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Dynamic-mechanical Investigation of Melt Compounded Poly(butylenterephtalate)/organoclay Nanocomposites

Domenico Acierno,[1] *Eugenio Amendola,*[2] *Pietro Russo**[3]

Summary: Nanocomposites constituted by neat or opportunely toughened polybuthylene terephtalate filled with a commercial organoclay (Somasif^{TM}MEE) were analysed to asses their potential use in the automotive field. In particular, hybrid systems including 3–6% by weight of MEE, in presence or not of a toughening agent such as an engineering thermoplastic elastomer (Pibiflex), and obtained by melt intercalation were considered. All materials were characterised in terms of dynamic-mechanical properties. Results clearly proved that the optimization of the formulation composition allows to achieve a considerable improvement of the ultimate damping performances.

Keywords: dynamic-mechanical; melt intercalation; nanocomposite; organoclay; poly buthylene therephtalate

Introduction

Polymer-layered silicate (PLS) nanocomposites have gained an increasing interest for ever more industrial applications. Their success, widely reported in the literature,[1–14] is essentially based on the occurrence of synergistic effects between organic and inorganic phases combined together.

It is well known that monitoring processing conditions it is possible to obtain different structures going from intercalated nanocomposite in which extended matrix chains remain between the host layers to exfoliated hybrid where silicate layers are randomly dispersed in a continuous organic matrix such that the interlayer distance is comparable with the radius of gyration of the polymer.

Nanostructured materials may be prepared by in situ polymerization, solution or melt intercalation. The first method relies on the swelling of the organo-clay by the monomer, followed by the in-situ polymerization initiated thermally and/ore by addition of a suitable additive (catalyst, initiator and so on). The chain growth in the clay galleries allows the lamellar exfoliation.

By solution intercalation a solvent is employed to mix the filler with the polymer, and an exfoliated structure is trapped when evaporating the solvent while a very promising alternative is offered by melt-intercalation. This last method is gaining an increasing attention for industrial purposes owing to its versatility and environmental benefits (absence of solvents). In this case, preformed polymers mixed at room temperature with the inorganic filler are processed by conventional compounding equipments, such as twin-screw extruders and injection moulding apparatus.

With the aim to identify new materials potentially useful for the automotive field our interest was focused on hybrid

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[1] Department of Materials and Production Engineering, University of Naples, P.le Tecchio, 80125 Naples, Italy

[2] Institute of Composite Materials & Biomaterials (IMCB), National Research Council of Italy (CNR), P.le Fermi, 1, 80055 Portici (NA), Italy

[3] Institute of Chemistry and Technology of Polymers (ICTP), National Research Council of Italy (CNR), Via Campi Flegrei 34, 80078 Pozzuoli, Naples, Italy
E-mail: russo_pietro@virgilio.it

Table 1.

Somasif™ ME100	DENSITY	Specific weigth (g/cm^3)	Thermal Resistance (°C)	Specific Surface (m^2/g)	pH	CEC (MEP/100g)
	2,60	0,20	800	9	9 ~ 10	120

formulations obtained by melt intercalation of an organoclay into a polybuthylentherephtalate opportunely toughened to compensate the expected stiffening of the organic matrix as a consequence of the rigid inorganic reinforcement inclusions.

Experimental Part

Materials

An injection moulding grade poly buthylentherephtalate (PBT) POCAN B 1505 was supplied by Bayer.

A synthetic organo modified mica commercially known as Somasif™MEE from CO-OP Chemical Co. LTD., the main physical properties of which are collected in Table 1, was used as reinforcing agent.

Finally a commercial elastomeric copolyester (Pibiflex® E4090 from P-Group s.r.l.) (PBF) was used as a toughning agent to prevent premature brittle failures normally due to the addition of nanofillers. Main physical properties of this component are indicated in Table 2.

Sample Preparation

All materials were opportunely dried before processing. In particular the PBT was dried in a vacuum oven at 90 °C for 16–18 h while the nanofiller was subjected to the same conditioning step for 1 hour.

Extrusions of the dried components, preliminarly mechanically mixed in the case of compounds, were performed with a Polylab Haake corotating twin-screw extruder (L/D = 40/2.5) applying a screw speed of 150 rpm and the temperature profile 210–230–230–228 °C from the hopper to the die.

The investigated formulations are indicated in Table 3.

The extrudates were pelletised at the die exit, dried and then injection moulded into standard rectangular bars (30 mm length, 5 mm width and 2 mm thickness) in an injection moulding machine for further mechanical characterisations.

Characterization Techniques

Dynamic Mechanical Analysis of neat PBT, subjected to the same processing history for comparison, and compounds was performed with a TRITON instrument (mod Tritec 2000B) in the single cantilever mode.

The temperature dependence of the dynamic storage modulus (G′), loss modulus (G″), and their ratio (tan δ) were measured at a constant frequency (ω) of 1 Hz, with a strain amplitude of 0.02%, in the temperature range from –30 °C to 180 °C with a heating rate of 5 °C/min.

Results and Discussion

Preliminary morphological investigations performed on the fracture surfaces of these materials emphasized that:

Neat PBT fracture surface is mildly plastically deformed as demonstrated by the presence of not uniformly distributed shear yielding bands;

Table 2.

PIBIFLEX®	DENSITY	Melting point (°C)	Resistance at break (MPa)	Elongation at break (%)	Flexural Modulus (MPa)
	1,14	212	15	300	110

Table 3.
Composition of the extruded materials (% by weight).

Neat PBT
90%PBT + 10%Pbf
80%PBT + 20%Pbf
97%PBT + 3%MEE
87%PBT + 10%Pbf + 3%MEE
74%PBT + 20%Pbf + 6%MEE

Pibiflex is partially phase separated in the polyester matrix and the relevant toughening improvement achieved for PBT/Pbf formulations, confirmed by the increased shear yielding of the matrix, was just ascribed to the elastomeric nature of the included additive;
additions of layered silicates cause an embrittlement of ternary formulations by a stiffening of the matrix as indicated by the reduction of deformation signs and the appearance of features typical of a brittle fracture surface.

In light of these remarks, interesting results have been drawn by dynamic-mechanical measurements comparing each formulation containing MEE with its reference matrix (e.g. 87% PBT + 10% Pbf + 3% MEE with 90% PBT + 10% Pbf).

In Figure 1 the dynamic elastic modulus curves as a function of the temperature for all investigated materials are collected.

First of all, comparing the reference matrices (neat PBT and PBT/Pibiflex systems including 10 and 20% by weight of Pibiflex), addition of the elastomeric phase yields to an evident reduction of the dynamic parameter G′ all over the temperature range under consideration. This effect, particularly marked in the glassy region, in line with the trend of the flexural modulus obtained from previous static measurements, has been reasonably ascribed to an improvement of the flexibility of structures' formulations.

This negative effect on the storage modulus, essentially confined in the glassy region for the formulation containing 10% of Pibiflex, covers also the rubbery region for a content of Pibiflex equal to 20% by weight.

For particulate filled composites, a gradually increasing slope of the elastic modulus in the glassy region with the nanofiller content, is observed. This effect is normally related to induced field of stresses generated by the difference between the values of the thermal expansion coefficients of the inorganic filler and the matrix. Taking into account that, as confirmed by previous morphological investigations on these formulations, the reinforcement is preferentially localised into the PBT phase, it is reasonable to assume that silica lamella modify the PBT phase in terms of crystalline degree and size distribution, orientation of amorphous zone or other features, changing its characteristic chemico-physical parameters.

As cited above, regarding formulations based on polyester matrix toughened with 20% by weight of Pibiflex, additions of Somasif seem to improve dynamic storage modulus also in the rubbery zone: behaviour usually explainable by the formation of an inorganic network giving consistency to the amorphous phase for temperatures higher than the characteristic glass transition one.

In Figure 2 dynamic loss modulus trends as a function of temperature are compared for the same materials.

In any case, a single peak (α-transition) at about 70 °C is displayed, in with the glass transition value already reported in literature for the main relaxation of PBT. On the other hand, it is clear that inclusions of both Pibiflex and lamellar clays, in general, do not influence the relaxation peak temperature of PBT, but significantly alter intensity and shape of this relaxation signal.

In particular, toughening, as expected, reduces this dynamic parameter decreasing the energy dissipated during the stress. In fact, the presence of a toughening agent in a semi crystalline matrix normally does not affect its crystallinity but it acts as a nucleating agent, reducing the spherulite size and, consequently, the intensity of the viscous responce of the neighbouring

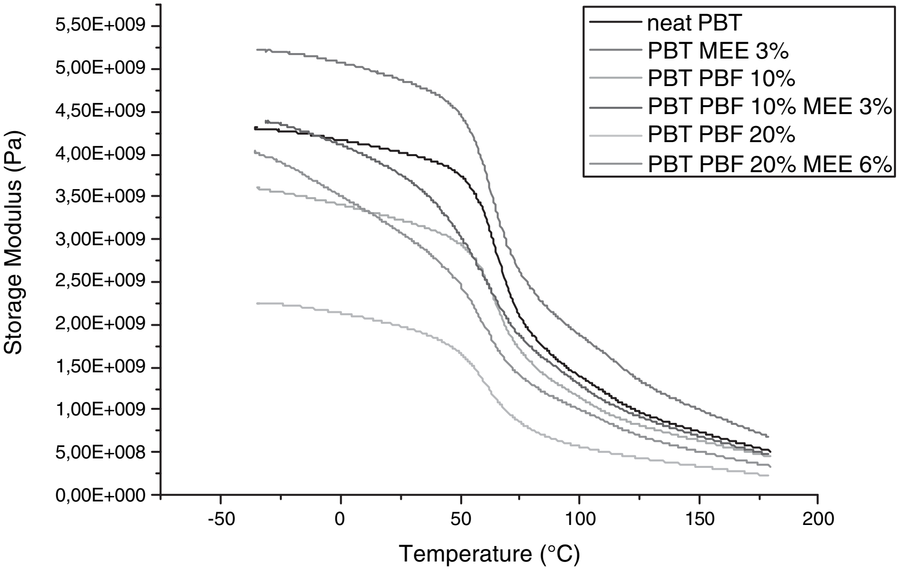

Figure 1.
Comparison of dynamic storage modulus curves.

amorphous phase. On the other hand, this is particularly true for these formulations because previous studies have already demonstrated that great increases of the impact strength can be justified by a crystalline morphology interference on the toughening mechanism.

For ternary formulations, instead, additions of clay always generate the raising and broadening of the loss modulus signals with

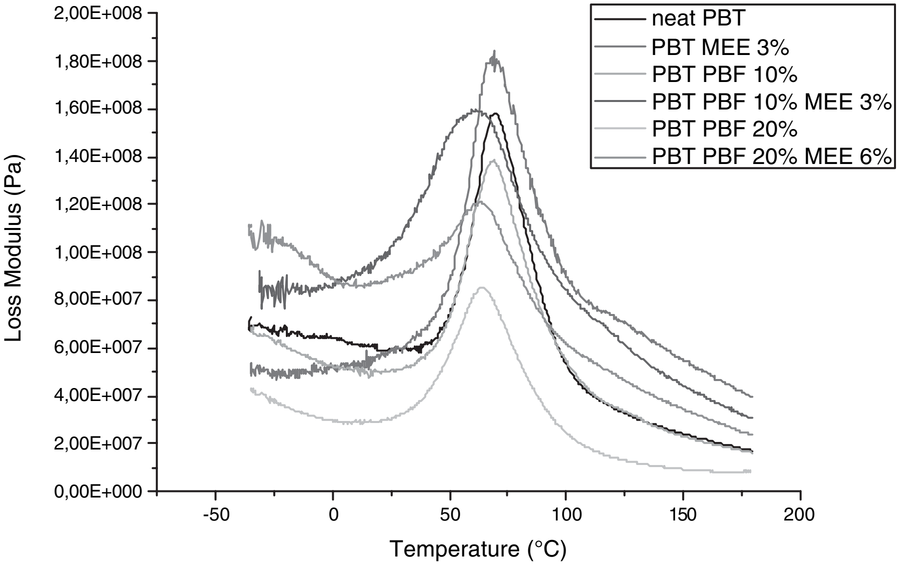

Figure 2.
Plot of loss modulus as a function of temperature for all formulations.

a little shift toward lower temperatures in the case of PBT + 20% Pbf + 6% Somasif MEE.

Thus, in line with the above consideration it is possible to assume that inclusions of inorganic lamella further modify the PBT morphology altering crystalline features. In details, curve raising may be ascribed to an increasing of the volume of the amorphous regions contributing to the damping phenomena while the signal broadening may represent the widening of the crystalline size distribution of the PBT component as a result of toughening.

Moreover, another loss signal seems to be centred at about −25°C for formulation containing the highest content of both toughening and reinforcing additive. This effect, perhaps related to Pibiflex relaxations, could be the object of further investigations.

Finally, Figure 3 compares tan δ curves of all investigated formulations as a function of the temperature. Once again, both toughening and inorganic nanofiller do not modify the temperature of the maximum tan δ signal, at least in the range of contents herein considered.

In more details, structure flexibility improvements, induced by addition of Pibiflex to the polyester matrix, deal to an increase of the maximum intensity of the damping peak. On increasing the content of the elastomer, there is a linear increase in the maximum intensity of the peak.

Moreover, the toughening effect seems to be limited for temperatures higher than the glass transition one in presence of 10% of Pbf but clearly it is extended also to lower temperature by increasing the toughening agent content.

Relevant effects are shown all over the temperature range by hybrid systems in which according to previous considerations a lowering of the matrix crystallinity indicate a high amorphous volumetric fraction and also a superior capacity of damping of this matrix at room temperature.

Anyway, a doubling of both additive contents does not seem to give further improvement of final performances of

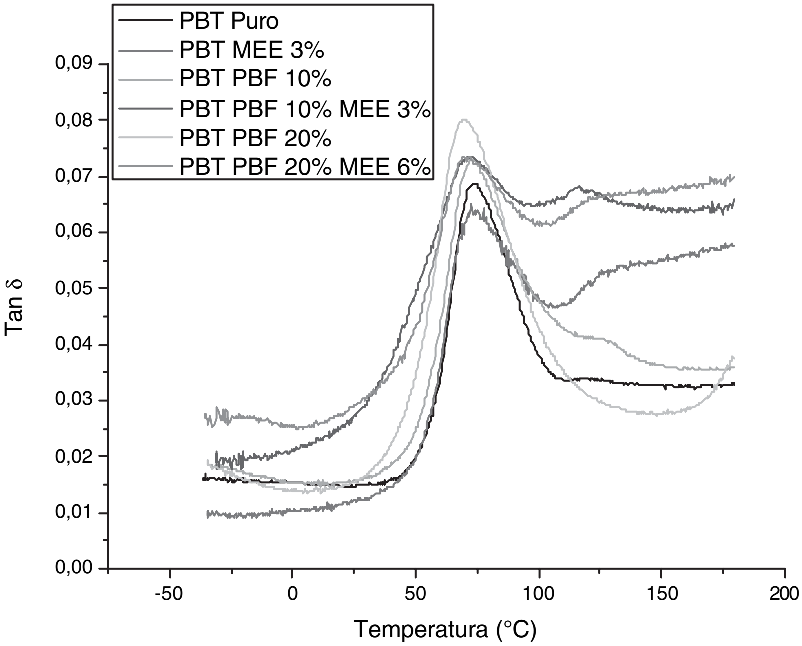

Figure 3.
Plot of tan δ as a function of temperature for all formulations.

products if not reducing their industrial competitiveness from an economical point of view.

Conclusions

Polybutylene terephtalate nanocomposites containing low contents (3–6% by weight) of a commercial organoclay Somasif MEE were characterised in terms of dynamic-mechanical properties. Toughening of the polyester matrix was also considered to prevent an excessive reduction of its toughness by the addition of the rigid filler. Dynamic mechanical characteristics (storage modulus, loss modulus and tan δ) of the PBT matrix appeared to be strongly influenced by both additives. Experimental data, particularly in line with mechanical investigations previously performed at low (flexural) and high deformation speeds (Charpy impact tests) were mainly interpreted by modification of the PBT crystal size distribution.

Finally, satisfactory findings indicated that the introduction of a right combination of an elastomeric phase with lamellar clay may offer interesting materials at least for automotive applications.

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