any improvement in flame retardation, relative to the original material (PET-B). Furthermore, addition of untreated glass fibres (PET-D) did not benefit flame retardation at all; the dripping behaviour persisted such that the material had the same UL94 classification as the unfilled matrix i.e., UL94-V2. A study of the flammability of PET-A showed that the structure of the filler phase was maintained after the flammability test and even after complete removal of the organic phase at 600°C. Thus, the treatment of the glass fibre with a coupling agent was considered as an important factor of the study, to reach a better flammability behaviour. It may be noted in the Scanning Electron Microscopy (SEM) micrographs that the interfacial adhesion between the PET matrix and the glass fibre phase does not exist in material PET-D (figure 1), while it is effective in material PET-A (figure 2).

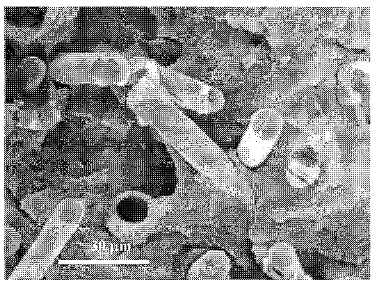

Figure 1. SEM micrograph of the fracture surface of PET-D: no adhesion between matrix and glass fibres.

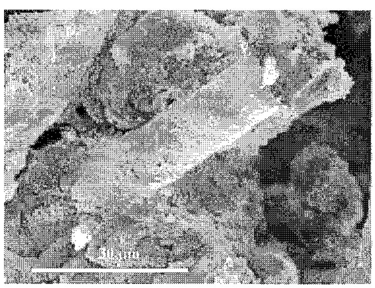

Figure 2. SEM micrograph of the fracture surface of PET-A: good interfacial adhesion between matrix and glass fibres.

Using as additives phosphorus-based halogen-free flame retardant and treated glass fibre, the first successful result was obtained for the material PET-C7, showing a V-0 rating. Next steps focused on optimising phosphorus and glass fibre contents.

A previous study [6] has observed that incorporation of glass fibres in a recycled PET in combination with a phosphorus-containing flame retardant significantly increases the stiffness of the char layer formed during combustion and limits the flow of the molten polymer. A condition to obtain this behaviour is good adhesion between the char layer and the glass fibres. The positive role of glass fibre can also be explained by the large amount of volatile combustibles that can be retained inside the char layer. This leads to the phenomenon of intumescence, which adds to the effect on fire resistance obtained by flame retardant, which contributes to create the char.

In table 1, phosphorus and glass fibre contents are shown in relative units related to phosphorus content of PET-C5, equal to 1.

Table 1. Relative composition, UL94 test and HDT of the studied materials.

Sample	P-cont.	GF-cont.	Burning time (s)	UL94 V-rating	HDT (°C)
PET-A	0.00	14.95	∞	V	>150
PET-B	0.00	0.00	29.1	V-2	65.5 ± 0.5
PET-C1	0.53	7.35	168.7	V	49.8 ± 1.1
PET-C2	0.55	9.95	162.4	V	50.0 ± 0.7
PET-C3	0.75	4.25	53.8	V-2	43.7 ± 2.1
PET-C4	0.85	10.80	93.2	V-2	42.9 ± 1.6
PET-C5	1.00	4.25	22.6	V-0	38.2 ± 0.5
PET-C6	1.09	10.10	32.3	V-0	37.7 ± 1.1
PET-C7	1.26	3.50	17.3	V-0	39.9 ± 0.1
PET-D	1.60	10.70	6.3	V-2	44.8 ± 0.2

HDT temperature decreases with increasing phosphorus content. The content of glass fibre does not seem to play a role, since pairs of values with a similar phosphorus content (and different glass fibre content) have a similar HDT temperature: PET-(C1/C2, C3/C4 and C5/C6).

Mechanical properties

In figures 3 and 4, results of impact tests are shown as a function of glass fibre and phosphorus content, respectively.

As expected, materials with treated glass fibre show better impact properties than the material with untreated glass fibre (PET-D). It is well known that adhesion of glass fibre to the matrix reduces propagation of cracks [7].

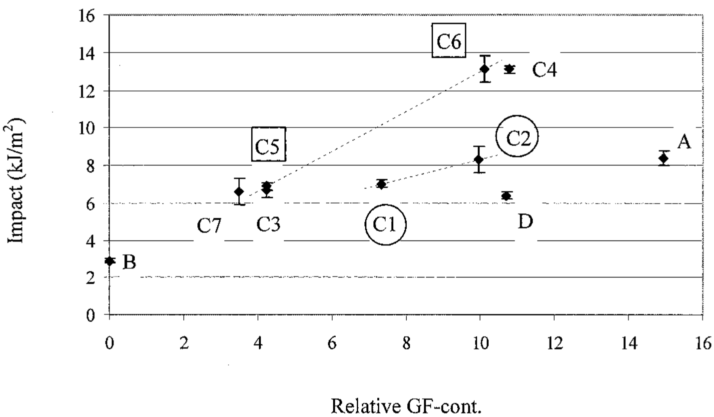

Figure 3. Impact strength of the studied materials as a function of relative glass fibre content. (Relative P-cont.: □ ≈ 1 and ○ ≈ 0.5).

For constant phosphorus content, a comparison of the materials PET-(C1/C2 and C5/C6) shows that increasing of glass fibre content leads to increasing of impact strength.

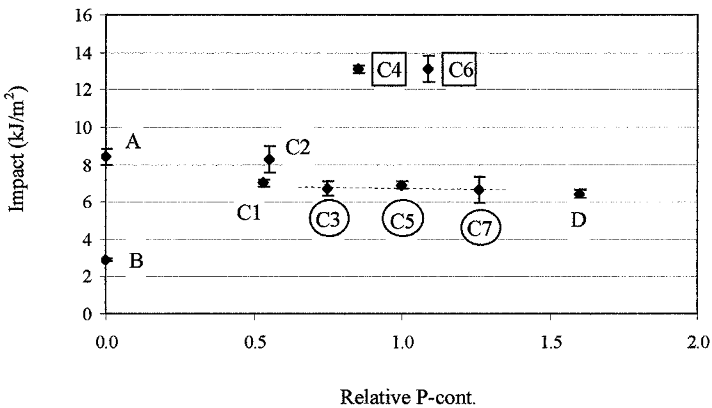

Figure 4. Impact strength of the studied materials as a function of relative phosphorus content. (Relative GF-cont.: □ ≈ 10 and ○ ≈ 4).

For constant glass fibre content, a comparison of the materials PET-(C4/C6 and C3/C5/C7) shows that impact strength is independent of phosphorus content. In the case of the materials PET-C2, a lower value is obtained, more tests should be performed to study this issue. Results obtained in the impact test are important to know the application range of the final product.

In figures 5 and 6, results of tensile tests are shown as a function of glass fibre and phosphorus content, respectively.

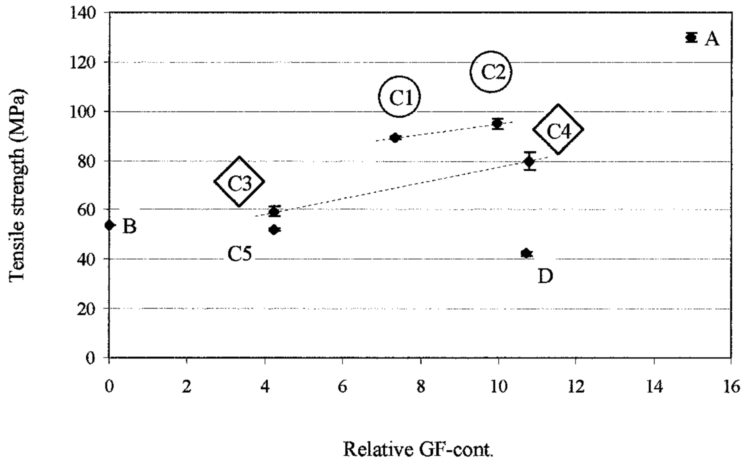

Figure 5. Tensile strength of the studied materials as a function of relative glass fibre content. (Relative P-cont.: ◊ ≈ 0.8 and ○ ≈ 0.5).

Material PET-D shows lower mechanical properties than PET-C# materials due to the lack of adhesion in the glass fibre as mentioned before. On the other hand material PET-A shows higher mechanical properties than PET-C# materials due to the high GF-cont with a good surface adhesion and because it is a virgin material (further research has shown that tensile strength of PET-A falls 23% after five recycling operations).

For constant phosphorus content, a comparison of the materials PET-(C1/C2 and C3/C4) shows that increasing of glass fibre content, leads to increasing of tensile strength.

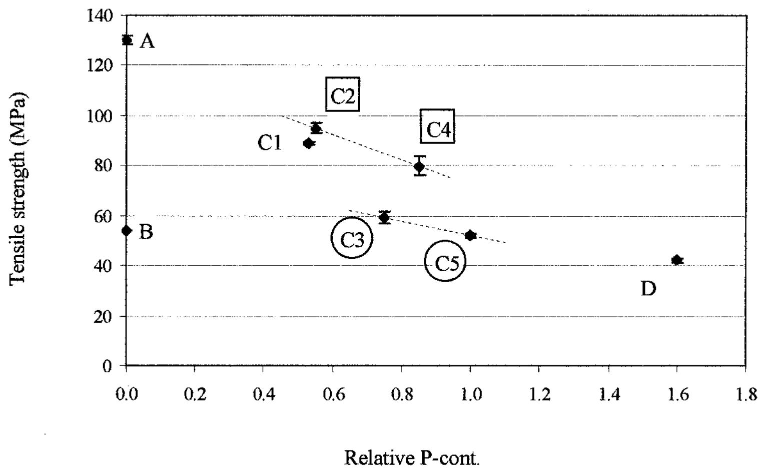

Figure 6. Tensile strength of the studied materials as a function of relative phosphorus content. (Relative GF-cont.: □ ≈ 10 and ○ ≈ 4).

For constant glass fibre content, a comparison of the materials PET-(C2/C4 and C3/C5) shows that increasing of phosphorus content leads to slight decrease of tensile strength.

Tensile tests also showed that Young Modulus, and therefore material stiffness, increases with increasing glass fibre fraction. This assessment was foreseeable, as the glass fibre is more rigid than the PET matrix.

Conclusions

A halogen-free recycled PET UL94 V-0 rating could be achieved with a combination of phosphorus-containing flame retardant and glass fibre.

The best way to avoid dripping in the flammability test of PET is the addition of glass fibre treated with a specific coupling agent for PET. Additionally, a compact structure is reached after the burning test.

Incorporation of a phosphorus-containing flame retardant neither seems to have an important influence on the mechanical properties, nor on the injection process. HDT temperature may be a limiting property for the incorporation of the flame retardant, but does not seem to be a disadvantage for the application of the reference material in TV components.

Further research could focus on optimising the synergistic effect of glass fibre and flame retardant with the assistance of an experimental design and analysis of the response surfaces obtained.

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