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Innovative Poly(Butylene Terephthalate) Based Nanocomposites: a Preliminary Investigation

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Summary: A polymer-clay nanocomposite based on Poly(butyleneterephthalate) (PBT) and an innovative organoclay has been synthesized via intercalation of Bis(hydroxyethyl terephthalate) (BHET) in Na-Montmorillonite layers. Chemical and physical properties of this nanocomposite have been studied in comparison to other PBT/nanocomposites based on two commercial organoclay: Cloisite 25A and Somasif MEE. Nanocomposites have been prepared via melt compounding using a twin-screw extruder, with extrusion rate of 150 rpm. Samples were characterized by using wide-angle X-ray diffraction, TEM, thermal and mechanical analysis.

Introduction

In recent years polymer/layered silicate (PLS) nanocomposites have attracting increasing interest in academia and industry because of their remarkable improvements in material properties with respect to pristine polymer or conventional micro and macro-composites. They exhibit high moduli,[1–3] increased strength and heat resistance,[4] decreased gas permeability[5–7] and flammability.[8,9]

Depending on the nature of the components used and the method of preparation, the addition of layered silicate to a polymer melt can result in three main types of composites. When the polymer is unable to intercalate between the silicate sheets, a phase separated composite is obtained, whose properties stay in the same range as traditional microcomposites. Beyond this classical family of composites, two types of nanocomposites can be recovered. Intercalated structure in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layers. When the silicate layers are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure is obtained.[10]

Polymer-clay nanocomposites are mostly synthesized by using three methods: solution intercalation,[11] in situ polymerization intercalation[12] and melt intercalation.[13] In the last one the layered silicate is mixed with a molten polymer matrix.[14,15] When the matrix is a thermoplastic polymer, elevated temperatures are required. If the processing temperature is higher than the thermal stability of the organoclay, decomposition occurs, altering the interface between the filler and the matrix polymer.

Poly(butylene terephthalate) (PBT) represents an important semicrystalline thermoplastic, with excellent processability and mechanical properties and widely used in various applications such as electronics and engineering materials. In order to improve PBT properties, many nanocomposites based on this matrix have been prepared. In order to facilitate the intercalation of polymer in silicate layers, hydrated Na^+ or K^+ ions in the structure of clays are generally replaced with alkyl ammonium cations, which render

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organophilic the normally hydrophilic silicate surface.[29,30]

Since these organophilic modifiers exhibit a thermal degradation temperatures lower than the PBT processing temperature,[17,18] much attention has been directed toward the preparation of high-temperature stable organoclay.[19–21]

The aim of this study was to synthesize an innovative nanocomposite based on PBT and an organoclay prepared via intercalation of Bis(hydroxyethyl terephthalate) (BHET), PET monomer, in Na-montmorillonite layers.

Thermo-mechanical properties and morphology of this new nanocomposite were investigated in comparison to other PBT hybrid composites, based on commercially clay. In fact, nanocomposite proposed in this paper shows an improved thermal stability due to the absence of alkyl ammonium cations in organoclay preparation.

All PBT hybrid composites were melt-extruded by using an intermeshing twin-screw extruder.

Experimental Part

Materials and Procedures

In this research thermal-mechanical properties of PBT-nanocomposite, reinforced with organoclay synthesized in our laboratory, were studied in comparison to PBT/commercial organoclay nanocomposites. The clay was preparated via dispersion of BHET Bis(hydroxyethyl terephthalate) (provided by Sigma-Aldrich) in Na^+-MMT (sodium montmorillonite) galleries; the matrix was PBT Pocan B 1505, provided by Bayer. The organophilic-Montmorillonite, supplied by Southern Clay Products Inc., with a cation exchange capacity of 98 meq/100 g. clay. Commercially available organoclay investigated in this study were Cloisite 25A and Somasif MEE.

The first one, purchased from Southern Clay Products Inc., is a natural montmorillonite modified with a quaternary ammonium salt (2MHTL8 - dimethyl, hydrogenatedtallow, 2-ethylhexyl quaternary ammonium) and has a cation exchange capacity of 95 meq/100 g. clay. MEE Somasif, supplied by UniCoOp Japan LTD, is a sodium synthetic flouromica. Its cation exchange capacity (CEC) is of 1.20 meq/g. clay.

MMT modified with BHET (NaMod) used in this research was synthesized according to the following procedure. 10.2 g of BHET were dissolved in 150 ml of ethanol at room temperature; and 6,0 g of Na^+-MMT were suspended in 210 ml of distilled water and stirred for 30 minutes at 70 °C and 5 rpm. BHET solution was poured into the MMT suspension and stirred for 3 h a 70 °C and 5 rpm. Solvents were subsequently evaporated by means of a rotovapor, at 75–80 °C. Once made solid, the material was dried in a vacuum oven at 250 °C for 30 minutes and milled by a porcelain mortar.

For nanocomposites preparation, PBT (pellets form) and organoclay (powder form) were first dried in vacuum oven overnight at 90 °C. Then 6% wt. of organoclay was mixed to the matrix by mechanical mixer. The mixture was melt-extruded by using an intermeshing twin-screw extruder (Haake Rheocord 9000). The temperature of the extruder was maintained at 210, 230, 230, 228 °C from hopper to die respectively. The screw speed was maintained at 150 rpm. The obtained nanocomposites were finally pelletized.

Characterization Methods

Thermogravimetric Analysis (TGA)

Thermal stability of nanocomposites is usually studied by thermogravimetric analysis. The weight loss due to the formation of volatile products caused by the degradation at high temperature was monitored as a function of temperature. Measurements were conducted by TA Instruments TGA951. The heating occurred under a nitrogen flow, from room temperature up to 600 °C with a heating rate of 10 °C/min. In order to assure the organic compounds degradation and so a precise value of

inorganic compounds weight, measurements were extended in oxidative atmosphere (in air) from 600 °C up to 800 °C at the same heating rate.

Differential Scanning Calorimetry (DSC)

The glass transition (Tg), melting (Tm) and crystallization (Tc) temperatures of pure PBT and PBT-nanocomposites were investigated by DSC-Q1000 (TA Instruments). Samples were investigated during a second scan in the temperature range between −30 to 300 °C, at heating rate of 10 °C/min, after preliminary 5 minutes isotherm at 300 °C and cooling at controlled rate, for previous thermal history erasure.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of pure PBT and resulting nanocomposites were investigated to detect the value of T_g and study temperature dependence of the storage modulus. Measurements were carried out using a TA Instruments DMA-930 with an oscillation frequency of 1 Hz, an amplitude of 0,25 mm. Specimens were heated from −50 °C to 180 °C in nitrogen atmosphere, with a heating rate of 2.5 °C/min.

Thermo-mechanical Analysis (TMA)

Coefficient of linear thermal expansion (CTE) of pure PBT and PBT/nanocomposites was studied by TA Instruments TMA-2940. Two different temperature range were investigated in the temperature range between 0 and 220 °C at 5 °C/min scanning rate.

Flexural Properties

In order to investigate the flexural properties, pure PBT and nanocomposites were first dried overnight at 90 °C in a vacuum oven. Then pellets were injection-molded by means of a mini injection molding. The temperature was maintained at 235 °C for barrel and 170 °C for mould. Specimens were tested according to ASTM D790-03 method using a INSTRON 4204 instrument.

Impact Tests

In order to determine the fracture toughness of samples, impact tests were performed according to ASTM D6110 with a Charpy pendulum (CEAST). Specimens were made with a milled notch, for stress concentration, minimize plastic deformation and direct the fracture to the part of the specimen behind the notch. On the top of this one, a sharp notch (length ∼0.5 mm) was cut with a fresh razor blade. The free clearance was 48 mm, the impact speed employed was 1 m/s. Tests were performed at room temperature.

X-Ray

Wide-angle X-ray diffraction (WAXD) experiments were performed with a Philips 1830 Powder diffractometer, using a Ni-filtered CuKα radiation. A flat camera with a sample-to-film distance of 140 mm was used to collect the data. The Fujifilm MS 2025 imaging plate and the Fuji Bio-imaging Analyzer System (mod. BAS-1800) were used for digitizing the diffraction patterns.

Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) analyses were performed using a Zeiss EM 900 operating at 80kV on ultra-thin specimens cryogenically microtomed.

Results and Discussion

Thermal Properties and Crystalline Morphology

The thermal properties of the organoclays, the pure PBT and its hybrids were analyzed by thermogravimetric analysis (TGA) at heating rate of 10 °C/min. The diffusion of BHET in the NA-MMT galleries assures an increased thermal stability of the organoclay with respect to the commercial ones. The onset degradation temperature of the NaMod is about 200 °C higher than Cloisite 25A and Somasif MEE (Fig. 1a).

In fact, the initial weight loss, at about 280 °C, can be attributed to BHET condensation, resulting in ethylen glycol

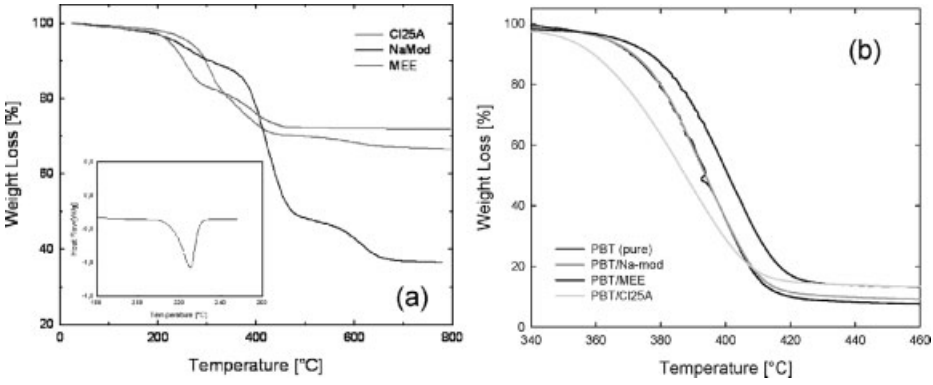

Figure 1.
Temperature dependence of the weight loss for organoclays (a), neat PBT and its hybrids (b).

by-product formation. In order to promote the PET precursor molecular weight increase and reduce the release of ethylen glycol into the PBT matrix, the obtained organoclay has been processed in a vacuum oven at 250 °C for 30 minutes.

TGA curves of PBT nanocomposites show that the thermal stability of PBT/NaMod does not increase considerably compared to neat PBT, but is considerably higher than C25A, wherein the presence of alkyl ammonium salts causes the char formation at lower temperature (Fig. 1b). The onset temperature (T_{onset}), the maximum decomposition temperature (T_{max}) and char residue at 600 °C are reported in Table 1.

DSC thermograms of the non-isothermal crystallization and remelting process for the PBT neat, PBT-NaMOD, PBT-25A and PBT-MEE systems are shown in Figure 2 and Figure 3.

In the cooling process during DSC, the hybrids show higher crystallization peak temperatures and narrower peak widths than the neat PBT. This indicates an increased crystallization rate in the hybrids. Increases in the crystallization rates have been widely observed in hybrids based on semicrystalline polymers, in which the clay nanolayers can adsorb polymer chains more easily and the clay particles act as nucleating agents. The differences in the peak temperatures for crystallization between the pure PBT and their hybrids (Figure 3) are more significant for the PBT-MEE, the peak temperature is increased from 195 to 203 °C, while it is increased from 195 to 201 °C for the PBT-NaMOD. In the remelting processes, shown in Figure 2, PBT-MEE shows only one melting peak at about 226 °C, while the other nanocomposites exhibits two melting peaks, The main one at 224 °C and 221 °C for PBT-NaMOD and PBT-25A respectively. PBT-NaMOD and PBT-25A investigated in this study also showed an additional secondary melting endotherm at around 211–214 °C during the second heating scan (Fig. 2b). The origin of this additional melting endotherm is not clear, but is thought to be due to the formation of small amounts of crystals having a different structure to that of the main PBT crystals in the nanocomposites. In order to elucidate this phenomenon, studies on the crystalline morphology, as well as the crystallization behavior of these nanocomposites under isothermal and non-isothermal conditions with different cooling rates, are currently in progress.

Table 1.
The onset temperature (T_{onset}), the maximum decomposition temperature (T_{max}) and char residue at 600 °C for neat PBT and its hybrid composites.

Sample	Residue (%)	T_{onset} (°C)	T_{max} (°C)
PBT	4.2	369	389
PBT/NaMod	5.4	370	388
PBT/MEE	9.2	373	392
PBT/C25A	8.6	359	390

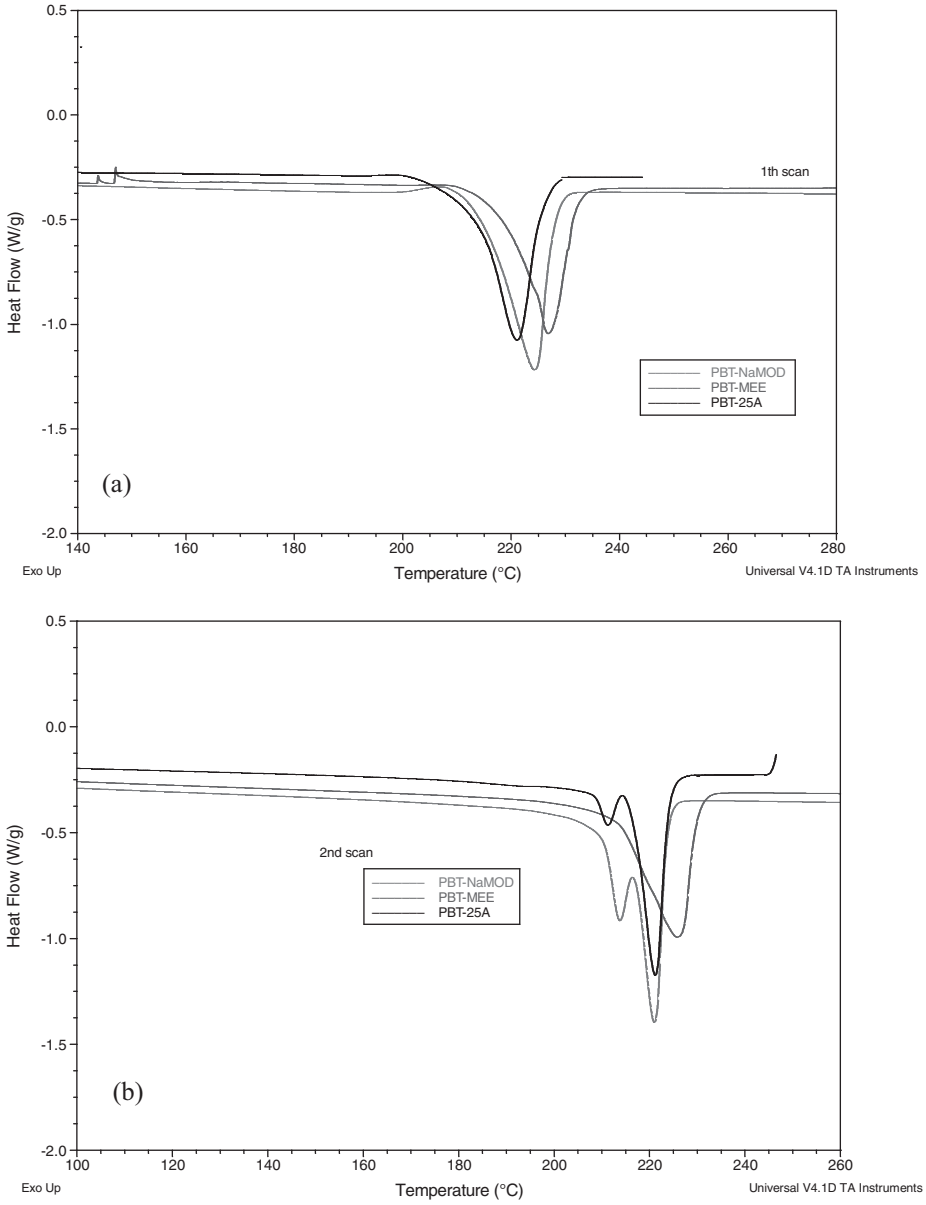

Figure 2.
DSC thermograms of PBT/organoclays (obtained at cooling/heating rates of 10 °C min^{-1}) (a) first scan (b) second scan.

In order to identify NaMod and PBT based nanocomposites structures, WAXD analysis and TEM observation were carried on.

Low-angle peaks in WAXD allow quantification of changes in layer spacing. As reported in Fig. 4, X-ray diffraction plots of organoclay reveals a new basal reflection that has been shifted towards a higher interlayer spacing. This indicates that a partial exfoliation has occurred (Fig. 4).

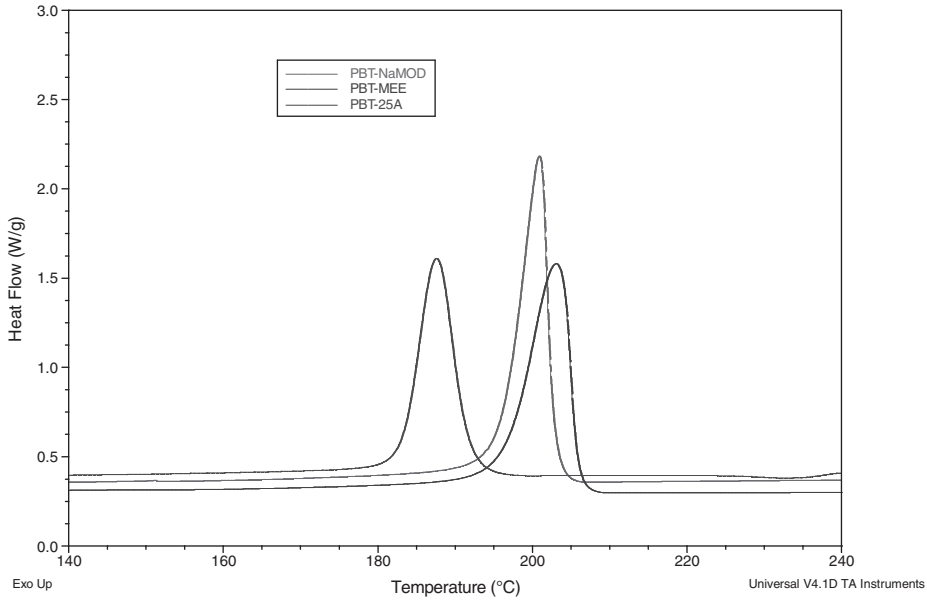

Figure 3.
DSC thermograms, Tc of PBT/organoclays (obtained at cooling/heating rates of 10 °C min^{-1}).

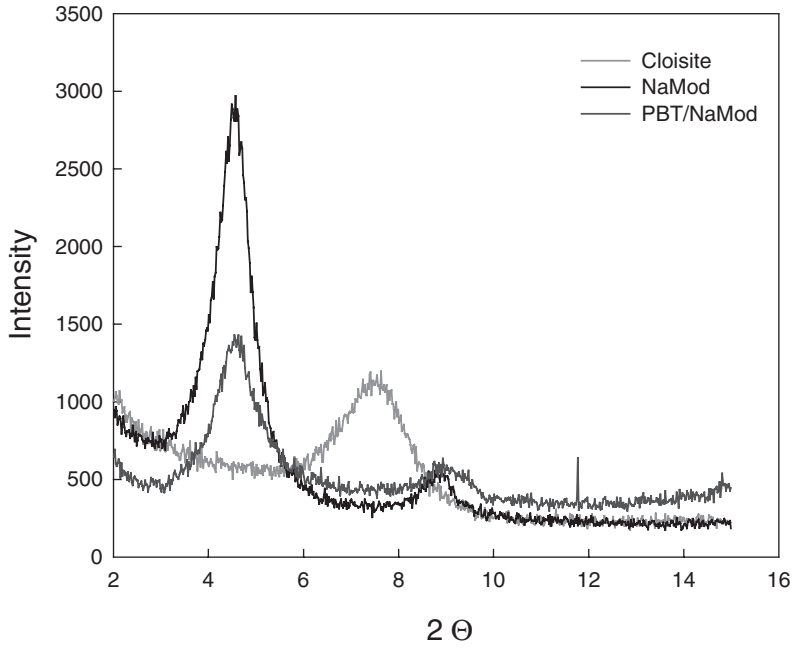

Figure 4.
WAXD patterns of Na-MMT, NaMod and PBT/NaMod nanocomposite.

Table 2.
Interlayer spacing values of Na-MMT, NaMod and PBT based nanocomposites measured by WAXD.

X-ray	
Sample	d (Å)
Na-MMT	11,58
NaMod	19,31
PBT-NaMod	19,39
PBT-MEE	16

An increase in the interlayer distance of about 7,5 Å has been observed in comparison to Na-MMT. All the values are listed in Table 2.

The nanoscale structure of PBT/nanocomposite was clarified by conventional TEM. Even though the investigation is very time-intensive and only gives qualitative information on the samples as a whole, Na-MMT and Cloisite 25A show clearly an intercalated morphology (Fig. 5a and Fig. 5b, respectively), with typical interlayer spacing reported in literature. NaMod exhibits a partial exfoliated morphology (Fig. 5c). This is consequence of the penetration of BHET in the layers.

Nanocomposites Mechanical Properties

Dynamic mechanical analysis (DMA) has been used to track the temperature dependence of the storage and loss moduli. The incorporation of NaMod and MEE into the PBT matrix results in a remarkable increase in storage modulus (Fig. 6a). It can be seen that the dispersed clay nanolayers result in significant increases in the dynamic storage moduli of the matrix polymer over the entire range of temperatures investigated.

The addition of NaMod into PBT matrix has two compensating effects on the matrix glass transition. On one hand, the presence of solid nanodispersed phase is reported to increase the Tg of matrix. On the other hand, the release of ethylen glycol into the matrix can result in PBT plasticization or reduction of molecular weight. The overall effect is a limited increase of PBT/NaMod Tg with respect to neat matrix (see Fig. 6b).

The evaluation of flexural properties of PBT and its nanocomposites confirmed the reinforcing effect of dispersed MMT particles.

Table 3 summarizes the mechanical properties of PBT and its hybrid composites measured at 25 °C. There was a significant increase in flexural modulus for all nanocomposites when compared with that of neat PBT. Even if PBT/MEE shows the highest E_f value; the incorporation of NaMod in the matrix galleries assures the highest σ_f.

Conclusion

PBT-based nanocomposite was prepared by melt compounding using BHET as organomodifier of Na-MMT, obtaining a partial exfoliated morphology. TGA results for organoclay show that the use of BHET/Na-MMT (NaMod) increases the onset degradation temperature of the hybrid over PBT process temperature in contrast to

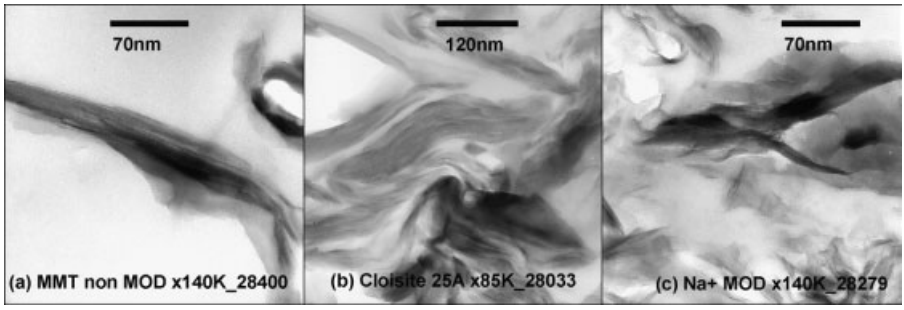

Figure 5.
TEM images: (a) Na-MMT; (b) Cloisite 25A; (c) NaMOD.

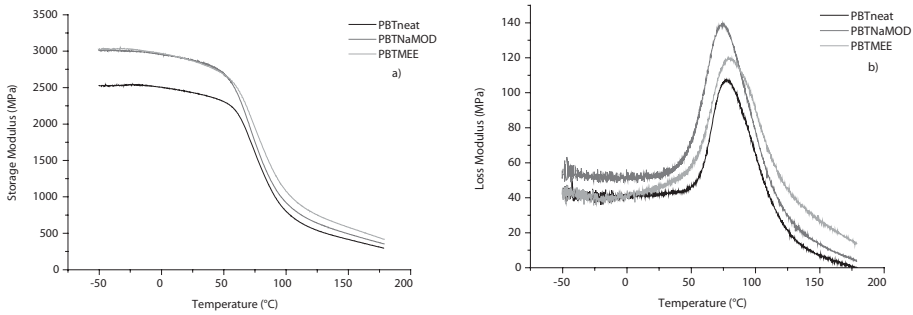

Figure 6.
Storage Modulus (a) and Loss Modulus (b) of neat PBT and PBT-NaMOD, PBT-MEE systems.

Table 3.
Comparison of material properties between neat PBT and PBT nanocomposites prepared with three different organomodified montmorillonite.

Material	E_f (Gpa)	σ_f (Mpa)
PBT	2.70 ± 0.09	89.9 ± 1.6
PBT/NaMod	2.86 ± 0.15	90.4 ± 3.1
PBT/MEE	3.12 ± 0.13	83.9 ± 1.6
PBT/C25A	2.87 ± 0.16	81.2 ± 3.7

commercial organoclays. The mechanical analysis reveals an increase of the storage modulus in comparison to neat PBT. However, the presence of the polymer precursor in the nanocomposites does not affect significantly the glass transition temperature of the polymer matrix. Future works will be focused on the optimization of the organic phase content and its molecular weight.

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