SUPPLEMENTARY INFO

Poly(butylene succinate) Bionanocomposites: A Novel Bio-Organo-Modified Layered Double Hydroxide For Superior Mechanical Properties

Grazia Totaro, Laura Sisti, Annamaria Celli, Haroutioun Askanian, Vincent Verney, Fabrice Leroux

1. SPECTROSCOPIC DATA OF PBS OLIGOMER

PBS oligomer was analyzed by ^{1}H NMR (Figure S1) and ^{13}C NMR (Figure S2). The resonance signal appearing at 2.6 ppm was associated with the methylene protons (Hb) in the succinic moiety. The resonances at 4.1 and 1.7 ppm were respectively assigned to the methylene protons (Hc) and (Hd) in the 1,4-butanediol unit. At 3.7 ppm the methylene protons near OH terminal groups are visible.

In ^{13}C NMR spectrum the methyl groups of glycol appear at 25 ppm, while the methyl groups of succinic unit are present at 29 ppm. At 64 ppm the methylene groups of the diol bonded to oxygen are present. The carbonyl carbons are visible at 170 ppm.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.60-1.80 (m, 4H; C^dH_2), 2.55-2.70 (s, 4H; C^bH_2), 3.65-3.70 (t, 2H; $C^{c'}H_2$), 4.06-4.16 (t, 4H; C^cH_2).

^{13}C NMR (400 MHz, $CDCl_3$, δ): 25.20 (C^dH_2), 29.01 (C^bH_2), 64.16 (C^cH_2), 172.35 (C^aO).

2. MORPHOLOGICAL CHARACTERISTICS OF ORGANO-MODIFIED LDHS

2.1 Composition of the intercalating agent in LDH

In order to better understand the composition of the intercalating agent, the samples prepared in this study were analyzed by comparing them with an LDH coprecipitated with sodium succinate (MgAl-SU), with the starting monomers succinic acid (SA) and 1,4-butanediol (BD), and with PBS oligomer (PBS_o).

Considering the FTIR analysis (see Figure S3), the main vibration bands of SA at 1680, 1410 and 1310 cm^{-1}, are respectively due to the carboxylic C=O stretching, OH bending and C-O stretching mode [1]. BD presents the hydroxyl group stretching vibration at 3441 cm^{-1}, the aliphatic -CH_2 stretching at 2940 cm^{-1} and a broad band between 1048-944 cm^{-1} (stretching of primary alcohol groups). By examining the LDH containing succinate as anion, the expected symmetric and asymmetric -COO^- group stretching at almost 1370 and 1560 cm^{-1} are present, while for the MgAl-PBS_o sample these bands shifted to 1387 and 1555 cm^{-1}: therefore the succinate seems to be present

in MgAl-PBS_o. On the other hand, the band at almost 1048 cm^{-1} is common to both BD and PBS_o hence it is not possible to exclude the presence of butanediol.
In conclusion, the FTIR spectra does not seem to clarify exactly the composition of the filler, in fact both succinate and butanediol in MgAl-PBS_o could be present, as highlighted by the dash lines in green and black in Figure S3b.

In order to better elucidate this point, a small part of a PBS oligomer, dissolved in acetonitrile, was subjected to ageing (24 h at 75 °C) in an aqueous basic medium (NaOH 1M), in accordance with the coprecipitation procedure reported for LDH synthesis (figure S4), but without the metal salts. After evaporation of the solvent, the product obtained resulted to be partially soluble in $CHCl_3$ and water, therefore it was analyzed by ^1H NMR both in $CDCl_3$ and D_2O.
The ^1H NMR analysis of the soluble fraction in $CDCl_3$ indicates the presence of condensation products such as bis(4-hydroxydibutyl)succinate (BSB) and butanediol. BSB is one of the hydrolysis products of PBS [2-4] suggesting, as expected, that the LDH coprecipitation procedure causes a partial hydrolysis of PBS oligomer. The second monomer SU is not visible because it is not soluble in chloroform. On the other hand, the ^1H NMR analysis in D_2O reveals mostly the presence of SU and BD. Since the oligomer is insoluble in water, it is reasonable that such signal is not visible in D_2O, as well as any possible condensation product. All the solubility tests of the substances involved were conducted and, to better clarify, the data are shown in Table S1.
Then the ^1H NMR spectrometry suggests the presence of monomers and a condensation product such as BSB.

Moreover, the presence of the oligomeric chains in the system is confirmed by XRD diffraction.
When comparing of the diffraction patterns of MgAl-SU, MgAl-PBS_o and PBS_o (Figure S5), the basal reflection of the sample with succinate anion (10.9 Å at $2\theta = 7.9°$) is positioned at a slightly higher angle with respect to the MgAl-PBS_o sample (12.0 Å at $2\theta = 7.4°$). Finally, and more significantly, it clearly appears that the nanofiller modified in this study presents the typical reflections of the polymer matrix into the angular domain $17° < 2\theta < 30°$. Hence, the oligomeric chains are also present into the nanofiller system.

In view of such considerations, the interlayer distance obtained by the novel organo-modified Layered Double Hydroxide prepared in this study probably results from more than one species, simultaneously present in the nanofiller system, that is butanediol, succinate, bis(4-

hydroxydibutyl)succinate and some oligomeric chains. Hence, the intercalation reaction provides a mixed organo-filler system (figure S6).

2.2 Presence of physisorbed PBS oligomer on the surface of LDH

With the aim of ascertaining that the oligomer was not just adsorbed on the surface of LDH but also grafted onto it, a small part of MgAl-PBS_o (denoted MgAl-PBS_{ow}) was washed with $CHCl_3$ in order to completely eliminate the oligomer simply physisorbed and the sample was characterized by ATR-FTIR, XRD and TGA.

The FTIR profile does not highlight any differences from the pristine organo-modified MgAl-PBS_o, and the XRD profile clearly demonstrates that the oligomer is also intercalated or grafted, because of the presence of the typical reflections of the polymer matrix (Figure S7). One should note that a new reflection appears close to the first, probably indicating a carbonate absorption, due to the greater solubility of CO_2 in chloroform with respect to water [5].

The amount of physisorbed oligomer was quantified by TGA, considering the difference in residual mass loss between pristine and washed samples: it corresponds to almost 15-20% by weight, but such value could be affected by the CO_2 uptake.

The presence of oligomers adsorbed or grafted onto the surface of LDH is a key factor in the preparation of composites because it clearly improves the compatibilization with the matrix.

REFERENCES

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3. A Lindström AC Albertsson, M Hakkarainen. *Journal of Chromatography A*, 1022, (2004), 171–177.
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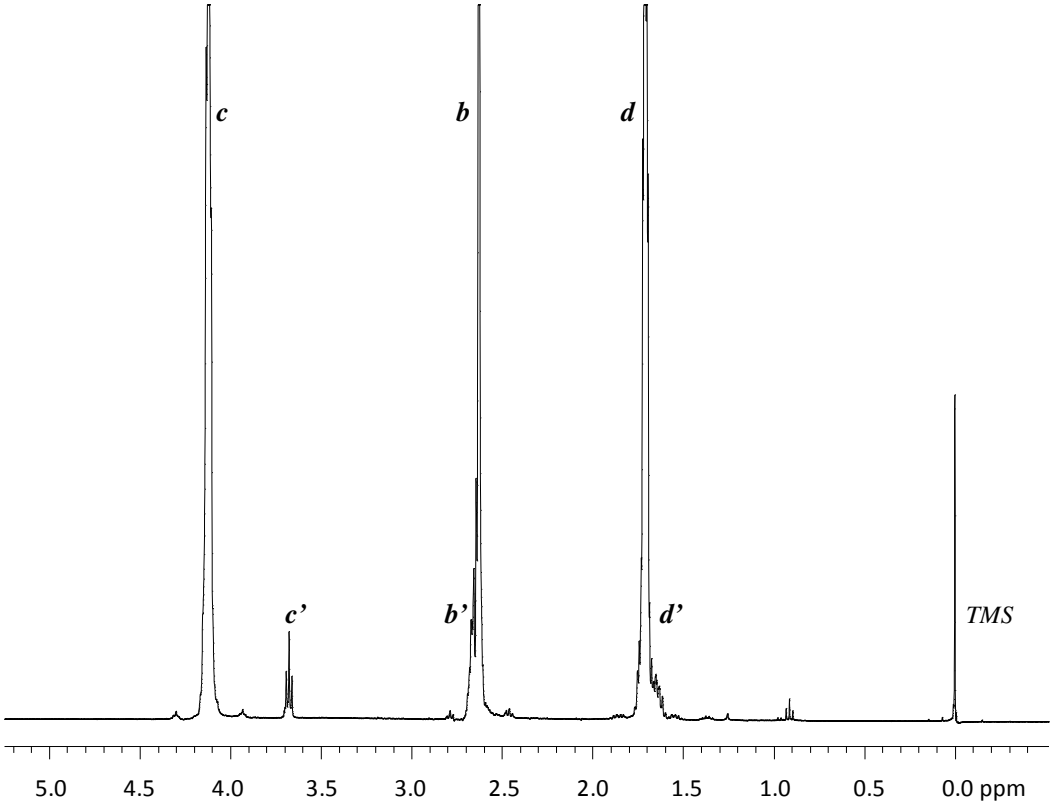
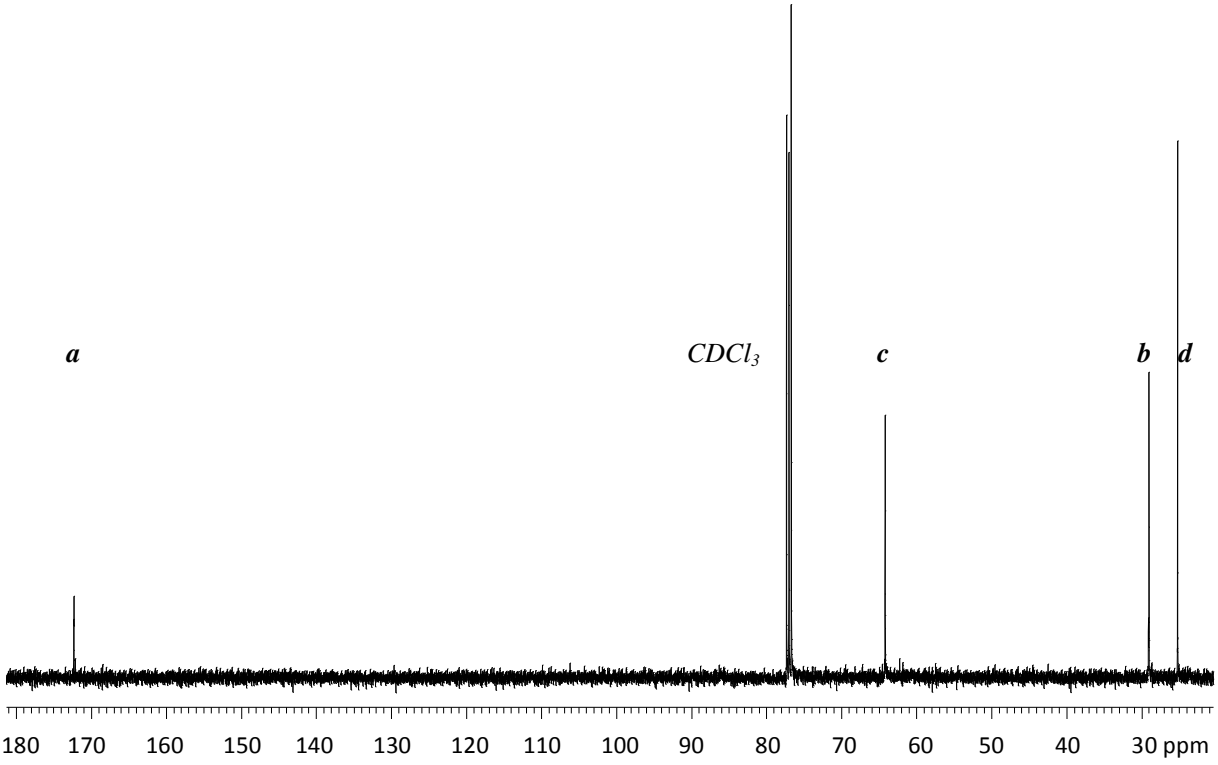


Figure S1. ^{1}H NMR of PBS oligomer (PBS_o).



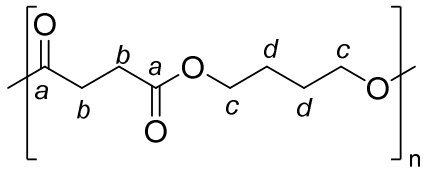


Figure S2. ^{13}C NMR of PBS oligomer (PBS_o).

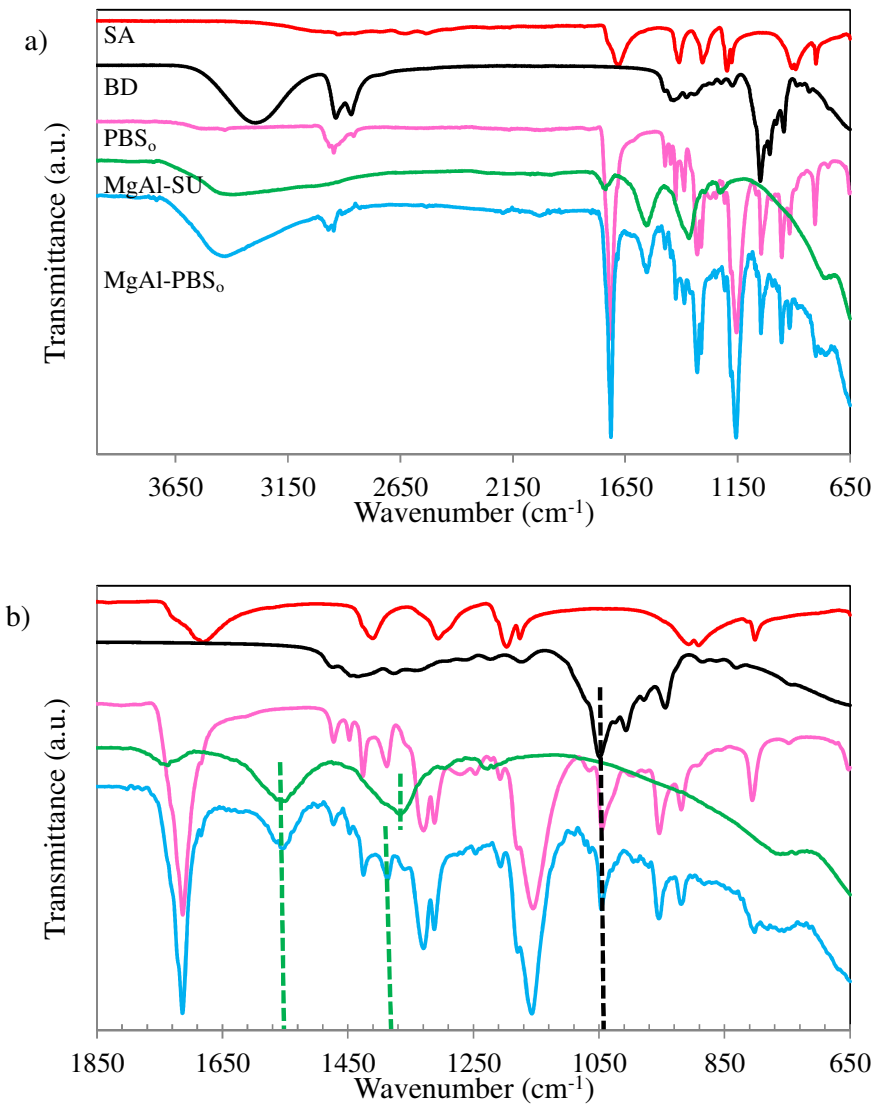


Figure S3. a) FTIR spectra of succinic acid (SA), 1,4 butanediol (BD), PBS oligomer (PBS_o), LDH with succinate anion (MgAl-SU) and LDH intercalated with PBS oligomer (MgAl-PBS_o); b) zoom region 1850-650 cm^{-1}.

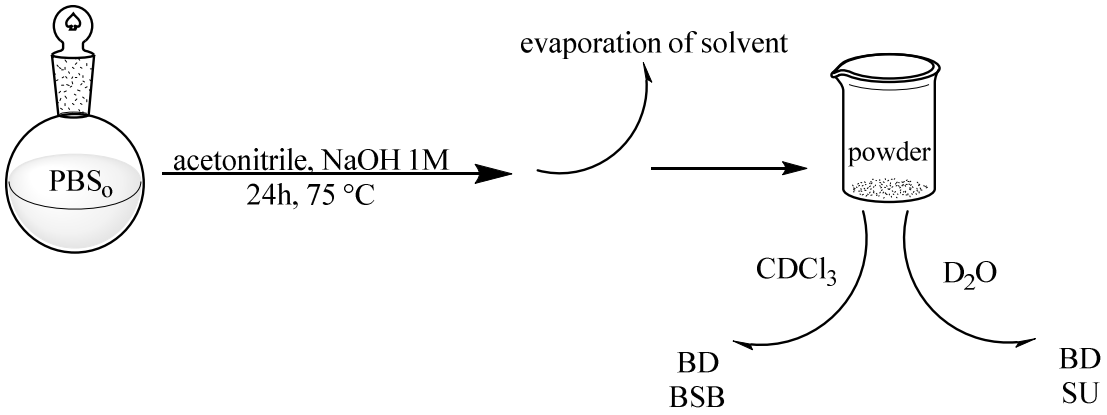


Figure S4. Schematic procedure for the ageing of PBS oligomer in an aqueous basic medium (24 h at 75 °C in acetonitrile and NaOH 1M) and substances identified by ^{1}H NMR

Table S1. Solubility of monomers, PBS_o, and the product from ageing of PBS_o in aqueous basic medium (I = insoluble, S = soluble, pS = partially soluble)

Substance	**$CHCl_3$**	**H_2O**
SA (Succinic Acid)	I	S
SU (Sodium Succinate)	I	S
BD (1,4-Butanediol)	S	S
PBS_o (PBS oligomer)	S	I
Product from ageing of PBS_o	pS	pS

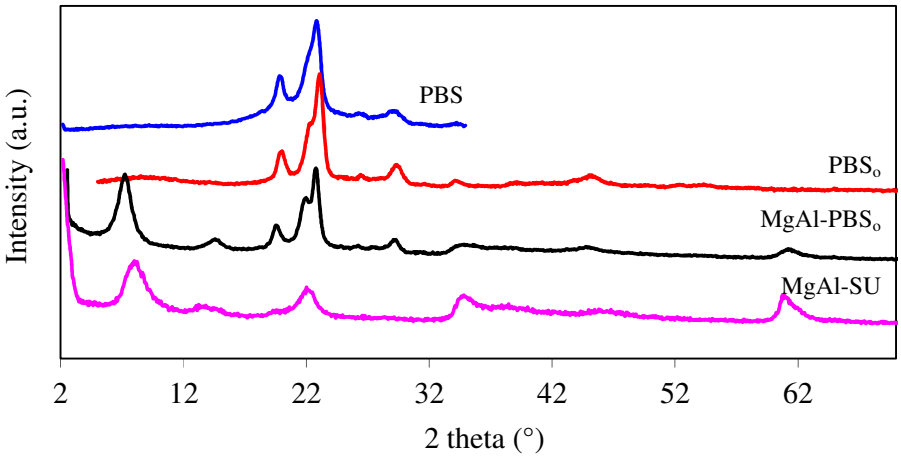


Figure S5. XRD spectra of PBS, PBS oligomer (PBS$_o$), LDH with PBS oligomer (MgAl-PBS$_o$), and LDH with succinate anion (MgAl-SU)

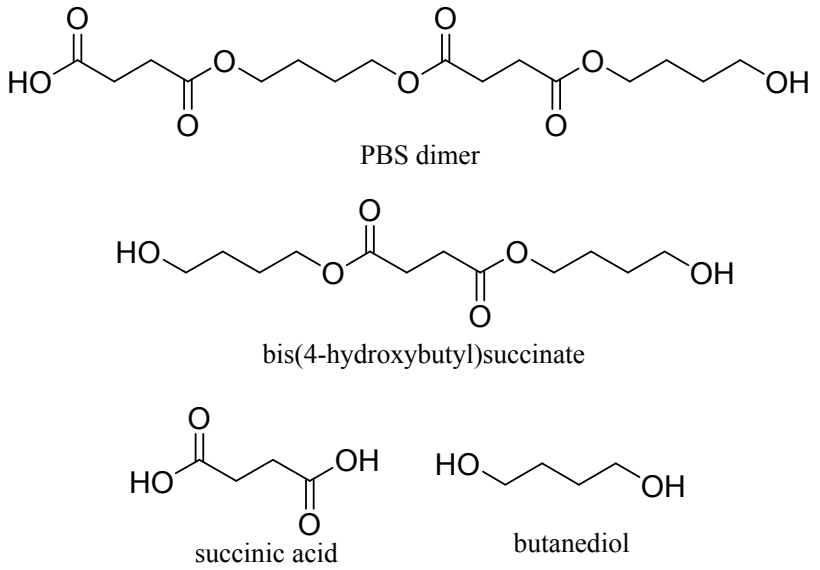


Figure S6. Molecular structures of the possible species simultaneously present in the nanofiller system: dimer of PBS (as example of oligomeric chains), succinic acid, bis(4-hydroxybutyl)succinate (BSB) and butanediol.

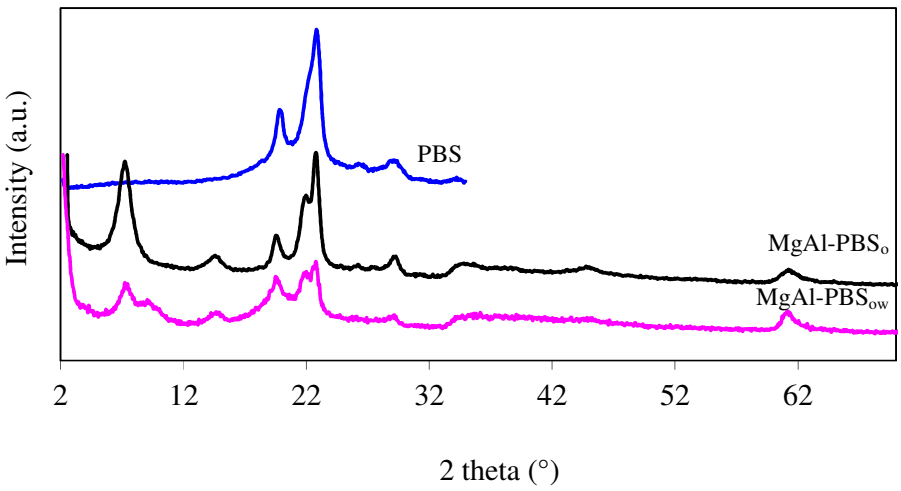


Figure S7. XRD spectra of PBS, LDH with PBS oligomer (MgAl-PBS$_o$) and LDH with PBS oligomer washed in $CHCl_3$ (MgAl-PBS$_{ow}$).