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Transesterification catalysts to improve clay exfoliation in synthetic biodegradable polyester nanocomposites

Eric Pollet, Cécile Delcourt, Michael Alexandre, Philippe Dubois *

Service des Matériaux Polymères et Composites (SMPC), Materia Nova Research Center, Université de Mons-Hainaut, 20, Place du Parc 7000, Mons, Belgium

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Abstract

We report here on the melt intercalation preparation of polymer/clay nanocomposites based on three commercial synthetic biodegradable polyesters: EastarBio Ultra, Ecoflex, and Bionolle, respectively. The montmorillonite clay addition is performed either by direct dispersion of Cloisite 30B in the polyester matrix or by dispersing a "PCL-grafted Cloisite 30B" masterbatch in the biodegradable polyesters. All obtained nanocomposites display an intercalated morphology as attested by X-ray diffraction measurements. The various analyses clearly show that the Bionolle (BIO) matrix gives the best results. Morphological characterization and mechanical properties of these nanocomposites also show that the "masterbatch route" leads to poor results as a consequence of the very low compatibility between the poly(ε-caprolactone) (PCL) of the masterbatch and the three other polyester matrices. In a second part, nanocomposites based on the BIO matrix are prepared by direct dispersion of the organo-clay in the presence of three different metal-based catalysts with the aim to promote transesterification reactions between the nanocomposite constituents. The mechanical properties and morphological characterization of these nanocomposites show that the tin-based catalyst (Sn) is the more efficient. Indeed, the effectiveness of transesterification reactions taking place between the ester functions of the BIO matrix and the hydroxyl groups of the organo-clay and the resulting "grafting" of BIO chains on the organo-clay surface are confirmed by thermogravimetric analyses performed after the extraction procedure. TEM observations show that this catalyst enhances the clay platelets exfoliation within the BIO matrix as a consequence of the transesterification reactions. Nanocomposites prepared in presence of Sn show better clay dispersion and enhanced stiffness with a 60% increase in Young's modulus.

Keywords: Clay; Biodegradable polyesters; Transesterification; Nanocomposites; Exfoliation

1. Introduction

During the last decade, nanocomposites based on biodegradable polyesters and layered silicates have been a subject of great interest [1–3]. Indeed, layered clays such as montmorillonite are environmentally friendly, naturally abundant, and thus available at relatively low cost. Their dispersion within polyester matrices leads to considerable improvements of various properties, in comparison with the neat biodegradable polymers, which broadens the application fields of these biopolyesters [1–5].

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* Corresponding author. Fax: +32 65 37 34 84.
E-mail address: philippe.dubois@umh.ac.be (P. Dubois).

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In general, polyester-layered silicate nanocomposites can be prepared by three different methods: polymer melt intercalation, solution adsorption/intercalation and in situ intercalative polymerization [1–3]. Among these techniques, the polymer melt intercalation has proven to be a very attractive method because of its versatility, its compatibility with current polymer processing techniques, and its environmentally friendly character due to the absence of organic solvents.

Among biodegradable polymers, the chemosynthetic aliphatic and/or aromatic (co)polyesters represent an important family. Nanocomposites based on such synthetic biodegradable polyesters have been prepared, by the three different techniques mentioned above, mainly with poly(ε-caprolactone) (PCL) [6–11], with poly(lactic acid) (PLA) [12–19], with poly(butylene succinate-co-butylene adipate) (PBSA) [20–22], with poly(butylene succinate) (PBS) [23–26] and very recently with poly(butylene adipate-co-butylene terephthalate) (PBAT) [27]. Poly(butylene succinate) (PBS) is an aliphatic thermoplastic polyester supplied by Showa High-Polymer under the trade name Bionolle®. PBS is obtained by polycondensation of 1,4-butanediol with succinic acid. Regarding PBAT, it is a new biodegradable aliphatic/aromatic copolyester obtained by polycondensation of 1,4-butanediol with adipic acid and therephtalic acid. Commercial PBAT can be found under the trade name Ecoflex® (supplied by BASF) and also under the name of EastarBio® (formerly supplied by Eastman Chemicals and now sold to Novamont).

Depending of the chosen grade, PBS and PBAT can be used for wide applications such as films, sheets, fibers and all kind of materials obtained by lamination, extrusion, molding, injection, etc. Nevertheless, PBAT is more flexible and has a higher elongation at break than PBS, and therefore is usually more suitable for film applications (e.g., food packaging and agricultural films).

To the best of our knowledge, all the results reported up to now on PBAT and PBS based nanocomposites concern intercalated/flocculated materials morphologies, with a very limited extent of clay platelets exfoliation. In all cases, the nanocomposites were prepared by polymer melt intercalation technique and several types and contents of organo-modified montmorillonite were studied [23–27].

The present article aims at studying the effect of the selected organo-clay (bearing hydroxyl functions) and more precisely its dispersion method (direct addition or masterbatch process) on the nanocomposites morphologies. In the masterbatch process, selected organo-clays were previously surface-grafted by aliphatic polyester chains, i.e., poly(ε-caprolactone) PCL via catalyzed ring-opening polymerization of ε-caprolactone. In a second approach, our aim was to enhance the clay dispersion and its exfoliation within the biopolyester matrix. Thus, the nanocomposite preparation has been conducted in the presence of various catalysts with the aim to promote transesterification reactions between the biopolyester chains and either the hydroxyl functions of the organo-clay or the polyester chains of the masterbatch (PCL-grafted organo-clay). Our attention has also been focused on the relationship between the nanocomposite morphology and its mechanical properties.

2. Experimental

2.1. Materials

Commercial grade poly(ε-caprolactone) PCL was supplied by Solvay (Belgium) under trade name CAPA® 6500 and CAPA® 1000, with $M_n = 50{,}000$ and 1000 g/mol, respectively. Aliphatic homopolyester poly(butylene succinate) (PBS) was supplied by Showa HighPolymer Co. (Japan) under trade name Bionolle® (grade #1003). Two aliphatic/aromatic copolyesters were also studied. These poly(butylene adipate-*co*-butylene terephtalate) were Ecoflex® F from BASF and EastarBio Ultra® formerly from Eastman Chemicals (now from Novamont). All along this document, these four polyesters matrices will be abbreviated PCL, BIO, ECO and EAS, respectively.

The commercial clay used in this study was a montmorillonite organo-modified by methyl bis(2-hydroxyethyl) (tallow alkyl) ammoniums and was supplied by Southern Clay Products (Texas, USA) under the trade name Cloisite®30B. The organo-modifier content of this clay is approximately 20 wt% as attested by thermogravimetry analysis (TGA, see hereafter).

Three transesterification catalysts were used in this study: dibutyltin dilaurate $Sn(Bu)_2(Lau)_2$, titanium (IV) butoxide $Ti(OBu)_4$ and antimony (III) oxide Sb_2O_3 and are abbreviated Sn, Ti and Sb, respectively. These catalysts were purchased from Aldrich Chemicals and used as received.

2.2. Nanocomposites preparation

Before processing, the organo-clay was dried at 40 °C under reduced pressure for 4 h. The polyester matrices were substantially dried in a ventilated oven before use. The polyester-layered silicate nanocomposites were prepared by mechanical kneading with an Agila two-roll mill for 10 min. The temperature was set at 150 °C for EAS and ECO and at 160 °C for BIO. When the objectives were to promote transesterification reactions, blending of polyesters with clay particles was conducted in the presence of 1 wt% of catalyst and 0.3 wt% of Ultranox®626 stabilizer (supplied by General Electric). Nanocomposites containing 3 wt% (in inorganics) of montmorillonite were prepared. The collected molten materials were compression-molded into 3 mm thick plates by hot-pressing at 170 °C under 150 bar for 3 min, then under 30 bar for three additional minutes, followed by cold pressing at 15 °C under 30 bar for 5 min.

A second method was used for the clay addition which consists in the dispersion of a "PCL-grafted organo-clay" masterbatch displaying a high loading in Cloisite 30B (36 wt%). In this case, all other experimental conditions for the nanocomposites preparation remain unchanged.

2.3. "PCL-grafted Cloisite 30B" masterbatch preparation

The experimental procedure has already been described elsewhere [9]. The e-caprolactone (CL) monomer was added, under nitrogen atmosphere, to previously dried Cloisite 30B in a polymerization reactor. The medium was stirred for 1 h at room temperature then a known amount of $Bu_2Sn(OMe)_2$ initiator solution in dry toluene was added such that the [CL]/[Sn] initial molar ratio was 230. The polymerization was allowed to proceed at 100 °C and the reaction was stopped, after a determined time, by quenching in liquid nitrogen. Residual monomer was further removed by evaporation under reduced pressure. The inorganic content of the "PCL-grafted Cloisite 30B" masterbatch, measured by TGA (see below), was found to be 36 wt%. This masterbatch displays an intercalated structure with an interlayer spacing of approximately 18 Å as determined by X-ray diffraction (see technical details below).

2.4. TGA characterization

All analyses were performed on approximately 5–15 mg samples, at a heating rate of 20 K/min from 25 to 600 °C on a Hi-Res TGA 2950 apparatus from TA Instruments. For all polyester/clay nanocomposites, the analyses were carried out under air flow (74 cm^3/min) and the clay content of each composite was assessed by TGA as the residue left at 600 °C. The organic content (in wt%) of the organo-modified clay was determined by the weight loss recorded between 150 and 425 °C, corresponding to the ammonium cations thermal degradation.

2.5. DSC characterization

The thermal behavior of the pristine polyester matrices and their respective nanocomposites was analyzed by Differential Scanning Calorimetry (DSC) using a DSC 2920 from TA Instrument. The analyses were performed on approximately 5–10 mg samples, at a heating rate of 10 K/min from -100 to 200 °C under nitrogen flow. The reported values were recorded during the second heating scan.

2.6. XRD characterization

X-Ray Diffraction (XRD) morphological analyses were performed on a powder diffractometer Siemens D 5000 using Cu (Kα) radiation (wavelength: 1.5406 Å) at room temperature in the range of $2\theta = 1.5–30°$ with a scanning rate of 2°/min. These analyses were performed on approximately 100–200 μm thick films obtained by hot pressing the nanocomposite samples.

2.7. TEM analysis

Transmission electron microphotographs (TEM) were obtained with a Philips CM200 apparatus using an accelerator voltage of 120 kV. The samples were 70 nm thick and prepared from 3 mm hot-pressed plates with a LEICA Ultracut UCT ultra-cryomicrotome cutting at -100 °C.

2.8. Mechanical testing

Tensile properties were measured with a Lloyd LR 10 K tensile testing apparatus, at 20 °C, at a constant deformation rate of 50 mm/min, with dumbbell-shaped specimens prepared from compression molded samples according to the 638 type V ASTM norm. Five specimens were tested for each nanocomposite sample and the mean values and standard deviation were calculated and reported.

2.9. Procedure for the clay extraction

As a first step, approximately 2 g of crude nanocomposite sample were dissolved, under stirring, in chloroform (100 mL) for 2 h at room temperature. After centrifugation at 4000 rpm for 30 min. the polymer containing supernatant was collected and the solid phase was carefully washed by redispersion in 100 mL of chloroform followed by a second centrifugation. This operation was repeated one more time then all supernatants were gathered, concentrated and precipitated into heptane. The resulting "clay-free" polyester was filtered and dried under vacuum at 50 °C up to constant weight. The solid "clay-rich" phase was recovered after vacuum drying, at 50 °C, up to constant weight.

3. Results and discussion

3.1. Thermal properties of commercial polyesters

As it can be seen in Table 1, EAS, ECO and BIO present similar thermal properties when analyzed by DSC. Nevertheless, EAS and ECO seem to be characterized by a lower crystallinity in comparison to the BIO matrix. The respective rate of crystallinity (X_c) were estimated using $X_c = \Delta H_m/\Delta H_m^0$ where ΔH_m^0 represents the theoretical heat of fusion for a 100% crystalline polymer (200 J/g for BIO and 115 J/g for EAS and ECO). It is worth noting that the low level of crystallinity for EAS and ECO leads to higher uncertainty of calculated values.

As far as TGA is concerned (Fig. 1), EAS and ECO present an almost identical behavior with a thermal degradation occurring between 230 and 580 °C with a maximum thermal degradation rate around 410 °C (maximum of the weight loss derivative curve). The BIO matrix presents only slight differences with a thermal degradation ranging from 250 to 515 °C with a maximum rate around 400 °C.

3.2. Preparation and characterization of biopolyester/Cloisite 30B nanocomposites

First of all, the DSC analyses (not shown here) demonstrated that the addition of 3 wt% of Cloisite 30B, either directly or via the masterbatch process (see next section), slightly increases the crystallinity of the BIO matrix (from ≈27% to 30%) but does not alter at all the extent of crystallinity of the EAS and ECO matrices.

The results of tensile tests and XRD measurements are presented in Table 2. The mechanical behavior of the three polyesters is very different since the BIO matrix is much more rigid than EAS and ECO. Thus, the tensile tests had to be carried out with different grips and load cells for these two set of samples which makes it difficult to make a direct comparison between the various values.

As far as XRD analyses are concerned, one may note that all the composite samples present an intercalated morphology with a distance between clay platelets, noted $d(001)$ in Table 2, increased from 18 Å (for the pristine clay or the masterbatch) to values ranging from 36 to 42 Å for the nanocomposites. Such results are in good agreement with those reported by Okamoto and co-workers [23–25] who obtained intercalated/flocculated PBS based nanocomposites. These materials displayed interlayer spacing ranging from 28 to 32 Å only, but in these cases the montmorillonite were organo-modified by less bulky cations (mainly octadecyl based ammonium). Someya et al. also prepared nanocomposites materials based on organo-modified montmorillonites dispersed within BIO or ECO matrices [26,27]. In these papers, the authors reported mainly intercalated morphologies and interlayer spacing ranging from 22 to 33 Å for the bulkier ammonium cations. Although in our case

Table 1
Thermal properties of the synthetic polyesters as measured by DSC

Matrix	Glass transition temperature T_g (°C)	Melting temperature T_m (°C)	Heat of fusion ΔH_m (J/g)	Crystallinity rate X_c (%)
EAS	−30	113–115	15	10–15
ECO	−30	108–112	13	10–15
BIO	−31	112–114	54	27

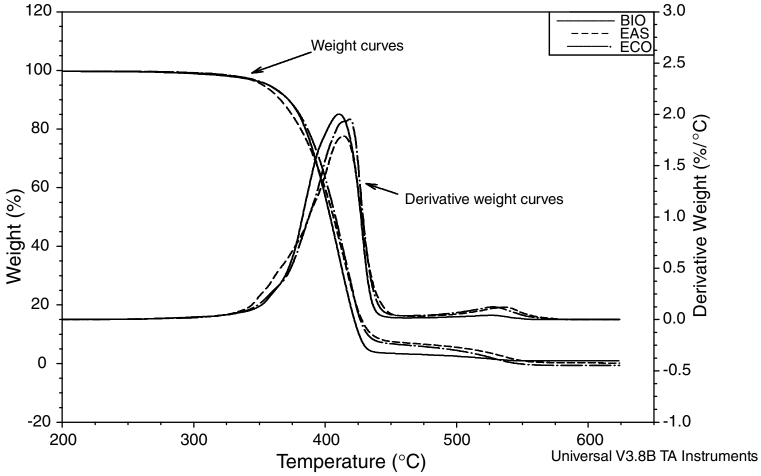

Fig. 1. Results from thermogravimetric analyses (time-dependent weight loss and related derivative) of the synthetic biopolyesters matrices (recorded at a heating rate of 20 °C/min, under air flow).

Table 2
Tensile properties of neat biopolyesters and their respective nanocomposites materials (filled with 3 wt% in inorganics)

Sample	d(001) (Å)	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
BIO	–	323 ± 16	36.0 ± 0.4	220 ± 8
BIO + Cl.30B	42	405 ± 19	27.3 ± 0.3	149 ± 10
BIO + Master.[a]	36	353 ± 25	24.9 ± 0.8	135 ± 19
EAS	–	82 ± 4	33.4 ± 0.8	1173 ± 34
EAS + Cl.30B	40	90 ± 2	29.2 ± 0.9	1072 ± 45
EAS + Master.[a]	38	90 ± 2	23.1 ± 1.7	862 ± 94
ECO	–	70 ± 3	35.0 ± 1.0	1250 ± 31
ECO + Cl.30B	38	76 ± 2	31.9 ± 0.4	1162 ± 33
ECO + Master.[a]	36	70 ± 3	28.5 ± 1.3	1139 ± 69

Organo-clay interlayer spacing *d*(001) of the obtained nanocomposites as measured by XRD.

[a] Dispersion of the "PCL-grafted Cloisite 30B" masterbatch in the selected biopolyester in order to reach a final inorganic content of 3 wt% (see experimental).

the organo-modified clay is different, the morphologies and interlayer spacing values reported in the literature are in good agreement with our observations.

In the present study, the composites obtained by dispersion of the "PCL-grafted Cloisite 30B" masterbatch are characterized by lower *d*(001) values in comparison to the samples obtained by direct addition of Cloisite 30B.

Regarding mechanical properties, the nanocomposites samples based on EAS and ECO matrices present only a small increase in their Young's modulus values (less than 10%). On the other hand, the direct addition of Cloisite 30B in the BIO matrix leads to a large increase of the polyester rigidity, with a 25% increase in Young's modulus. Nevertheless, the addition of clay particles through the dispersion of the masterbatch does not lead to such an increase. These results are in apparent contradiction with previously reported results about the dispersion of such a masterbatch in a high molecular weight PCL matrix [9]. This could be explained by a very low compatibility between the three different polyester matrices studied here and the PCL chains (actually grafted at the clay surface) of the masterbatch.

3.3. Miscibility of biopolyester matrices with PCL chains

It is worth pointing out that Bhattacharya et al. have studied the compatibility between these biodegradable polyesters [28]. The reported results show that the polyester blends are mostly immiscible showing separate melting and glass transition temperatures. Nevertheless, small shifts in the T_g are an indication of interaction between some of the investigated matrices. Furthermore, the authors have demonstrated that ester-interchange reactions can sometime occur between these polyesters. Thus, in order to check if the limited polyester intercalation and low modulus enhancement observed in the present study are the consequence of a poor compatibility between the biopolyester and PCL chains, thermal properties of their respective blends were studied by DSC.

The first set of samples consisted in melt blending BIO with PCL ($M_n = 50{,}000$ g/mol) in order to obtain 95–5, 90–10 and 80–20 compositions (in weight). The second set of samples was obtained by co-dissolving BIO and PCL (with $M_n = 1000$ g/mol) in chloroform and casting the mixture. BIO/PCL compositions ranging from 95/5 to 50/50 were prepared. All DSC analyses (not shown here) made on these blends have demonstrated that the mixtures present two distinct melting temperature peaks (identical to those of the neat polyesters) and composition-independent glass transition temperature. Thus, BIO was found to be immiscible with PCL in this composition range as recently confirmed by the results reported by Qiu et al. [29]. The poor intercalation of polyester chains and low mechanical properties observed for the masterbatch dispersion are most probably due to the immiscibility of these synthetic polyesters.

Keeping in mind the assertion of Bhattacharya et al. about the ester interchange reactions between these polyesters, we tried to promote transesterification reactions between the polyester matrix and either the OH groups from the Cloisite 30B organo-modifier or the PCL chains of the "PCL-grafted Cloisite 30B" masterbatch. Our objectives were to check if such transesterification reactions could improve the clay dispersion (exfoliation) and thus enhance the mechanical properties of the nanocomposites. Since the clay addition to EAS and ECO matrices gave rather poor results, it has been decided to focus our attention on the poly(butylene succinate) matrix (BIO).

3.4. Preparation of BIO/Cloisite 30B nanocomposites in the presence of transesterification catalysts

We chose three different chemical metal-based compounds known to promote and catalyze transesterification reactions with polyesters matrices such as poly(ethylene terephtalate) (PET) or poly(ε-caprolactone) (PCL) [30,31]. These transesterification catalysts are dibutyltin dilaurate $(Bu)_2Sn(Lau)_2$, titanium(IV) butoxide $Ti(OBu)_4$ and antimony(III) oxide Sb_2O_3 and are abbreviated Sn, Ti and Sb, respectively, for sake of clarity.

Three blends were prepared as reference samples by mixing BIO with the Sn, Ti and Sb catalysts (1 wt% of catalyst). Tensile tests were performed on these reference samples and are reported in Table 3. As can be noticed, these results clearly demonstrate that the addition of the catalyst to the BIO matrix does not affect its mechanical properties. Thus, any difference, which could be observed further on nanocomposites samples, would be a consequence of transesterification reactions.

The first attempts to promote transesterification reactions were carried out on materials prepared by dispersing the "PCL-grafted Cloisite 30B" masterbatch (36 wt% in inorganics) within the BIO matrix. XRD characterization of the obtained nanocomposites (not shown here) demonstrated that the addition of a catalyst had no influence on the material final morphology. Indeed, all nanocomposites present an intercalated structure and their interlayer spacing remained unchanged at approximately 36 Å.

Tensile tests were also performed on these samples and the obtained results are summarized in Table 4. When looking at these values, it appears that the addition of these catalysts has no influence on the mechanical properties of the final nanocomposite material since the Young's modulus or the stress at break values are similar to those of the pristine BIO matrix. Furthermore, a sharp decrease of the ultimate elongation is even observed in the presence of Sn and Ti catalysts.

Table 3
Mechanical properties of "BIO + catalyst" reference samples (prepared in the presence of 1 wt% catalyst)

Sample[a]	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
BIO	323 ± 16	36.0 ± 0.4	220 ± 8
BIO + Sn	327 ± 35	35.2 ± 0.8	214 ± 10
BIO + Sb	321 ± 18	34.4 ± 1.6	214 ± 9
BIO + Ti	325 ± 22	35.6 ± 1.2	216 ± 11

[a] Sn, Ti and Sb refer to $(Bu)_2Sn(Lau)_2$, $Ti(OBu)_4$ and Sb_2O_3, respectively.

Table 4
Mechanical properties of nanocomposites prepared by dispersing the "PCL-grafted Cloisite 30B" masterbatch in BIO added with 1 wt% of catalysts

Sample[a]	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
BIO	323 ± 16	36.0 ± 0.4	220 ± 8
BIO + Master.	353 ± 25	24.9 ± 0.8	135 ± 19
BIO + Master. + Sn	315 ± 15	24.1 ± 0.9	19 ± 2
BIO + Master. + Sb	361 ± 18	25.6 ± 1.3	147 ± 43
BIO + Master. + Ti	335 ± 22	15.0 ± 4.1	55 ± 22

Final content in clay = 3 wt% in inorganics.

[a] Sn, Ti and Sb refer to $(Bu)_2Sn(Lau)_2$, $Ti(OBu)_4$ and Sb_2O_3, respectively.

One can assume that the incompatibility between PCL and BIO is too high and prevents the reaction between their respective implied chemical functions, even in presence of a transesterification catalyst.

As a second series of attempts, nanocomposites were prepared by direct dispersion of Cloisite 30B within the BIO matrix in presence of the transesterification catalysts. Then tensile tests were performed on these nanocomposites samples and the results are presented in Table 5. It is worth noting that the Sb and Ti based catalysts seem to have a very limited effect on the mechanical properties since the Young's modulus values are in the same range as the one of the nanocomposite sample obtained by direct dispersion of Cloisite 30B without adding any catalyst.

Nevertheless, the Sn based transesterification catalyst seems to have a great influence on the material stiffness since a 27% increase is observed for the Young's modulus along with a significant decrease of the stress and strain at break values (4.9 MPa and 66%, respectively).

As a next logical step morphological studies were performed on these nanocomposites using the usual characterization methods such as XRD and TEM. The X-ray diffractograms of these samples are presented in Fig. 2. Next to the intense diffraction peaks characteristic of the crystallinity of the polyester matrices (from ≈20° to 25°) one notices that the signal intensity at low 2θ angle range is quite low for the BIO + Cloisite 30B sample and that makes difficult the comparison with others traces.

Nevertheless, it seems that the nanocomposite sample prepared with Sn catalyst shows a much broader and less intense intercalation peak compared to the samples obtained with Sb and Ti catalysts. This may be the result of a better dispersion of the organo-clay platelets (with less order) and thus a higher degree of exfoliation could be expected that would also explain the higher modulus value for this material. However, XRD analyses suffer a lack of precision and only provide averaged information about the clay dispersion quality and thus must be completed by TEM observations.

Fig. 3 shows representative TEM photographs, at low and high magnification, of the nanocomposites prepared in the absence (pictures (a) and (b)) and in the presence (pictures (c) and (d)) of Sn catalyst, with pictures (b) and (d) displaying higher magnifications. Pictures (a) and (b) highlight the intercalated–flocculated structure of the Cloisite 30B within the BIO matrix (dark entities are the cross section of organo-clay platelets). These morphologies are in good agreement with those previously observed by Okamoto and co-workers [23–25] on similar systems.

Microphotographs (c) and (d) clearly demonstrate that the addition of the Sn based transesteri-

Table 5
Mechanical properties of nanocomposites prepared by direct dispersion of Cloisite 30B in BIO added with 1 wt% of catalysts

Sample[a]	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
BIO	323 ± 16	36.0 ± 0.4	220 ± 8
BIO + Cl.30B	405 ± 19	27.3 ± 0.3	149 ± 10
BIO + Cl.30B + Sn	515 ± 11	4.9 ± 1.5	66 ± 19
BIO + Cl.30B + Sb	388 ± 10	27.9 ± 1.1	113 ± 20
BIO + Cl.30B + Ti	438 ± 23	14.4 ± 4.2	106 ± 21

Final content in clay = 3 wt% in inorganics.

[a] Sn, Ti and Sb refer to $(Bu)_2Sn(Lau)_2$, $Ti(OBu)_4$ and Sb_2O_3, respectively.

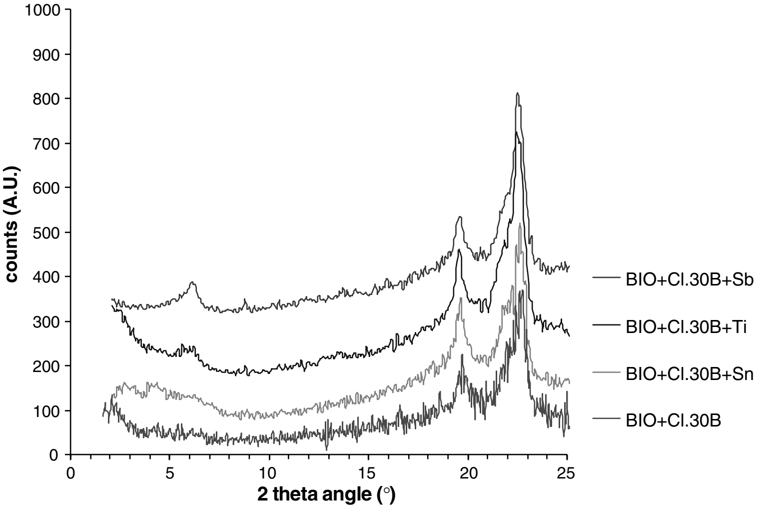

Fig. 2. XRD traces of the materials prepared with and without transesterification catalysts (see Table 5).

fication catalyst has a great and positive influence on the quality of clay platelets dispersion, leading to higher degree of exfoliation for this material. The TEM observation also showed that the Ti based catalyst improves the clay dispersion, but in a less extent (photographs not shown here).

3.5. Evidence of effective promotion of transesterification reactions: nanocomposite extraction

Highlighting the effective occurrence of transesterification reactions is not trivial work. Indeed, common spectroscopic techniques (e.g., FT-IR) did not bring us any obvious proof on this point. Thus, we have tried to separate the clay from the BIO matrix by centrifugation of the material previously dissolved in chloroform. This technique has already been successfully used in similar nanocomposite systems to extract (organo-)clays from PCL matrices [8–10]. The clay, being heavier, settles down while the poly(butylene succinate) chains, soluble in chloroform, stay in the supernatant medium allowing for the separation of the two entities. Such extraction has been performed on the nanocomposite prepared with Sn catalyst and on a nanocomposite prepared without any catalyst, the later being the reference sample. TGA was then performed on the extracted moieties. Fig. 4 presents the traces of temperature-dependent weight loss for the clay rich phase extracted from the two samples. All characteristics data obtained from the TGA are summarized in Table 6.

Regarding the TGA of the clay-rich phase, the weight loss recorded between 150 and 425 °C is related to the organic content of the clay, that is to say its amount of organo-modifier (organic ammonium cations). Such analysis performed on dried Cloisite 30B gives an organic weight content of approximately 20% for this pristine clay [9,17]. When looking at the values reported in Table 6, one may notice that the organic content of the clay extracted from the "BIO + Cl.30B" nanocomposite is almost the same as for the pristine Cloisite 30B: 19% and 20%, respectively. On the other hand, the clay extracted from the nanocomposite prepared in presence of Sn catalyst shows a greater organic content (28%). In this last case, the thermograms overlay presented in Fig. 4 shows that the thermal degradation extends on a larger temperature range with an important additional weight loss occurring between 500 and 600 °C. This higher value of organic content could be explained by the presence of polyester chains linked to the clay as a result of effective transesterification reactions. This consideration is confirmed by the TGA of the "polyester-rich" extracted phase. Indeed, when the nanocomposites were prepared without any transesterification catalyst, the extracted polymer chains totally degrade when heated up to 600 °C, leaving no residue. This thermal treatment, performed under air flow, and the recorded value of the residue at 600 °C have proved to be very effective means for determining the inorganic content (from the alumino-silicate) of nanocomposite materials. When such analysis was performed on polyester chains extracted from the

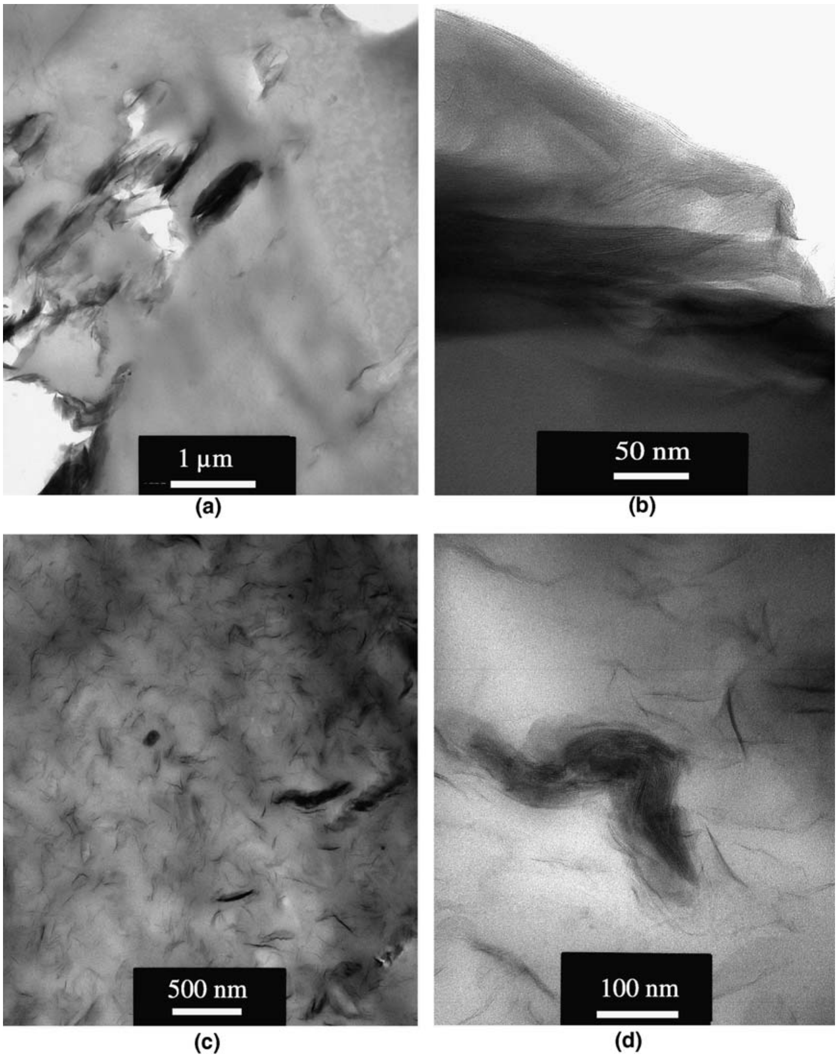

Fig. 3. TEM photographs of the nanocomposites prepared by direct addition of Cloisite 30B in absence (a,b) and presence (c,d) of Sn based transesterification catalyst (1 wt%). Final clay content is 3 wt% in inorganics.

nanocomposite prepared in presence of Sn catalyst, the final residue at 600 °C was found to be approximately 1.9% (see Table 6). This relatively high value is clearly an indication of the presence of clay particles strongly linked to the poly(butylene succinate) chains. The impossibility to remove these clay platelets from the polyester chains could only be explained by the formation of some chemical covalent bonds between the clay organo-modifiers and the polyester chains, which resulted from the occurrence of transesterification reactions between these two entities.

One may also consider that these transesterification reactions could cleave the polyester chains and thus reduce the average molecular weight of BIO macromolecules. This phenomenon could be positive as it may favor the intercalation of these smaller polyester chains between the clay platelets but on the other hand, it could have a detrimental effect on the mechanical properties and thermal stability of the biopolyester matrix. Nevertheless, the tensile tests showed us that the addition of transesterification catalysts into the unfilled biopolyester matrices had no influence on the mechanical properties. In addition, TGA (not shown here) also demonstrated that the polymer thermal stability was not influenced by these catalysts (at least within the investigated compositions and experimental conditions) thus one may suppose that the average length of the polyester chains is more likely not significantly altered.

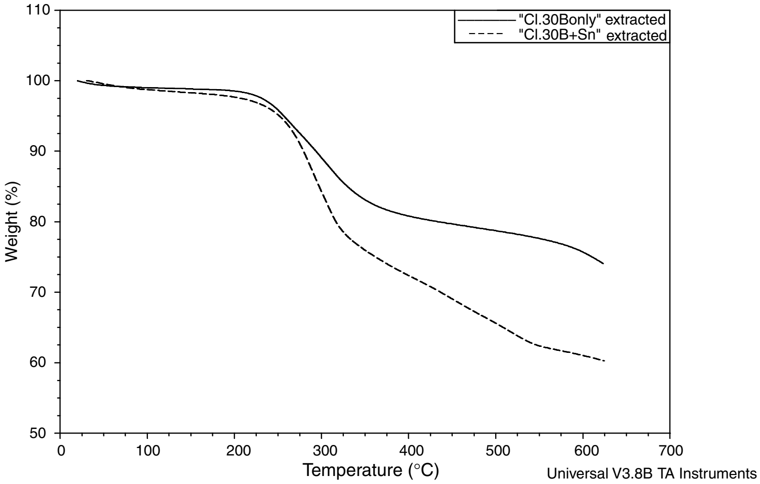

Fig. 4. TGA thermograms of the clay-enriched phase solvent-extracted from the BIO-based nanocomposites prepared by direct addition of Cloisite 30B in absence (full line) and presence (dotted line) of Sn based transesterification catalyst (see entries 2 and 3; Table 5). Analyses performed at a heating rate of 20 °C/min, under air flow.

Table 6
Data from TGA analyses performed on extracted phases from the nanocomposite samples (see Fig. 4)

Sample[a]	"Clay-rich" extracted phase, Weight loss between 150 and 425 °C (wt%)	"BIO-rich" extracted phase, Residue at 600 °C (wt%)
BIO + Cl.30B	19	0
BIO + Cl.30B + Sn	28	1.9

[a] Cl.30B and Sn stand for Cloisite30B and $(Bu)_2Sn(Lau)_2$, respectively.

This is also confirmed by the DSC analyses where no change in the melting temperature (T_m) was observed for the BIO chains when the nanocomposite was prepared in presence of the transesterification catalyst ($T_m = 113.5\ °C \pm 1\ °C$). Nevertheless these DSC traces (not shown here) also demonstrated that the crystallinity rate of the biopolyester is increased (from 30% to 40%) for the nanocomposites prepared in presence of Sn or Ti catalyst, that is to say for the nanocomposites displaying enhanced levels of clay exfoliation. Indeed, it is well known that a finer dispersion of the clay platelets may increase the number of crystal nuclei forming agents and thus the overall crystalline rate of the polymer in the nanocomposite material.

4. Conclusions

In this study biopolyester nanocomposites have been successfully prepared by dispersing an organo-modified montmorillonite (Cloisite 30B) within three different synthetic biodegradable polyesters. The structural analyses performed on the final materials showed that intercalated nanocomposites were obtained in all cases. The tensile tests performed on the intercalated nanocomposites evidenced that the clay dispersion within the ECO and EAS matrices did not increase significantly the biopolyester rigidity whereas an important enhancement of the Young's modulus was observed for the BIO-based nanocomposites. Nevertheless, whatever the biopolyester used, both morphological characterization and tensile tests clearly demonstrated that the addition of clay via the dispersion of a "PCL-grafted Cloisite 30B" masterbatch gives poor results. Thermal characterization of PCL blended respectively with the BIO, EAS and ECO biopolyesters clearly showed that the restricted intercalation and poor mechanical properties were the results of the PCL immiscibility with these synthetic biodegradable polyesters and this was confirmed by previously reported studies. We further aimed at enhancing the compatibility between the nanocomposite components and thus we tried to promote transesterification reactions by testing several catalysts for the preparation of nanocomposites based on the BIO matrix.

All attempts to promote transesterification reactions between BIO macromolecules and the PCL chains of the masterbatch gave poor results. It appears that the incompatibility between BIO and PCL is too high and prevents transesterification reactions between their respective reactive functions even in the presence of a catalyst. Regarding the nanocomposites obtained by direct addition of the organo-clay, dibutyltin dilaurate $(Bu)_2Sn(Lau)_2$ gave the best results among the tested metallic catalysts. Indeed, XRD and TEM morphological characterization clearly evidenced higher levels of clay platelets exfoliation. The extraction procedures performed on these samples and the related TGA tend to prove that the BIO macromolecules are covalently linked to the clay surface (more precisely to its organo-modifier) as a result of effective transesterification reactions occurring between the polyester chains and the hydroxyl functions of the organo-clay. As a direct consequence of the transesterification reactions and enhanced clay exfoliation, the nanocomposite prepared by direct addition of Cloisite 30B in presence of $(Bu)_2Sn(Lau)_2$ catalyst displays a tremendous increase in the stiffness of the BIO matrix (60% increase in Young's modulus compared to the neat polyester). It is worth pointing out that the results presented here were obtained without optimizing the nature of the catalyst and its content, thus one may expect getting even better results by an appropriate selection of the transesterification catalyst.

In conclusion, promoting in situ transesterification reactions during the preparation of biopolyester/clay nanocomposites by a melt intercalation process seems to be a very effective method to improve the organo-clay dispersion and exfoliation within the polyester matrix. This original approach could allow for the preparation of nearly-exfoliated nanocomposites by the quite simple polymer melt intercalation technique and thus could make it competitive with the less environmentally friendly in situ intercalative polymerization method. Such optimized technique could possibly lead to an industrially viable method to easily produce exfoliated polyester/clay nanocomposites in a one-pot procedure.

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