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R. Scaffaro, L. Botta, E. Passaglia, W. Oberhauser, M. Frediani, L. Di Landro
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Comparison of different processing methods to prepare poly(lactid acid)–hydrotalcite composites

R. Scaffaro, L. Botta, E. Passaglia, W. Oberhauser, M. Frediani, L. Di Landro

Abstract

The effect of the compounding method on the morphology and on the properties of poly(lactic acid) (PLA)–hydrotalcite (HT) composites was studied. Moreover, the influence of two different kinds of HT—organically modified (OM-HT) and unmodified (U-HT)—and their concentration was evaluated. The composites were prepared using either a single screw extruder (SSE), a counter rotating twin-screw compounder (TSC) or a corotating twin-screw extruder (TSE). The prepared materials were characterized by scanning electron microscopy, gel permeation chromatography (GPC) analysis, mechanical and rheological measurements. The results indicated that the best morphology, i.e., particles dimension and distribution, is exhibited by materials prepared by TSE while the worse ones by the samples processed by SSE. The viscosity of all the materials containing the HT is lower in comparison with the viscosity exhibited by the neat matrix, in particular, when the OM-HT is used. These results were correlated to degradation phenomena occurring during the processing of the materials as revealed by the results of GPC analysis. The addition of HT caused only a slight increase of elastic modulus of filled materials even when 5% of filler was incorporated. However, in full agreement with morphological analyses, the best performances were exhibited by materials prepared by TSE while the worse ones by the samples processed by SSE.

INTRODUCTION

Over the past decades there has been a growing interest toward polymeric materials obtained by renewable sources and with potential biodegradability or compostability to reduce the overall environmental impact **1**-**5**. In this view, the request of performing materials to satisfy the market pushed both industry and academia in investigating new candidate polymers adequate for different applications. In this context, poly(lactic acid) (PLA) is one of the most interesting materials as its chemical-physical properties allow the substitution of conventional petrochemical based polymers in several common applications including the food packaging **6**-**11**. On the other hand, a more diffused use of PLA is limited by the need to improve some functional properties such as mechanical and gas/vapour barrier. The addition of small amounts of lamellar particles or nanoparticles to a polymer can remarkably improve the mechanical properties of the matrix and enhance the barrier properties **2**, **12**-**17**. However, the characteristics of these multiphase systems certainly depend on the nature of the components but also on the final morphology achieved in the materials. Controlling the dispersion and the dimension of the particles is, therefore, a critical factor for the success in practical applications.

Among inorganic materials, recently, attention has been turned to layer double hydroxides, also known as hydrotalcites (HT), as inorganic filler **13**, **18**-**20**. The structure of these materials consists of positively charged brucite-like infinite layers, where trivalent cations replace a fraction of the bivalent cations in octahedral coordination. The positive charge of the layers is balanced by the intercalated hydrated anions. The HT interlayer anions are highly tuneable and a wide variety of organo-HT can be prepared, also bearing specific functionalities **21**, **22**.

Aim of this work was to evaluate the effect of the compounding method, namely a single screw extruder (SSE), a counter-rotating twin-screw compounder (TSC) and a co-rotating modular extruder on the morphology and on the properties of PLA–HT composites. Moreover the influence of two different kinds of HT—organically modified and not modified—and their concentration was evaluated. The prepared materials were characterized by scanning electron microscopy (SEM), gel permeation chromatography (GPC) analysis, mechanical, and rheological measurements, paying particular attention on the effects of the degradation phenomena of PLA on the composite properties.

EXPERIMENTAL

Materials and Preparation

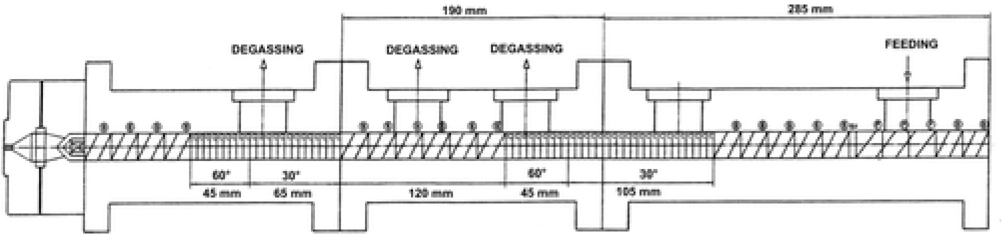
The polymer matrix adopted to prepare the composites is a sample of PLA (PLA 2002D, Natureworks, melt flow index (210°C/2.16 kg) = 6 g/10 min, melting temperature = 151°C).

Two commercial samples of HT have been used as filler. The first is an unmodified hydrotalcite (U-HT) (Perkalite LD, Akzo Nobel), the second is organically modified with hydrogenated fat acids (OM-HT) (Perkalite F100S, Azko Nobel, modifier content = 55 wt%). In our previous work, the OM-HT was characterized by FT-IR and TGA analyses and briefly, it was shown that it is most likely modified with stearate and palmitate anions and the amount of adsorbed/free surfactant molecules is low (roughly around 3 wt%) **18**. The use of both HT samples for manufacturing of plastic material intended to come into contact with foodstuffs is approved by the EU.

To protect the polymeric matrix by possible hydrolytic scission during processing, both the PLA and the HT samples were dried overnight under vacuum at 110°C.

The composites (containing 1, 2, and 5 wt% of filler) have been prepared adopting three different processing equipments: modular co-rotating twin-screw extruder (TSE), counter-rotating TSC and SSE. In all three extruders, the materials were prepared by premixing them in the solid state and then feeding them all together into the extruder.

The thermal profile of the TSE (OMC Italy, $D = 19$, $L/D = 35$) was set to 180–190-190–200-200-200-190°C while the rotational speed was 180 rpm. Under these conditions, the residence time, measured by feeding a colour tracer to the extruder, was about 60 s. The molten material coming out the die of the extruder was cooled on line in a water bath, pelletized and then used for further characterization. A schematic of the TSE is shown in Scheme 1. The screws are modular with segments of simple transport alternated with mastication sections having the elements of mastication o inclined by 30° or 60°.



Scheme 1

Schematic of the modular co-rotating twin-screw extruder used in this work.

The thermal profile of the counter-rotating TSC (Brabender, $D = 42$ mm, $L/D = 7$, depth of thread = 6.5 mm, pitch = 10 mm) was set to 180–190-200-190°C while the rotational speed was 64 rpm. Under these conditions, the residence time, measured by feeding a colour tracer to the extruder, was about 100 s. The molten material coming out the die of the extruder was cooled in air and afterwards pelletized to be used for further characterization.

The thermal profile of the SSE (Brabender, $D = 19$ mm, L/$D = 25$, equipped with ribbon die) was set to 180–190-200-190°C while the rotational speed was 90 rpm. Under these conditions, the residence time, measured by feeding a colour tracer to the extruder, was about 90 s. The molten material coming out the die of the extruder was cooled in air and afterwards pelletized to be used for further characterization.

For comparison, the pure PLA matrix was processed in all the three equipments under the same conditions.

Characterizations

The morphology of the materials was studied by using a scanning electron microscope (SEM) FEI Quanta ESEM. The samples were obtained by cryogenic fracture of the extruded materials under liquid nitrogen and then sputter coated with a thin layer of gold to avoid electrostatic charging under the electron beam.

The rheological characterization in dynamic mode was carried out by using a parallel plate rheometer (SR5, Rheometrics) at the temperature of 200°C on samples obtained by compression moulding ($T = 200$°C, $P = 100$ bar, $t = 3$ min) using a Carver laboratory press.

Tensile tests were carried out using an Instron 3365 dynamometer on specimens cut off from compression moulded sheets prepare as above indicated. The crosshead speed was 50 mm/min, kept constant for the whole duration of the test.

GPC analysis was carried out using a Waters instrument equipped with pumps model Binary HPLC 1525, refraction index Optilab® T-rEX Refractive Index Detector (refractometer with EXtended range) and three columns Shodex KF ($L = 300$ mm, $D = 8$ mm). The analysis have been carried out at 30°C using chloroform as eluting solvent, a flow speed of 1.0 mL/min and a polystyrene standard for the calibration line.

RESULTS AND DISCUSSION

SEM analysis, Fig. **1**, showed that the best morphology, i.e., particles dimension and distribution, is exhibited by materials prepared with the corotating twin-screw extruder if compared with the corresponding materials prepared with the other two extruders. In particular, the filler is well dispersed and the dimensions of HT aggregates are smaller than the dimensions of the aggregates visible in the materials prepared with TSC and SSE.

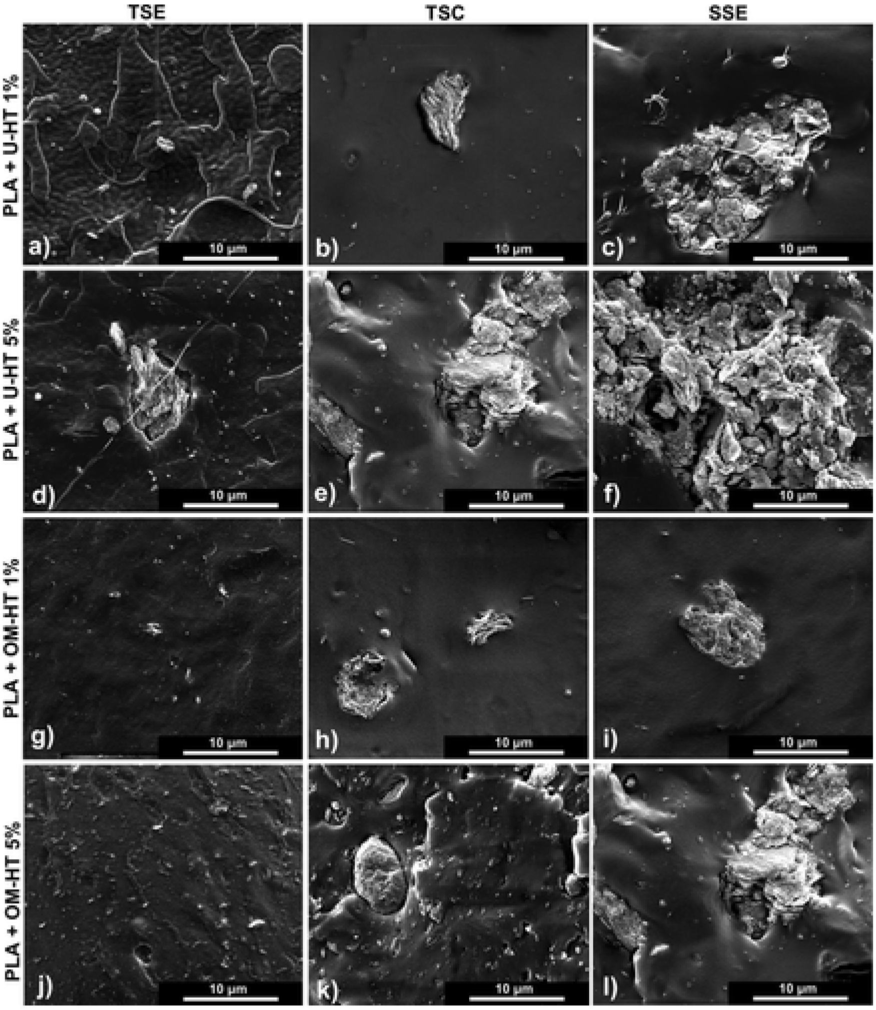


Figure 1
SEM micrographs of PLA + U-HT 1%; PLA + U-HT 5%; PLA + OM-HT 1%; PLA + OM-HT 1% processed by TSE, TSC, and SSE.

On the contrary, the samples processed with the SSE showed the worse morphology as large aggregates of HT are well visible even to the naked eye.

The composites prepared with TSC exhibited an intermediate morphology. In particular, the micrographs showed the contemporary presence of large aggregate and small particles.

In all the cases, when the concentration of HT increases, the morphology becomes coarser, i.e., the HT aggregates are larger and their dispersion worse. However, the materials containing the organic modified filler show a better morphology in comparison with the samples incorporating the unmodified HT for all the compounding methods, i.e., the HT is best dispersed and the dimensions of the aggregates are smaller. Nevertheless, a suboptimal morphology has been obtained also in this case probably because of the inadequate organic modification.

The rheological tests, Figs. 2-4, revealed that, for all three kind of processing, the viscosity of all the materials containing the HT is lower than the viscosity exhibited by the pure matrix processed with the same apparatus in the whole range of investigated frequencies. In particular, the viscosity decreases progressively by increasing the content of incorporated HT. This result, apparently surprising, was reported in the scientific literature for similar systems **23**. This decrease of the viscosity can be probably explained considering that relevant degradation phenomena of the matrix occurred during processing. As reported in the scientific literature, three suppositions of degradation of PLA should be possible: radical degradation, hydrolysis and/or transesterification with residual catalysts **24**.

The decrease of the viscosity is more intense in the case of materials incorporating the modified HT since probably the degradation phenomena involve also the organic modifier. In particular, it can be hypothesized that the degradation products of HT modifier accelerates the degradation of the PLA matrix, thus causing a further decrease of the melt viscosity. Indeed, on increasing the HT concentration, there is an increase of the total organic modifier amount that can undergo degradation. This can explain the further decrease of viscosity observed when the concentration of modified HT increases.

However, even if all the viscosity curves of the filled materials are lower than that of the neat PLA, it is worth noting that the pure matrix shows an almost Newtonian behaviour in the whole frequency range here investigated, while the filled materials exhibit a non-Newtonian behavior at the lowest frequencies. This behavior is more evident for the composites with the higher amount of filler. This different rheological behavior can be probably explained assuming that three-dimensional structures are present in the material and revealed at lowest frequencies. These structures are due to the matrix–filler interactions and exert a resistance to the flow which finds its macroscopic outcome in the appearance of a yield stress. When the shear rate increases, however, the three-dimensional structures are disrupted and the filled materials behave basically as a suspension of solid particles in a melt phase **25**-**27**. These assumptions were corroborated by the analysis of storage e loss moduli, here reported for sake of conciseness only for PLA and PLA + U-HT 5% processed with TSE (Fig. 5). Indeed, although both PLA and PLA + U-HT 5% show loss moduli higher than of the respective storage moduli, indicating a liquid-like behavior, it is worth noting that the slope of G' of PLA + U-HT

5% in the low frequency region is smaller than that of neat PLA suggesting an interaction between the HT particles and their tendency to form a three-dimensional structure **28**, **29**. The composites with lower filler content (i.e., 1% and 2%) and those processed with the other extruders (i.e., TSC and SSE), even if less accentuated, show a similar trend.

Comparing the viscosity curves of the materials prepared with the three different extruders, Figs. 2-4, it is evident that the decrease of the viscosity of the filled materials with respect to that of neat PLA is more relevant when TSE processing is adopted (Fig. 2). These results can be explained considering that the better dispersion of the filler achieved with this extruder lead to a larger contact surface between the filler and the polymer thus promoting a more intense degradation. Moreover, it is worth noting that also neat PLA samples processed with the three different extruders show different values of viscosity. In particular, the PLA processed with TSE shows the highest viscosity, while the PLA processed with TSC the lowest one. This result can be reasonably attributed to two concurrent effects: different residence times and different shear stresses generated during the extrusion. Indeed, as reported in the experimental part, the average residence time of extrusion in TSE is the lowest, i.e., 60 s while the average residence time of extrusion in TSC is the highest one, i.e., 100 s. Moreover, the materials extruded by TSE are immediately cooled in a water bath while the materials extruded by TSC and SSE are cooled in air. Nevertheless, even if the residence time of extrusion in SSE (90 s) is close to TSC, the shear stress applied by a counter-rotating extruder is certainly greater of that of the SSE. These considerations can explain why the neat PLA processed with TSE, unlike the composites, showed a higher viscosity.

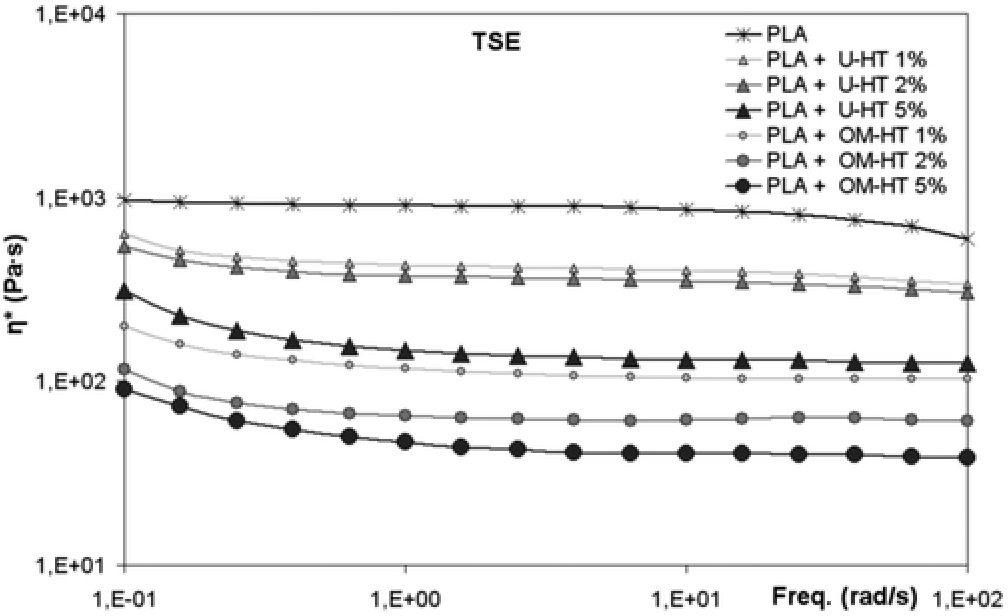


Figure 2

Complex viscosity as a function of frequency of all the materials processed by TSE.

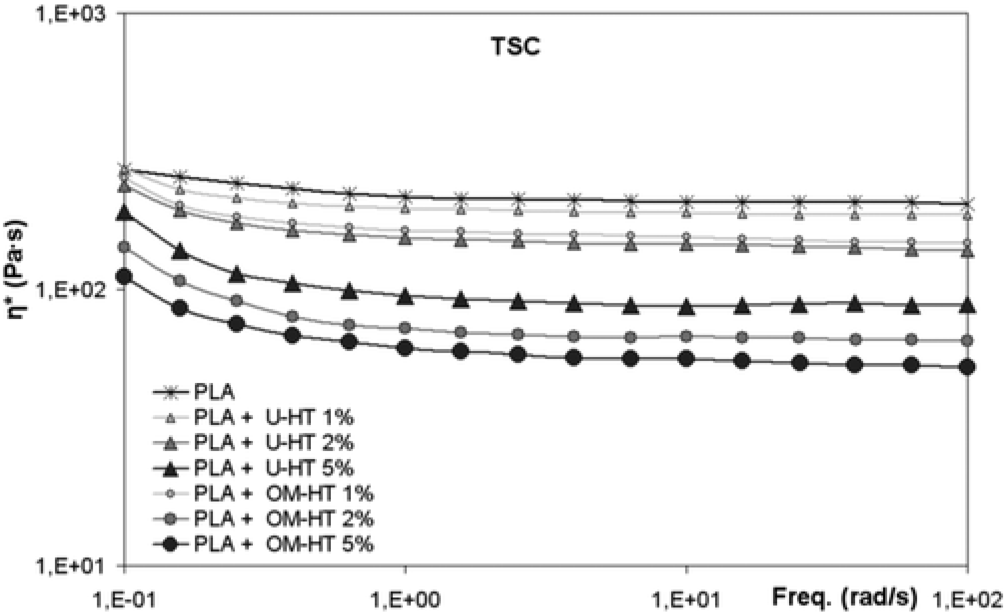


Figure 3

Complex viscosity as a function of frequency of all the materials processed by TSC.

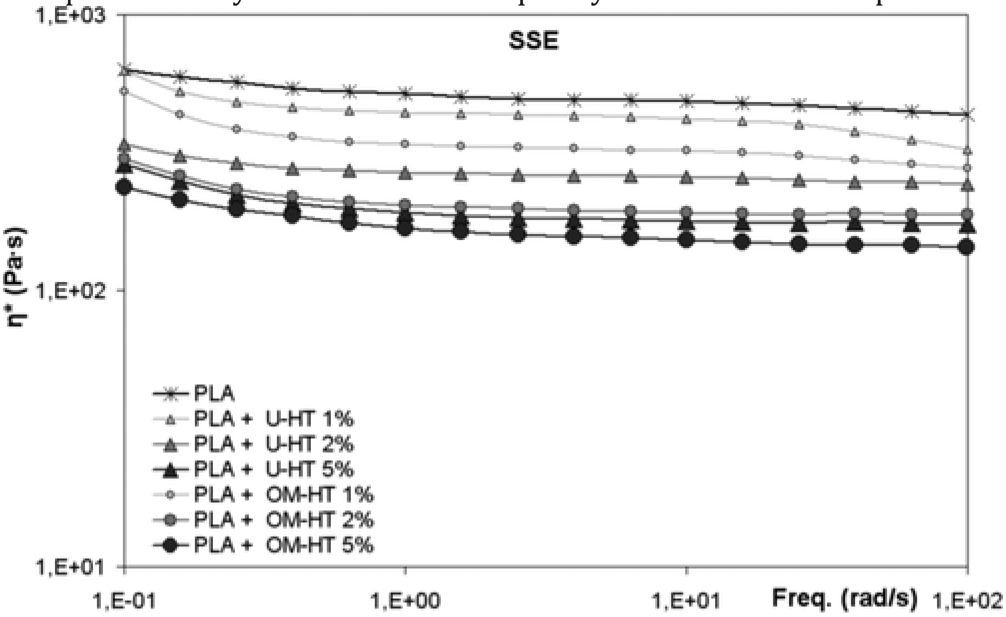


Figure 4

Complex viscosity as a function of frequency of all the materials processed by SSE.

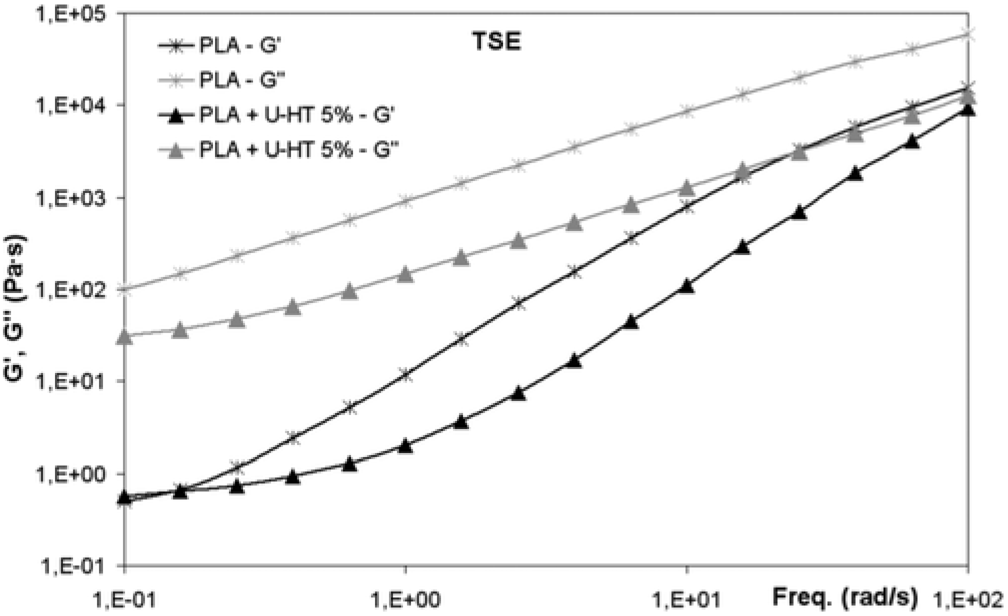


Figure 5
Storage and loss moduli of PLA and PLA + U-HT 5% processed by TSE.

To confirm the hypothesis of significant degradation phenomena of the matrix occurring during processing, measurements of the molecular weights by GPC analysis were performed (Table **1**).

Table 1. Values of M_n, M_w, and PDI of all the materials prepared by TSE and of neat PLA and PLA containing 5% of OM-HT prepared by TSC and SSE

Sample	M_n (g/mol)	M_w (g/mol)	PDI
Virgin PLA	113,300	181,600	1.60
PLA (TSE)	81,000	168,400	2.08
PLA (TSC)	59,403	116,700	1.96
PLA (SSE)	69,080	132,200	1.91
PLA + U-HT 1% (TSE)	77,550	1,61,800	2.09
PLA + U-HT 2% (TSE)	66,660	147,800	2.22

Sample	M_n (g/mol)	M_w (g/mol)	PDI
PLA + U-HT 5% (TSE)	56,610	109,400	1.93
PLA + OM-HT 1% (TSE)	52,340	110,400	2.11
PLA + OM-HT 2% (TSE)	43,120	82,440	1.91
PLA + OM-HT 5% (TSE)	31,850	80,040	2.51
PLA + OM-HT 5% (TSC)	41,970	84,070	2.00
PLA + OM-HT 5% (SSE)	64,430	130,700	2.03

In Table 1, the values of M_n, M_w, and PDI of all the materials prepared by TSE and of neat PLA and PLA containing 5% of OM-HT prepared by TSC and SSE are reported. The results show that the molecular weight of PLA incorporating HT decreases and this reduction is more intense on increasing the amount of HT incorporated. The reduction is even more marked when OM-HT is used. These results confirm that the presence of HT causes the degradation of the PLA matrix and that the organic modifier further promotes the PLA depolymerization.

Comparing the materials prepared with the three different extruders it is evident that the decrease of the molecular weight of the filled materials with respect to the neat PLA is more relevant in the case of samples processed by TSE. As reported about the rheological characterization, these results are probably due to the better dispersion of the filler achieved with this extruder that lead to a larger contact surface between the filler and the polymer thus promoting the degradation of the matrix. All these findings are therefore according with the rheological results.

Moreover, the molecular weight values of the neat PLA processed with the three different extruders corroborate the assumption that the cause of the different viscosity curves of the PLA is to be ascribed to different degradation intensity of the polymer during the extrusion. Indeed, the PLA processed with TSE exhibits the highest molecular weight, while the PLA processed with TSC the lowest one. As observed in the rheological analysis, this result can be reasonably attributed to the different residence times and shear stresses applied during the extrusion. Actually, the effect of the extrusion equipment is different for neat PLA in comparison with the composites. Indeed, neat PLA processed with TSE shows the highest values both of M_n and M_w in comparison with those exhibited by PLA processed with the other two extruders. On the contrary, the PLA + OM-HT 5% extruded with TSE exhibits the lowest molecular weight if compared with the respective composites prepared with TSC and SSE. Probably, the effect due to the higher mixing intensity in TSE is counterbalanced by its lowest residence time in the case of PLA, but in the case of composites the higher mixing efficacy yields a better dispersion of the filler that further promotes the degradation phenomena.

As regards the mechanical properties, the addition of HT caused only a slight increase of the elastic modulus (E) of filled materials even when the 5% of filler was incorporated, Fig. 6a. The tensile strength (TS) of the filled materials, Fig. 6b, decreased if compared with neat PLA, particularly for the composites with 5% of HT. The elongation at break (EB), Fig. 6c, slightly decreased on increasing the HT amount. Moreover, the composites incorporating the unmodified HT showed, for all the three methods of extrusion, better mechanical properties than those observed for the materials filled with the modified HT. In order to explain these results, it must be considered that there are two phenomena that influence the mechanical behavior of the filled materials: from one hand the dispersion of the HT, from the other the degradation of the matrix. The former is improved by the presence of the organic modifier, as demonstrated by SEM micrographs, but at the same time the degradation products of OM-HT causes a more intense degradation of the PLA matrix as revealed by the measurements of the molecular weights. Nevertheless, it is worth noting that a suboptimal morphology has been obtained in all the cases probably because of the inadequate organic modification.

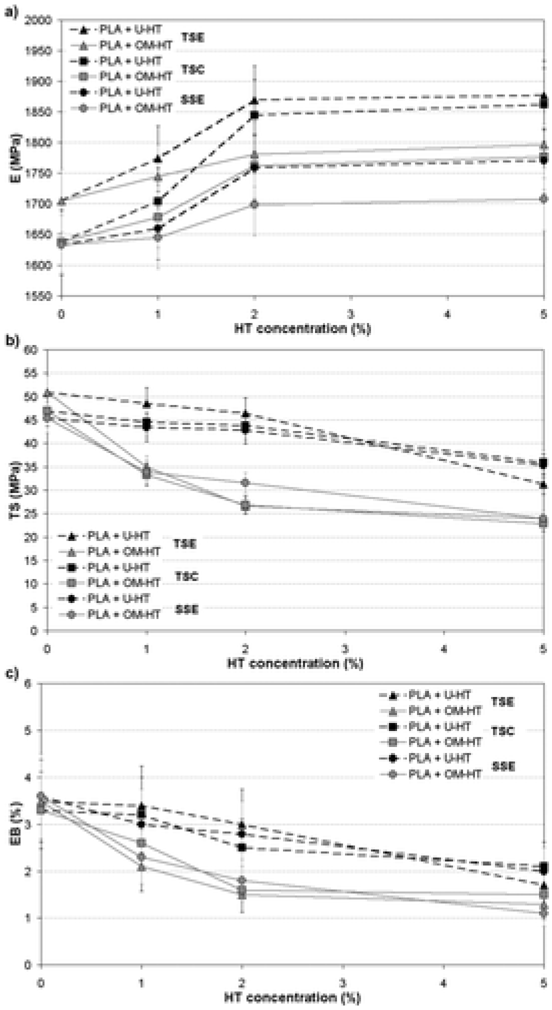


Figure 6

Elastic modulus (*E*), tensile strength (TS), and elongation at break (EB) of all the materials prepared in this work.

Moreover, it is worth noting that, even if the two HTs were added at the same concentration, the composites incorporating the OM-HT contain less inorganic fraction with respect to the materials incorporating the U-HT. Indeed, as reported by technical data of the supplier, the inorganic fraction of OM-HT used in this work, is only the 45% in weight **18**.

However, by comparing the three compounding methods, in full agreement with the results of the other characterizations, the best mechanical performances were exhibited by materials prepared by TSE while the worse ones by those processed with SSE.

CONCLUSIONS

The compounding method, the kind of HT used and its amount clearly influence the morphology and consequently the properties of PLA–HT composites prepared using either a corotating twin-screw extruder (TSE), a counter rotating TSC and SSE. The best morphology, i.e., particles dimension and distribution, is exhibited by materials prepared by TSE while the worse one by the samples processed by SSE. The increase of the HT concentration leads to a worsening of the morphology. However, the materials containing the organic modified filler showed a finer morphology, i.e., the HT is best dispersed and the dimensions of the aggregates are smaller. Nevertheless, a suboptimal morphology has been obtained also in this case probably because of the inadequate organic modification.

The viscosity of all the material containing the HT is lower in comparison with the viscosity exhibited by the neat matrix in particular when modified HT is used. This is due to degradation phenomena occurring during the processing of the materials as revealed by the results of GPC analysis.

As regards the mechanical properties, the addition of HT caused only a slight increase of the elastic modulus of filled materials even when 5% of filler was incorporated. The tensile strength and the elongation at break of the filled materials decreased if compared with the neat PLA. Probably, the improvements that should be related to dispersion of the filler in the systems are counterbalanced by the degradation of the matrix.

ABBREVIATIONS

GPC	Gel permeation chromatography
HT	Hydrotalcite
OM	Organically modified
PLA	Poly(lactic acid)
SEM	Scanning electron microscopy
SSE	Single screw extruder
TSC	Twin-screw compounder
TSE	Twin-screw extruder

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