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Processing and Dynamic-Mechanical Properties of Poly(butylen terephthalate) Based Nanocomposites

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Summary: Effects related to the simultaneous presence of an Al-phosphinate based fire retardant and of relatively low amounts of nanosized metal oxide particles on processability and mechanical performances of a commercial polyester resin have been investigated. In more details, ternary poly(buthylene terephtalate) based compounds, obtained by melt processing and first of all validated in terms of flammability, were analysed to verify the relative extrudability and ultimate dynamic mechanical performances of compression moulded samples. Preliminary rheological tests confirmed both a minimum of matrix degradation as a result of the process while applying an appropriate protocol drying of raw materials and a marked reduction of the apparent shear viscosity of the three-phase melts with respect to the neat matrix processed under the same conditions. Regarding the evaluation of dynamic-mechanical parameters such as storage modulus, loss modulus and the ratio tan δ, besides the expected stiffening of the matrix by inclusion of a rigid inorganic phase, a slight reduction of damping behaviour without no significant variation of the glass transition temperature of the polyester matrix have been observed.

Keywords: dynamic-mechanical properties; nanocomposites; poly(butylen therephtalate)

Introduction

Poly butylen therephtalate resins are semi-cristallyne thermoplastic resins widely used in many industrial applications that go from electronic/electric components, automotive, textile and so on, owing to their very interesting properties in terms of high dimensional stability under heat, high stiffness and hardness, good bearing strength, good electrical properties, good resistance to chemicals, oils, greases and chemical fluids,[1,2] good stress-cracking resistance and excellent flow characteristics.

But, as usually revealed for petroleum based resins, thermoplastic polyesters show a remarkable drawback related to their intrinsic chemical structure that limit their use. Owing to their poor resistance,[3–5] specific attention must be paid for application in which high temperature resistance is required and in fields such as transport where safety against accidental burning phenomena must be assured.

On the other hand, recent researches on nanostructured polymer formulation have shown promising perspectives of these new kind of materials in terms of fire performances.[6–12] Indeed, it seems that barrier (char) formation, nanoparticle networks and increasing of the melt viscosity are recognised as the main general fire retardancy mechanisms of polymer nanocomposites. This is witnesses by the huge amount of papers already available in the literature demonstrating that:

- small amounts of nanoclays (<5% by weight) enhance char formations and induce a drastic reduction of the heat release (flammability) of polymer matrices[13–17];

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- nanoscale metal oxide particles, accumulating on the surface of the burning polymer, form a barrier against flame propagation front[18–21];
- increased melt viscosity is the main reason for the fire behavior improvement demonstrated for polyamides reinforced with small contents of multiwall carbon nanotubes[22]; and so on.

But, in these cases, it is obvious that technical difficulties may arise from the need to have a good distribution of the nanoscaled filler within the polymer matrix in order to achieve satisfactory results: this target is usually not ease to approach mainly owing to the high viscosity of the matrix at operative conditions and/or intrinsic chemical features of the host nanofiller that prefer to cluster rather than distribute within the sea of the neighborhood matrix. Clearly these difficulties could be overcome by operating in solution at the expence of the final productivity or modifiying the interphase not always acceptable from an economic standpoint.

Thus, aim of the present work was to verify processability and dynamical mechanical properties of new nanostructured poly(butylen therephthalate) based formulations with improved fire resistancy.

Experimental Part

Materials

The matrix was a standard PBT (Pocan B 1505) by LANXESS. About additives, a traditional phosphorous based flame retardant (P-FR) purchased from Clariant and best known under the trade name Exolit OP 1240, and two different rigid particles of metal oxides, purchased by Sigma Aldrich, were considered. Regarding these latter, attention was paid on the use of iron and antimonium oxides having pseudospherical shape and nanometric sizes specified below:

$$Fe_2O_3(d < 50\ \text{nm; BET area} = 50 - 245\ m^2g^{-1})$$

$$Sb_2O_3(d < 250\ \text{nm; BET area} = 50\ m^2g^{-1}).$$

Compound Preparation

Formulations listed in Table 1 were prepared by using a twin-screw lab extruder under operative conditions previously optimized on the base of morphological observations. In more details, the applied procedure was chosen following a systematic morphological investigation aimed to verify the entity of eventual segregation of metal oxide nanoparticles or, in other words, the efficiency of achieved dispersion of nanoadditives within the polyester matrix.

A drying protocol performed at 90 °C overnight in a vacuum oven was applied to both matrix and additives, before blending, and compounds, before testing.

All extruded materials were pelletized and pressure moulded at 250 °C in 3 mm thick rectangular plaques with a hot press apparatus and subsequently cut to obtain 10 mm width rod samples for further characterization.

Characterization Techniques

Taking into account that that all materials were analysed taking neat PBT, processed under the same condition, as the reference one, samples of each formulation were systematically characterised in terms of flammability, rheological and dynamic-mechanical properties.

Flammability of rod samples were verified by using the UL94 Vertical burning test protocol. In details we measured the self-extinction ability of the sample and eventual dripping during the combustion test.

To assess any effect of additives on the processability of the hosting matrix,

Table 1.
Studied formulations

Material
PBT + 20 wt% Exolit
PBT + 5 wt%Exolit + 2 wt%Fe_2O_3
PBT + 8 wt%Exolit + 2 wt%Fe_2O_3
PBT + 5 wt%Exolit + 2 wt%Sb_2O_3
PBT + 8 wt%Exolit + 2 wt%Sb_2O_3

preliminary rheological measurements were carried out by using a capillary rheometer (Model RH 7) equipped with a pressure transducer positioned in front of the die entry. Tests were performed by extruding melts through a capillary die ($L/D = 16$ mm, $D = 1$mm) at pre-selected speeds of the cross-head and at 240 °C. No corrections related to end effects and non-Newtonian behavior of melts were applied. Data in terms of apparent shear stress and apparent shear rate were evaluated by the following equations:

$$\tau_{app} = \frac{\Delta P \cdot D}{2L} \text{ and } \dot{\gamma}_{app} = \frac{32Q}{\pi \cdot D^3}$$

where ΔP is the total pressure drop during the extrusion, D and L are diameter and length of the capillary die, Q is the volumetric flow rate. Thus, the apparent shear viscosity, reported in the pictures herein reported, was evaluated by:

$$\eta_{app} = \frac{\tau_{app}}{\dot{\gamma}_{app}}$$

Finally, for dynamic mechanical characterizations a lab instrument DMA Tritec 2000 by Triton Technology Ltd operating in single cantilever mode was used. Operative conditions were: heating rate: 4 °C/min, frequency: 1Hz and thermal range from 25 °C to 130 °C.

Results and Discussion

Experimental results, derived from flammability tests performed according to the procedure cited within the previous paragraph and averaged on at least 3 samples for each material, are summarized in Table 2. Clearly, for all considered formulation, a significant improvement of the fire behaviour is achieved with respect to the reference one, for simplicity cited as "*processed PBT*". The effect, well expected by inclusion of a relatively high amount of the traditional P-based FR, is satisfactorily verified also by replacing a relevant amount of the same with only 2% by weight of metal oxide nanoparticles. In particular, comparing the behaviour of compounds with respect to extruded and pressure moulded PBT samples, a strong reduction of the average time of combustion is shown with disappearance of dripping phenomena with exception of the ternary compound containing amounts of Exolit and Sb_2O_3 equal to 8% and 2% by weight, respectively, showing just 1 drop during the test.

From a rheological point of view, first of all research curiosity was driven by the well established consideration according to polyesters, as all resins synthesized by polycondensation routes (e.g. polyamides), are subject to thermo-mechanical degradation during the process, especially if not properly pre-dried. In our particular case, considering the double process of extrusion and subsequent pressure molding, interest was preliminarily focused on the comparison of the rheological behavior of as received and processed matrix resin. Results in terms of apparent shear viscosity as a function of apparent shear rate are indicated in the logarithmic plot of Figure 1. Clearly, a non-Newtonian (pseudoplastic or shear thinning) behavior is shown but even if, in both cases, an adequate pre-drying protocol was applied, the apparent flow curve of processed PBT shows a downward shift with a reduction of the shear viscosity approximately equal to 30%, all over the range of shear rates considered. Now, albeit

Table 2.
Flammability results

Sample	UL94-V ranking	$t_1 + t_2$ (s)	Dripping
Neat PBT	Failure	40	Heavy
PBT + 20 wt% Exolit	V0	3.0	No
PBT + 5 wt%Exolit + 2 wt%Fe_2O_3	V0	7.5	No
PBT + 8 wt%Exolit + 2 wt%Fe_2O_3	V0	8.0	1 drop
PBT + 5 wt%Exolit + 2 wt%Sb_2O_3	V0	4.6	No
PBT + 8 wt%Exolit + 2 wt%Sb_2O_3	V0	4.0	No

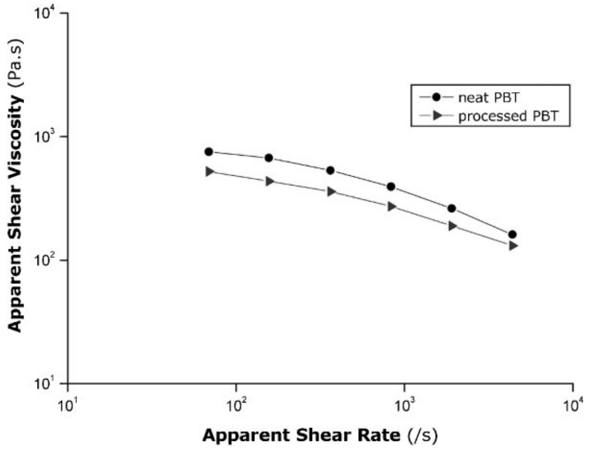

Figure 1.
Flow curves comparison of as received "neat PBT" and "processed PBT".

reasons of this adverse effect are not so clear by now, it has to say that its occurrence was partially expected since, as already explained, the optimization of processing conditions was based on dispersion criteria rather than on minimization of matrix degradation phenomena.

In line with the above results, Figure 2 shows the comparison of flow curves of all compounds with respect to extruded and pressure molded neat PBT. Before to discuss melt flow results, it is important to note that, generally, flame retardant additives acts increasing the matrix viscosity in order to reduce dripping during burning phenomena. In light of this consideration, first of all, it is possible to emphasize that, contrarily to the expectation, inclusion of Exolit OP 1240 involves a marked reduction of the matrix shear viscosity especially for shear rates lower than 1000 s^{-1}. Furthermore, a remarkable change of the rheological behavior may be highlighted noting that while processed PBT show a shear thinning behavior all over the examined range of shear rates, addition of 20% by weight of Exolit involve the occurrence of a Newtonian plateau at least till 300 s^{-1}.

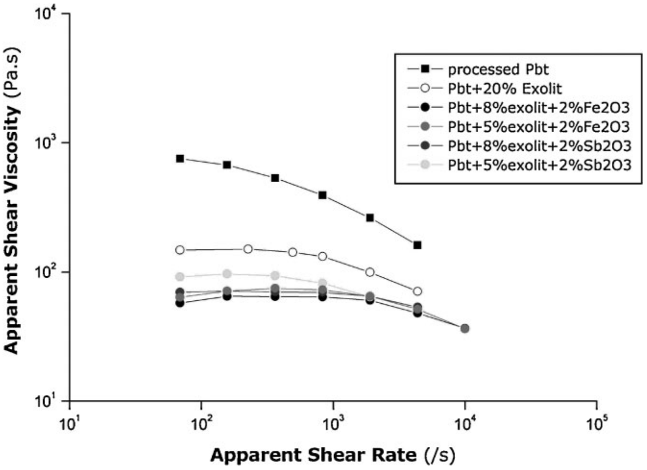

Figure 2.
Flow curves of examined compounds relative to processed PBT.

Regarding ternary compounds the above cited effects appeared to be amplified with a major reduction of the shear viscosity but also with a widening of the Newtonian region.

In other words, the improved extrudability, guaranteed by addition of an adequate amount of Exolit, is not compromised by replacing most of the same with small contents of nanosized metal oxides. This behavior, could be ascribed to disentanglement effects, already reported elsewhere,[23] just promoted by inclusions of rigid nanoparticles and/or to slipping effects related to eventual migration of the inorganic dispersed phase toward the surface of the extruded materials. With particular reference to the latter hypothesis, investigations are in progress to verify the extent of this morphological aspect.

About dynamic-mechanical behaviour, Figure 3 compare the trend of the elastic component of the dynamic modulus (storage modulus) as a function of the temperature on the thermal range between 25 and 130 °C. In particular, for clarity of exposition, taking always signals of processed PBT and of the binary compound with

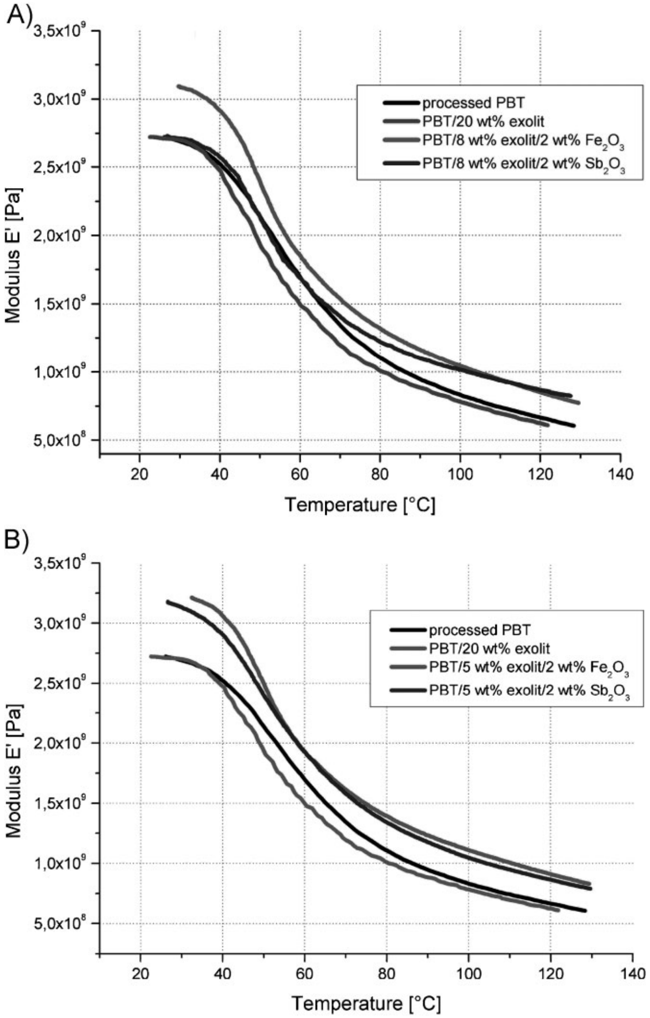

Figure 3.

(A) and (B) Storage modulus (E′) as a funtion of temperature for investigated materials.

Exolit alone as the references, curves are divided into two different charts (A) and (B) related to Exolit contents equal to 8 and 5% by weight, respectively. The same criteria will be followed for the loss modulus (E″) and for the ratio between the dissipative and storage components (Tan δ).

Taking the black curve as our reference, the Exolit slightly reduce this parameter especially in the glass transition region. While the inclusion of rigid metal oxide nanoparticles, evidently, improves the stiffness of samples all over the considered thermal range except in the case of PBT/8 wt%Exolit/2 wt%Sb_2O_3 for which improvements of the storage modulus values are limited to the rubbery region. This effect is usually attributed both to increased stiffness of the dispersed phase including the formation of a network of nanoparticles within the hosting matrix that improves the consistency of the amorphous phase.

Trends of the dissipative component of the dynamic modulus (E″) as a function of the temperature are reported in Fig. 4(A) and (B). It is evident that Exolit additions deal to lowering and shifting to higher temperatures of the E″ signal while ternary systems show opposite effects by increasing both height and width at medium height of the signal, without any relevant influence

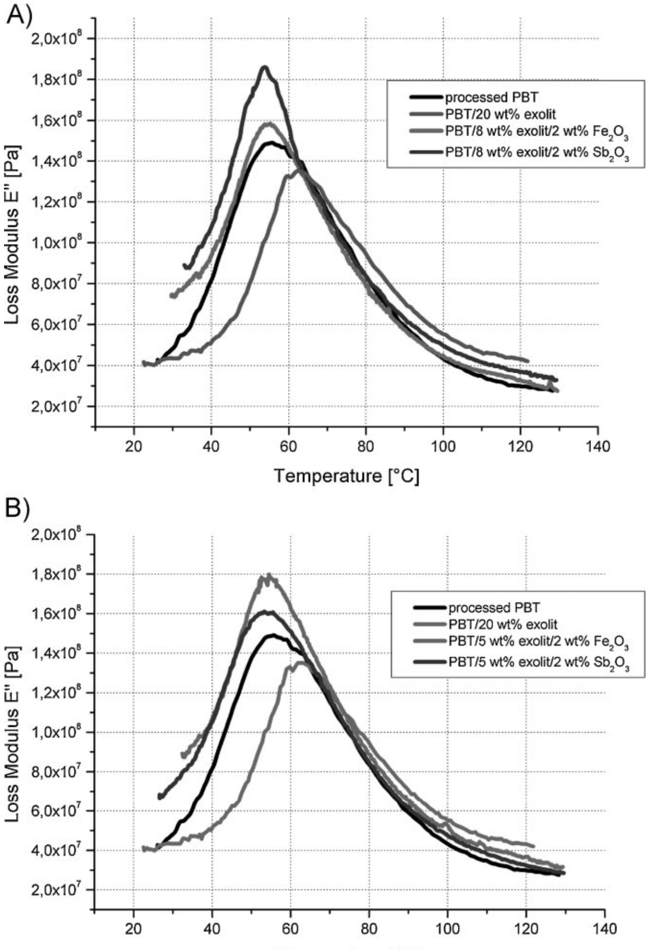

Figure 4.

(A) and (B) Loss modulus (E″) as a funtion of temperature for investigated materials.

Table 3.
Storage modulus and glass transition temperature of all materials

Material	E′ (GPa) Err ± 0.5	Tg (°C) ± 2
Neat PBT	2.7	63
PBT + 20 wt% Exolit	2.7	68
PBT + 5 wt%Exolit + 2 wt%Fe_2O_3	3.3	60
PBT + 8 wt%Exolit + 2 wt%Fe_2O_3	3.0	58
PBT + 5 wt%Exolit + 2 wt%Sb_2O_3	3.2	59
PBT + 8 wt%Exolit + 2 wt%Sb_2O_3	2.7	62

on the glass transition temperature of the polyester matrix.

This behavior can be explained assuming that the amount of included Exolit, on one side strictly necessary to achieve an adequate level of fire-retardancy, is, on the other hand, responsible of increasing the level of macromolecular constrains with consequent lowering of the dissipative and increasing of the relative glass transition temperature. Vice versa, replacing most of the P-FR content with low amounts of nanoparticles the final structure could be perturbed in such a way to have a macromolecular flexibility comparable with the neat PBT one and, simultaneously, to allow a higher dissipation of energy during the test.

A quantitative comparison in terms of dynamic modulus components for all studied formulations is reported in Table 3 from which especially evident are the cited stiffening effect caused by the P-FR replacement with rigid isodimensional nanoparticles and a slight increase of the glass

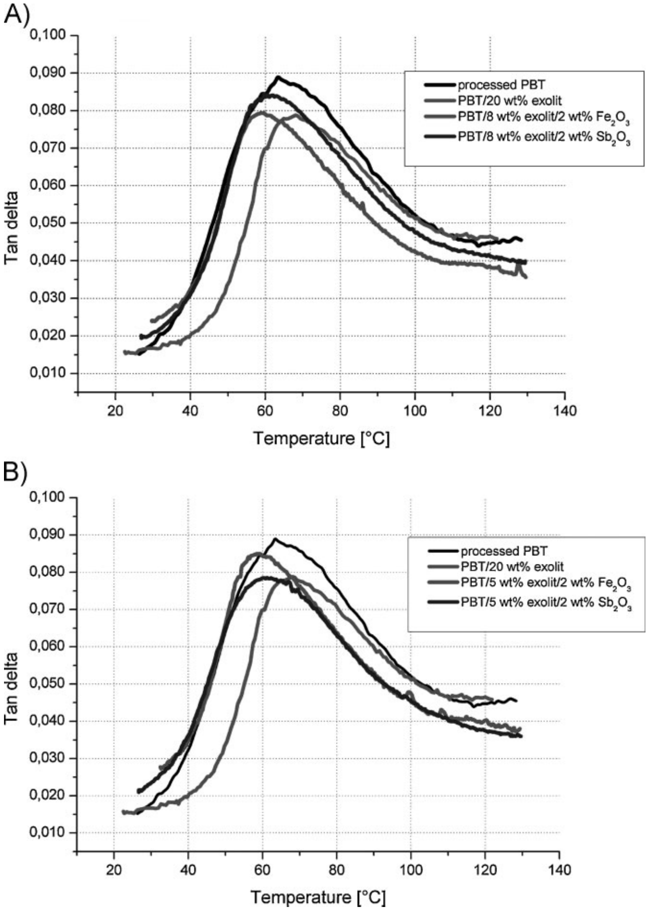

Figure 5.
(A) and (B) Damping (Tand δ) as a funtion of temperature for investigated materials.

transition temperature for the binary compound containing only the Exolit.

Finally, major restrictions at macromolecular level for the binary compound was further confirmed by the lowering of the tan δ signal (see Figs 5 (A) and (B)). Regarding ternary formulations, the same signal appeared slightly shifted to lower temperatures and, in all cases, narrower and slightly lower ($\sim$10%) than the one characterizing the reference material. Reasons for this behaviour (content of additives, interactions at interphases, extent of nanoparticle dispersion) are still under investigation.

Conclusion

The replacement of phosphinate-based flame retardant with metal oxides nanoparticles influences the fire performance, the processability and the dynamic-mechanical properties of plain PBT.

According to UL-94, with the addition of small percentages of nanoparticles it is possible to consistently reduce the content of Exolit without losing the fire performance of PBT based compounds.

The formulation containing 8 wt% Exolit and 2 wt% Sb_2O_3 seems to be the best one in terms of self-extinguishing and reduction of the combustion times.

Rheological measurements exhibit a clear improvement of the matrix extrudability by modifying the flow behavior, presumably for the occurrence of structural changes as a result of the matrix phase compounding, and further lowering the viscosity than the processed matrix one also at shear rates likely by effects of slipping related to the nanoparticles distribution. These results help to predict processing benefits reducing the working temperature and the motor load during the extrusion step.

DMA measurements show that Exolit does not alter the elastic modulus of PBT but reduces its damping, probably by restricting the macromolecular mobility.

Inclusion of nanoparticles of metal oxides deal to an increase of the matrix stiffness, in particular with the addition of Fe_2O_3 but no relevant benefits were achieved in terms of mechanical damping, at least for the examined formulations.

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