Peer-reviewed version available at *Materials* **2018**, *11*, 2527; doi:10.3390/ma11122527

Article

Optimization of Thermoplastic Blend Matrix HDPE/PLA with Different Nature and Level of Coupling Agent

Alessia Quitadamo [1,2], Valérie Massardier [2], Carlo Santulli [3] and Marco Valente [1,*]

[1] Università di Roma La Sapienza, Dept. of Chemical and Material Engineering, via Eudossiana 18, 00184 Rome; alessia.quitadamo@uniroma1.it
[2] Université de Lyon 69003, INSA de Lyon, Ingénierie des Matériaux Polymères CNRS UMR 5223,69621 Villeurbanne, France; valerie.massardier@insa-lyon.fr
[3] Università di Camerino, School of Architecture and Design, Viale della Rimembranza, 63100 Ascoli Piceno, Italy; carlo.santulli@unicam.it
* Correspondence: marco.valente@uniroma1.it; Tel.: +39-06-44585582

Abstract: High density polyethylene (HDPE) and poly(lactic) acid (PLA) blends with different ratios of both polymers, namely 30:70, 50:50 and 70:30, were produced. Polyethylene grafted maleic anhydride and a random copolymer of ethylene and glycidyl methacrylate, were also proposed as compatibilizers to modify HDPE-PLA optimal blends and were added in the amounts of 1, 3 and 5 wt.%. Blends properties have been evaluated through different aspects by performing tensile tests, scanning electron microscopy to analyze blend morphology and interfaces, and thermomechanical analysis through differential scanning calorimetry, thermo-gravimetric analyses and infrared spectroscopy. The second blend, the one with equal amounts of HDPE and PLA seems to represent a good balance between high amount of bio-derived charge and acceptable mechanical properties. This suggests a good potential of these blends, which would be a good starting point for the production of composites with lingo-cellulosic fillers.

Keywords: Blend; Bio-derived polymers; Compatibilization; Thermoplastic matrix for composite

1. Introduction

Blending is one of the simplest and widespread methods to improve polymer properties. In fact, low cost processing, typical of common blend manufacturing, allows obtaining desired properties and high variability of products [1]. As a consequence, nowadays polymer blends represent around half of total plastic production [2]. The main limit of polymer blend is the mutual miscibility of polymers. In fact, as established with the second law of thermodynamics, the variation of free energy ΔG is usually positive, because of the high polymerization degree of polymers (affecting the variation of entropy ΔS) and the poor affinity between polymers (affecting the variation of enthalpy ΔH) [3].

One of the main parameters affecting polymers miscibility is interfacial tension, in particular higher interfacial tension leads to higher phase separation [4]. In spite of this limit, polymer blend can be compatibilized in order to increase dispersion and adhesion between polymers [5]. Many strategies developed in this context, among which the introduction of a compatibilizer is one of the most adopted [6]. Recently, higher sensitivity to problems of oil-based polymer pollution develops, stimulating research to bio-derived polymer production for application as potential substitute of oil-based polymers [7-10]. Among bio-derived polymers, poly(lactic) acid (PLA) seems to be one of the most studied and applied thanks to its properties comparable or in some cases higher than traditional polyolefins [11-14]. PLA, in fact, has been frequently selected as bio-derived polymer to obtain blend with high amount of biodegradable polymer, reducing the amount of polyolefin. Moreover, depending on the compatibilizer added, oil-based/bio-derived blend can be optimized and has

Peer-reviewed version available at *Materials* **2018**, *11*, 2527; doi:10.3390/ma11122527

specific properties. For example, a recent study compatibilized PLA-HDPE polymer blends with cobalt stearate in view of a possible oxo-degradation process: this demonstrates the wide range of opportunities attributed to the addition of the right type and amount of compatibilizer [15]. Several compatibilizing methods have been studied in order to improve oil-based/bio-derived polymeric blends, such as the use of functional molecules for reactive compatibilization during extrusion or the addition of a commercial modified polymer as coupling agents [16-18].

The development of an oil-based/bio-derived thermoplastic blend is therefore the preliminary requirement of this work. In particular, an optimized high density polyethylene and poly(lactic) acid blend could be produced in order to obtain oil-based/bio-derived thermoplastic blends with high amount of bio-derived charge, keeping good mechanical properties.

Two kinds of compatibilizers have been tested in order to improve blend properties. Polybond 3029 and Lotader AX8840 seem to be effective thanks to the presence of maleic anhydride grafted on polyethylene chains for the former and polyethylene random copolymer with glycidyl methacrylate for the latter.

2. Materials and Methods

Eraclene MP90, commercial name of high-density polyethylene (HDPE) from ENI (Versalis), has been selected as oil-based polymer. Among its properties are: a melt flow index (MFI) of 7 g/10 min (190°C/2.16kg), a nominal mass of 0.96 g/cm^3, a tensile strength of 21 MPa, a tensile modulus of 1.2 GPa, a Shore D hardness of 50. Poly(lactic acid) (PLA) Ingeo Biopolymer 3251D from Nature Works was selected as bio-derived thermoplastic polymer, with a MFI of 35 g/10min (190°C/2.16 kg). This polymer is characterized by density 1.24, crystalline melting temperature in the range 155-170 °C and a glass transition temperature in the range 55-60°C. Polybond 3029 has been selected as additive, suitable for cellulosic fillers. In fact, Polybond 3029 is a maleated polyethylene with a melt flow index of 4 g/10min (190°C/2.16 kg) and the MA content is 1.7 wt.% (high). Generally, it is sold as pellets of 3-4 mm diameter. Lotader AX8840 has been selected with the same purpose. It is a random copolymer of ethylene and glycidyl-methacrylate, with a melt flow index of 5 g/10min (190°C/2.16 kg). The GMA content is about 8 wt. %. PLA has been dried for one night at 80°C, in order to avoid possible bubble formation due to water evaporation during production process.

A Micro 15 Twin-screw DSM research extruder was used in order to produce samples. Temperature of 180°C, screw speed of 75 rpm, nitrogen atmosphere and a resident time of 4 min in the extruder have been selected to avoid PLA degradation during the process.

Injection moulding has been used to obtain dog-bone specimens, with a mould temperature of 55°C and pressure parameters depending on polymer viscosity. For each family of samples, ten specimens have been produced. Table 1 sums up the formulations produced.

Table 1: Formulations produced (10 samples for each family).

Samples	HDPE (%)	PLA (%)	Polybond 3029 (%)	Lotader AX8840 (%)
HDPE70-PLA30	70	30		
HDPE50-PLA50	50	50		
HDPE30-PLA70	30	70		
HDPE50-PLA50-Poly1	49.5	49.5	1	
HDPE50-PLA50-Poly3	48.5	48.5	3	
HDPE50-PLA50-Poly5	47.5	47.5	5	
HDPE50-PLA50-Lot1	49.5	49.5		1
HDPE50-PLA50-Lot3	48.5	48.5		3
HDPE50-PLA50-Lot5	47.5	47.5		5

Tensile tests

Tensile tests were performed in accordance with the ASTM D638 standard using Zwick/Roell Z010, load cell of 10 kN was used and a 50 N preload was applied. A crosshead speed of 5 mm/min has been used. The tensile tests were performed on five dog-bone samples per series with a gauge length section 30x4x2 mm3 (LxWxT). For each family, five samples have been tested.

Scanning Electron Microscopy (SEM)

Samples have been observed with Hitachi S2500 and 25 kV in order to analyse blend morphology and interfaces. Samples have been sputter-coated with gold particles before surfaces characterization.

Quartering

Samples produced, in the majority of cases, are characterized by some heterogeneity because of multiphase matrices. In order to obtain reliable results from thermal analysis, and analyse a representative amount of sample, a cryogenic mill was adopted to obtain samples in the form of powders. A subsequent statistical approach, quartering, was used to select an exemplary amount of samples used for chemical and thermal analysis. This method is based on the separation of the total amount of charge in four parts equal in weight. Then, two parts at the opposite side are mixed together and the other two are separated.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) tests were performed on a Q20 Thermal Analysis instrument from 25°C to 180°C at 10°C/min under a nitrogen flow of 50 mL min^{-1}. Two cycles were performed with a 4 minutes interval between them at 180°C to eliminate trace of thermal history. The first cycle provides information about properties after injection moulding, while the second one gives materials properties. Cold crystallization, melting and crystallization parameters (temperature and enthalpy) and glass transition temperatures were analysed.

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) tests were carried out on a Q500 Thermal Analysis instrument, up to 600°C with a scanning temperature of 10°C/min under a nitrogen flow of 50 mL min-1. From these analyses, we derived temperatures at which degradation started (Tonset), evaluated through the extrapolated onset temperature from TGA curve, and Δm, mass variation during the test.

Infrared Analysis Attenuated Total Reflection (ATR-FTIR)

Infrared Analysis Attenuated Total Reflection (ATR-FTIR) tests were carried out to evaluate interactions between HDPE, PLA and compatibilizers. The tests were performed with a thermo-scientific Nicolet IS10 spectrometer, with a spectral range 4000-400 cm-1 and 32 scans.

3. Results

3.1. Tensile tests

HDPE-PLA blends properties were first analyzed through tensile tests of HDPE70-HDPE30, HDPE50-PLA50 and HDPE30-PLA70 to evaluate mechanical performances and identify the influence on polymer blend. Table 2 sums up results of these three blends compared to neat HDPE and PLA while figure 1 displays tensile tests curves of HDPE-PLA blends.

Table 2: Tensile tests results of HDPE-PLA blends without compatibilizers.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 15 November 2018 doi:10.20944/preprints201811.0351.v1

Peer-reviewed version available at *Materials* **2018**, *11*, 2527; doi:10.3390/ma11122527

Samples	E (GPa)	σ (MPa)	ε (%)
HDPE	1.16±0.08	21.59±0.18	>400
PLA	3.04±0.02	57.34±1.00	7.1±0.3
HDPE70-PLA30	1.51±0.05	30.76±0.73	>400
HDPE50-PLA50	1.88±0.05	38.73±0.18	99.4±2.1
HDPE30-PLA70	2.41±0.05	49.51±0.60	2.3±0.5

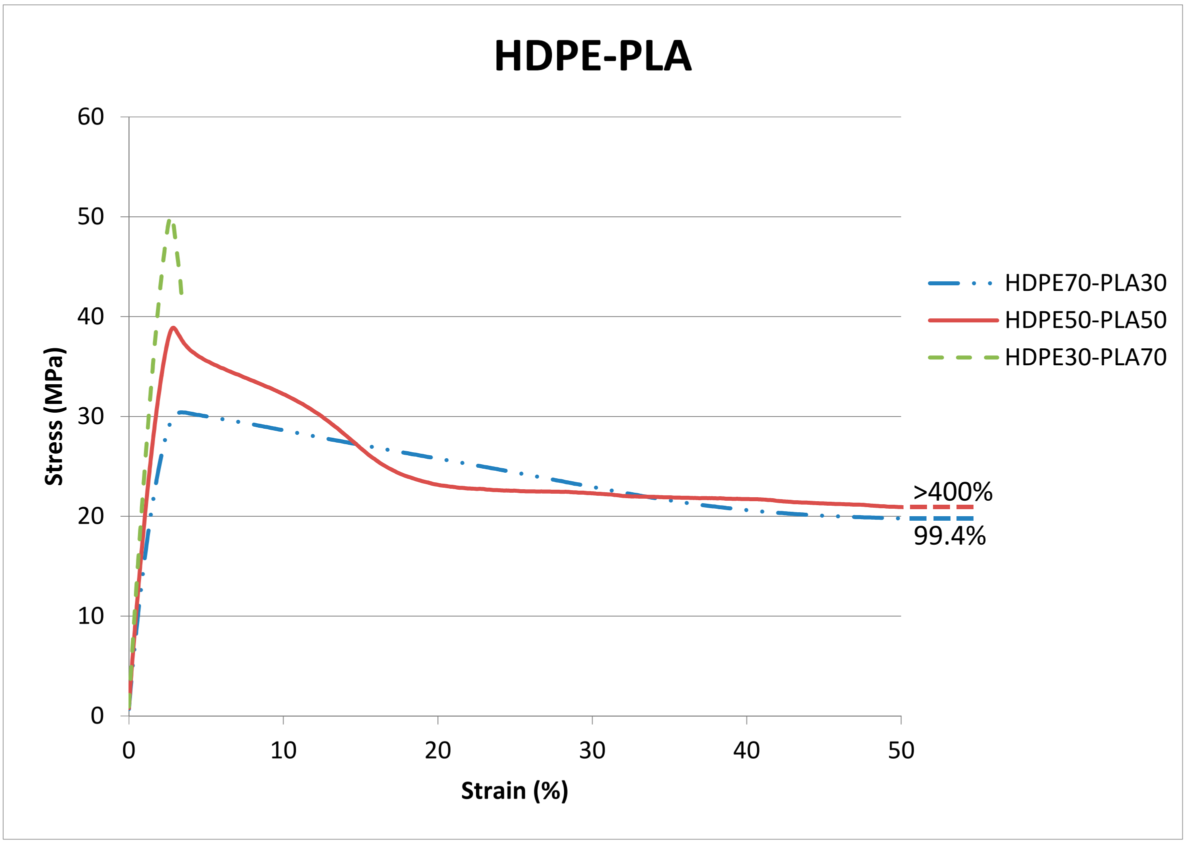

Figure 1:HDPE70-PLA30, HDPE50-PLA50 and HDPE30PLA70 tensile tests graphs.

The presence of 30 and 50 wt.% PLA allowed reaching a good tensile stiffness and strength, with respect to neat HDPE, while keeping at the same time an acceptable elongation at break: this is a significant result regarding the considerable amount of a brittle polymer (PLA) blended with HDPE. In contrast, increasing the amount of PLA up to 70 wt.% strongly reduced the elongation at break, at a level even lower than for neat PLA, while offering a tensile strength and stiffness near to neat PLA. Starting from these results, HDPE50-PLA50 was selected as a promising blend considering a compromise of mechanical properties and amount of bio-based material. As a consequence, analyses on blends with 50 wt.% PLA have been considered for deeper studies. The use of three different percentages of compatibilizers was investigated to elucidate their effects on HDPE50-PLA50 and to identify the most suitable compatibilizer and related amount. In particular, Lotader AX8840 and Polybond 3029 were investigated as compatibilizing agents in the amount of 1, 3 and 5 wt.%. Table 3 and figure 2 display main tensile tests results.

Table 3: Tensile tests results for HDPE-PLA blend with Lotader AX8840 and Polybond 3029 in different amount (1, 3, 5wt.%). Purple colour is for Polybond 3029 addition, while green one is for Lotader AX8840.

Peer-reviewed version available at Materials 2018, 11, 2527; doi:10.3390/ma11122527

Samples	E (GPa)	σ (MPa)	ε (%)
HDPE50-PLA50	1.88±0.05	38.73±0.18	99.4±2.1
HDPE50-PLA50-Poly1	2.24±0.76	43.30±2.76	86.2±17.3
HDPE50-PLA50-Poly3	2.31±0.14	42.80±2.65	71.9±46.9
HDPE50-PLA50-Poly5	1.92±0.03	39.74±0.41	34.1±13.1
HDPE50-PLA50-Lot1	2.18±0.21	40.70±3.99	175.3±84.2
HDPE50-PLA50-Lot3	2.14±0.07	41.70±1.93	193.0±59.1
HDPE50-PLA50-Lot5	1.75±0.13	34.28±1.52	173.2±56.2

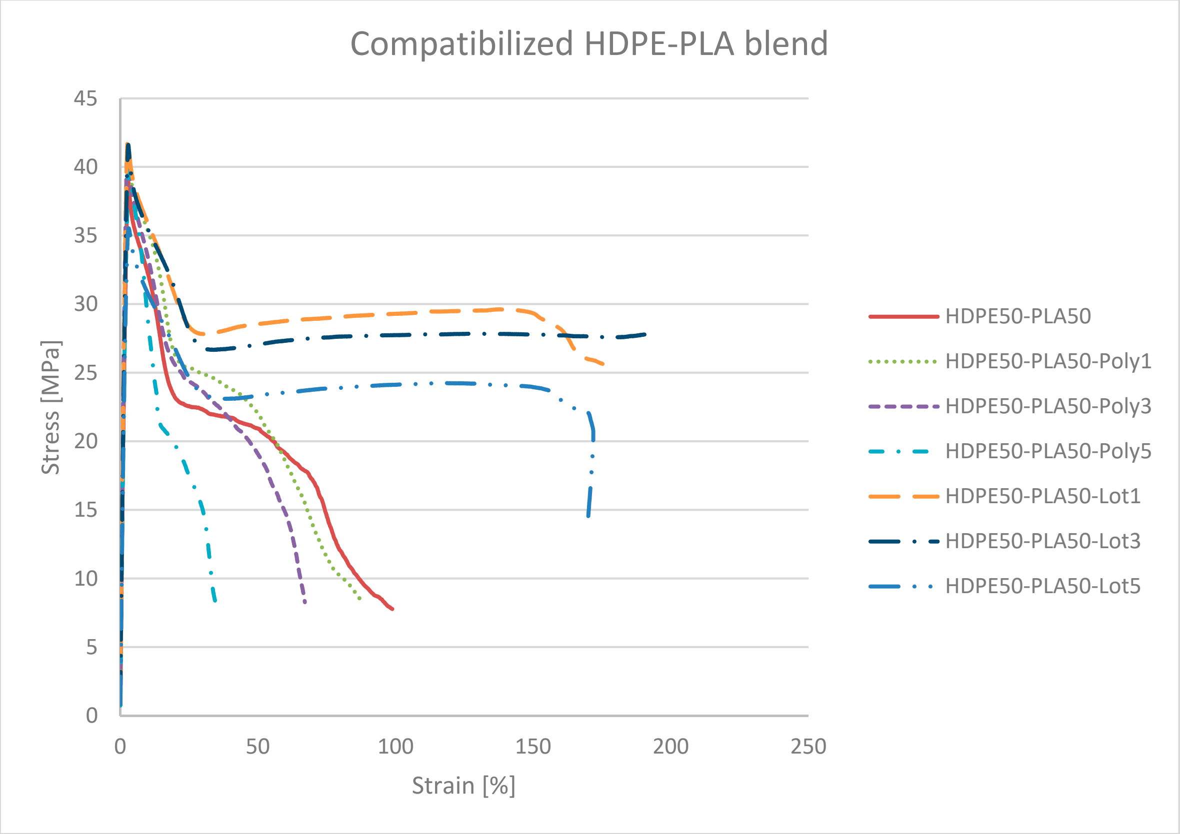

Figure 2: Effect of Lotader AX8840 and Polybond 3029 in 1-3-5 wt.% on PE50-PLA50 blend.

Lotader AX8840 and Polybond 3029 were selected because of their ability to interact with both polyethylene and polymers with polar groups such as poly(lactic)acid. The addition of Lotader AX8840 seems to be very effective to improve compatibility between HDPE and PLA. In fact, a significant improvement in elongation at break was displayed for all compatibilizer percentages. At the same time, slight reductions in elastic modulus and tensile strength have been displayed for the highest compatibilizer percentage. Moreover, Polybond 3029 similarly displays a reduction of σ and ε when 5wt.% is added. As a consequence, an optimal amount of Lotader AX8840 and Polybond 3029 need to be applied: in both cases, the best results were obtained for 3 wt. % of compatibilizer.

3.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analyses aimed at investigating both HDPE-PLA compatibility and the influence of compatibilizers on the blend. HDPE-PLA SEM images displays typical immiscible blend morphology between hydrophobic (polyethylene) and hydrophilic (poly (lactic) acid) (figure 3). In fact, a visible phase separation of HDPE and PLA was displayed: as expected for polymer with different hydrophilicity, a weak interface between HDPE and PLA is

Peer-reviewed version available at *Materials* **2018**, *11*, 2527; doi:10.3390/ma11122527

evident. The problem of compatibilization between polyethylene and poly(lactic) acid polymers is of paramount importance in recent resin manufacturing, and has been partially addressed with interfacially localized catalysts, based for example on stannous octoate [19]. However, the problem appears generally far from being totally resolved.

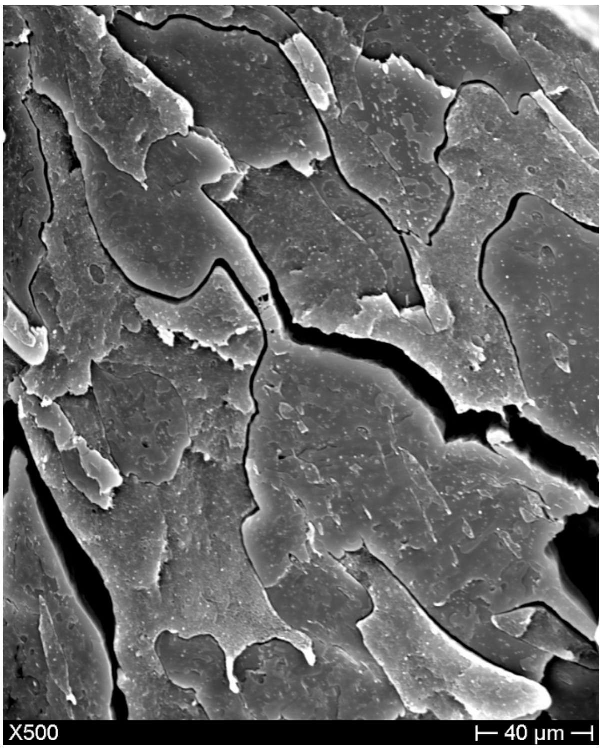

Figure 3: HDPE50-PLA50 blend morphology of cryo-fractured surface

The addition of compatibilizers to HDPE50-PLA50 blend allows a reduction in dimension of different phases, suggesting a higher compatibility between HDPE and PLA. This result is more evident for Lotader AX8840 (figure 4a) than for Polybond 3029 (figure 4b): in fact, a higher phase separation and easier distinction between polymers was displayed for samples compatibilized with Polybond 3029. The higher affinity of PLA for Lotader AX8840 was already displayed in our previous work [11], revealing the presence of smaller spherical secondary phase for Lotader AX8840 than for Polybond 3029 when blended with PLA.

Peer-reviewed version available at Materials 2018, 11, 2527; doi:10.3390/ma11122527

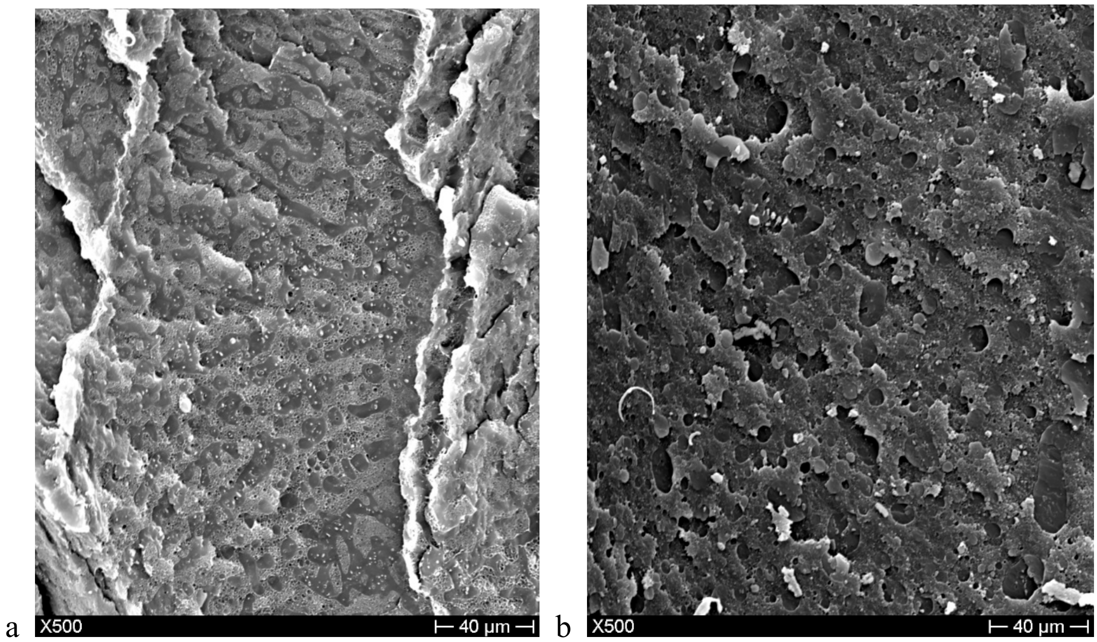

Figure 4: Blend morphology of cryo-fractured surface a) HDPE50-PLA50-Lot3
b) HDPE50-PLA50-Poly3

3.3. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was useful for analysing the combined effects of blending HDPE with PLA, and the effects of adding compatibilizers. ΔH_{mPE} (J/gPE) and ΔH_{mPLA} (J/gPLA) refers enthalpies value to the exact amount of Polyethylene and poly(lactic acid) in the samples. For example, HDPE50-PLA50 displayed ΔH_{mPE} of 113 J/g but a division by 0.5 is needed to obtain the real amount of enthalpy referred to HDPE; as a consequence, the effective ΔH_{mPE} is 226 J/g_{PE}. Table 4 sums up DSC results for HDPE, PLA and HDPE50-PLA50.

Table 4: DSC results for HDPE, PLA and HDPE50-PLA50.

	ΔH_{ccPLA} (J/g_{PLA})	T_{cc} (°C)	ΔH_{mPE} (J/g_{PE})	T_{mPE} (°C)	ΔH_{mPLA} (J/g_{PLA})	T_{mPLA} (°C)	T_{gPLA} (°C)
HDPE	-	-	215	134	-	-	-
PLA	7	98	-	-	41	168	61
HDPE50-PLA50	8	97	226	132	40	168	62

The typical PLA cold crystallization process [20] is still revealed by HDPE50-PLA50. Moreover, slightly higher crystallinity of HDPE phase is demonstrated, in agreement with both higher mechanical properties of the blend and with a phase separation because of the presence of crystals [4]. The effect of Lotader AX8840 and Polybond 3029 on HDPE50-PLA50 properties was also analysed (table 5). Both Polybond 3029 and Lotader AX8840 addition reveal the presence of cold crystallization. Higher enthalpies values were measured for Lotader AX8840 addition with respect to Polybond 3029, but in both cases, the influence of adding different amounts of compatibilizers is not evident. A possible interpretation for higher enthalpies is that the addition of compatibilizers results in an increased PLA chain mobility with respect to neat HDPE50-PLA50.

A more evident effect of compatibilizer addition is displayed by Lotader AX8840, with lower melting enthalpy for HDPE phase. This result suggests an interaction between HDPE and PLA through Lotader AX8840, hindering HDPE macromolecules mobility [21].

Table 5: DSC results of HDPE50-PLA50 with 1-3-5 wt.% of Lotader AX8840 and Polybond 3029.

	$\Delta H_{cc_{PLA}}$ (J/g_{PLA})	T_{cc} (°C)	$\Delta H_{m_{PE}}$ (J/g_{PE})	$T_{m_{PE}}$ (°C)	$\Delta H_{m_{PLA}}$ (J/g_{PLA})	$T_{m_{PLA}}$ (°C)	$T_{g_{PLA}}$ (°C)
HDPE50-PLA50	8	97	236	132	40	168	62
HDPE50-PLA50-Poly1	15	94	195	132	45	168	61
HDPE50-PLA50-Poly3	15	100	190	132	41	168	61
HDPE50-PLA50-Poly5	16	101	198	132	41	168	61
HDPE50-PLA50-Lot1	20	103	192	132	40	168	61
HDPE50-PLA50-Lot3	21	103	182	132	41	168	61
HDPE50-PLA50-Lot5	20	104	192	132	36	168	61

3.4. Thermogravimetric Analysis (TGA)

In order to evaluate thermal stability of polymer, analyses have been performed to measure degradation onset temperature (T_{onset}) (table 6). PLA revealed a lower thermal stability compared to HDPE: in fact, T_{onset} is around 319°C for PLA and 458°C for HDPE, in agreement with literature results [22]. Blending HDPE and PLA (HDPE50-PLA50) results in a Tonset near to neat PLA, confirming a reduced thermal stability of the blend (322°C) with respect to neat HDPE (458°C). All formulation displayed a complete degradation of polymers, without the formation of a residual char (100% of mass variation Δm between the total amount of sample before the test and the residual mass after the test). The addition of Lotader AX8840 increased blend thermal stability, with higher Tonset with increasing Lotader AX8840 amount. Blend formulations, either compatibilized or not, displayed two separated thermal degradations, the first refers to poly(lactic)acid and the second to polyethylene. A maximum rate of weight loss corresponds to each degradation: blend formulation exhibited two separated temperature of the peak value for the first derivative of the TGA curve (T_{DTG}).

Table 6: TGA results for HDPE-PLA blends with different compatibilizer percentages and HDPE50-PLA50 matrix composites with 3 wt.% of compatibilizer. T_{onset} (°C) is evaluated with the extrapolated onset temperature from TGA curve. T_{DTG} (°C) Temperature of maximum DTG curves peaks. Δm (%) is the mass variation percentage between the total amount of sample before the test and the residual mass after the test.

	T_{onset} (°C)	T_{DTG} (°C)	Δm (%)
HDPE	458	474	100
PLA	319	351	100
Poly	459	480	100
Lot	434	464	100
HDPE50-PLA50	322	345/471	100
HDPE50-PLA50-Poly1	316	351/444	100
HDPE50-PLA50-Poly3	322	358/438	100
HDPE50-PLA50-Poly5	313	342/432	100
HDPE50-PLA50-Lot1	325	350/470	100
HDPE50-PLA50-Lot3	325	350/468	100

Peer-reviewed version available at Materials 2018, 11, 2527; doi:10.3390/ma11122527

HDPE50-PLA50-Lot5	334	351/474	100

3.5. Infrared Spectroscopy Attenuated Total Reflection (ATR-FTIR)

Infrared spectroscopy has been done to evaluate interactions between polymers, and the main results are displayed in figure 5. As expected, HDPE50PLA50 did not display peaks variation confirming the presence of an immiscible blend without interactions between HDPE and PLA. The addition of Lotader AX8840 slightly shifts typical ester peak of PLA (1749 to 1752 cm-1), suggesting interactions between glycidyl methacrylate and C=O group of PLA. Polybond 3029 addition, on the contrary, did not display variation of HDPE50-PLA50 peaks, confirming the hypothesis of poor interactions between maleic anhydride and C=O group of PLA.

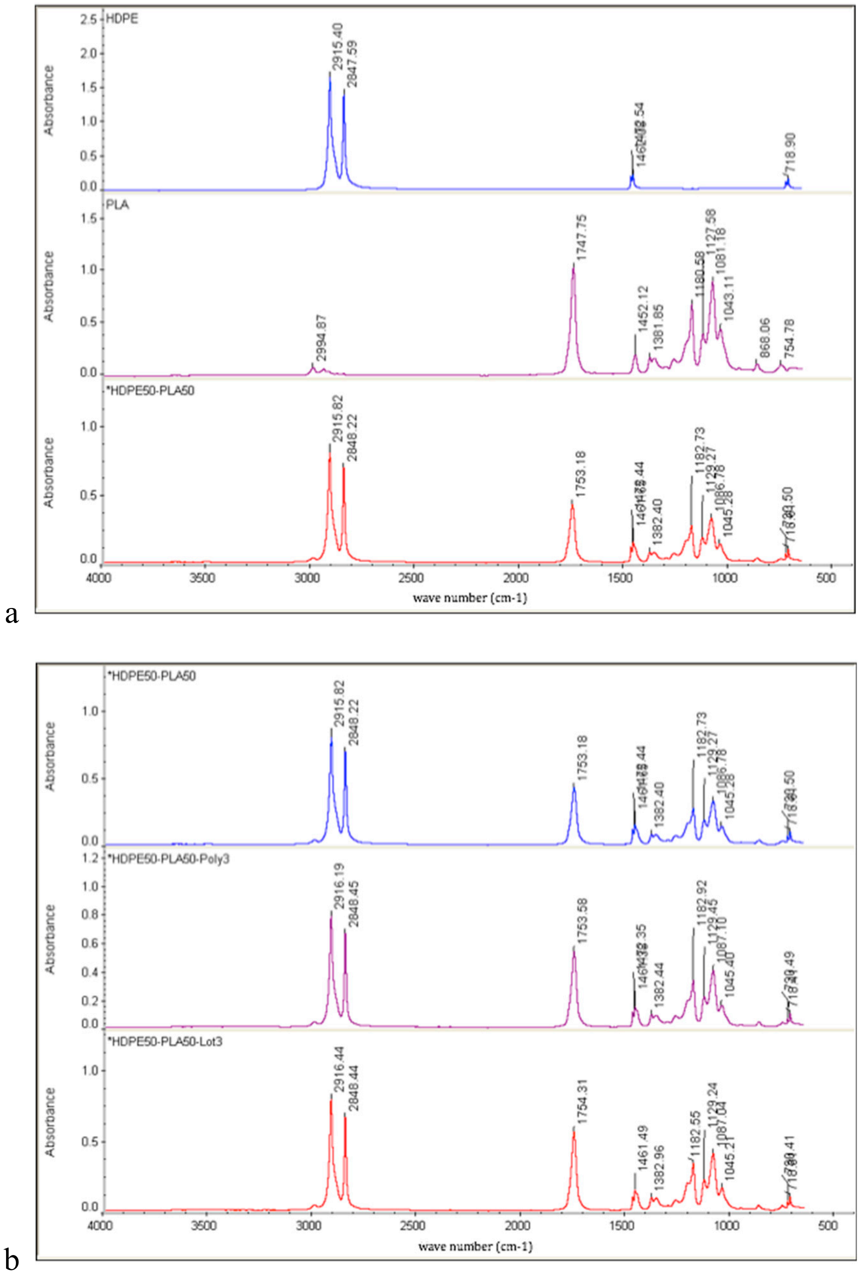

Figure 5: ATR-FTIR spectra of: a) HDPE, PLA and HDPE50-PLA50,
b) HDPE50-PLA50, HDPE50-PLA50-Lot3 HDPE50-PLA50-Poly3

Peer-reviewed version available at *Materials* **2018**, *11*, 2527; doi:10.3390/ma11122527

Further research on compatibilization could involve the use of nanostructure, such as SiO_2 nanoparticles, graphene platelets or carbon nanotubes [23].

4. Conclusions

After a preliminary study on HDPE-PLA blends, the one containing equal amounts of HDPE and PLA appears to be the most suitable towards keeping good mechanical properties and a significant reduction of non bio-derived charge. The addition of compatibilizer, especially Lotader AX8840 because of high content of glycidyl methacrylate, seems to increase homogeneity of the blend. An appropriate percentage of compatibilizer has to be selected in order to optimize blend properties. In fact, 3wt.% of compatibilizer seem to optimize (considering strength and plasticity) mechanical properties and affinity between HDPE and PLA. SEM images revealed a typical immiscible morphology between HDPE and PLA when blended without compatibilizer. Both Lotader AX8840 and Polybond 3029, more moderately, seem to increase homogeneity of the blend thanks to functional groups interaction with PLA, in agreement with FTIR results. Further analyses have to be done in order to evaluate biodegradation behavior of oil-based/bio-derived polymer blends with the ratio analyzed in this study.

References

1. Polypetchara, N.; Suppakul, P.; Atong, D.; Pechyen, C. Blend of polypropylene/poly(lactic acid) for medical packaging application: physicochemical, thermal, mechanical, and barrier properties. *En. Proc.* **2014**, *56*, 201-210, 10.1016/j.egypro.2014.07.150 .
2. Parameswaranpillai, J.; Thomas, S.; Grohens, Y. Polymer blends: state of the art, new challenges and opportunities. In Characterization of Polymer Blend, 1st Ed; Thomas, S.; Grohens, Y; Parameswaranpillai, J., Publisher: Wiley-VCH, 2015, pp. 1-6,
3. Higgins, J.A.; Lipson J.E.G.; White, R.P. A simple approach to polymer mixture miscibility, *Philos T Roy Soc A* **2010**, *368*, 1009-1025, 10.1098/rsta.2009.0215
4. Utracki, L.A. Compatibilization of Polymer Blends, *Can J Chem Eng* **2008,** *80,* 1008-1016.
5. Cook, S. *Polymeric Compatibilizers: Uses and Benefits in Polymer Blends*, John Wiley & Sons.: Akron, United States, 1997; ISSN 00359475
6. Kim, Y.F.; Choi, C.N.; Kim, Y.D.; Lee, K.Y.; Lee, M.S. Compatibilization of immiscible poly(l-lactide) and low density polyethylene blends, *Fiber Polym* **2004**, *5*, 270-274, https://doi.org/10.1007/BF02875524.
7. Quitadamo, A.; Massardier, V.; Valente, M. Oil-based/Bio-Derived Thermoplastic Polymer Blends and Composites, In *Introduction to Renewable Biomaterials: First Principles and Concepts*, Lucia, L.; Ayoub, A.; Wiley Hoboken, New Jersey, USA, pp. 239-268.
8. Ebnesajjad S. Handbook of Biopolymers and Biodegradable Plastics. 1st , ed. William Andrew, Elsevier, Oxford, UK, 2013, ISBN 978-4557-2834-3
9. Zhu Y, Romain C, Williams CK. Sustainable polymers from renewable resources. *Nature*. **2016**;*540*, 354–62.
10. Ermolovich , O.A.; Makarevich, A.V. Effect of Compatibilizer Additives on the Technological and Performance Characteristics of Biodegradable materials based on starch-filled polyethylene, *Russ J Appl Chem+*, **2006,** *79*, 1526-1531, https://doi.org/10.1134/S1070427206090266 .
11. Quitadamo, A.; Massardier, V.; Valente, M. Interactions between PLA, PE and wood flour:effects of compatibilizing agents and ionic liquid , *Holz*, **2017,** *72*, 691-700, https:*//doi.org/10.1515/hf-2017-0149*
12. Luyt, A.S. Polyolefin Blends, In *Polyolefin Compounds and Materials,* 1st ed; AlMa'adeed M.; Springer International Publishing, Switzerland, 2016, 978-3-319-25980-2.
13. Baiardo M.; Frisoni G.; Scandola M.; Rimelen M.; Lips D.; Ruffieux K.; Wintermantel, E. Thermal and Mechanical Properties of Plasticized Poly(L-lactic acid). *J Appl Polym Sci.***2003;***90,* 1731–1738. https://doi.org/10.1002/app.12549
14. Mekonnen T.; Mussone P.; Khalil H.; Bressler D. Progress in bio-based plastics and plasticizing modifications. *J Mater Chem A.* **2013;***1*, 13379–13398
15. Madhu, G.; Bhunia, H.; Bajpai, P.K.; Nando, G.B. Physico-mechanical properties and biodegradation of oxo-degradable HDPE/PLA blends, *Polym Sci A* **2016**, *58*, 57-75, https://doi.org/10.1134/S0965545X16010077.

Peer-reviewed version available at *Materials* **2018**, *11*, 2527; doi:10.3390/ma11122527

16. Sailaja, R.P.N.; Chanda, M. Use of Maleic Anhydride Grafted Polyethylene as Compatibilizer for HDPE Tapioca Starch Blends: Effects on Mechanical Properties, *J App Polym Sci* **2001**, *80*, 863-872.
17. Quiroz-Castillo, J.M.; Rodrigues-Felix, D.E.; Grijalva, H.; Castillo-Castro, T.; Plascencia-Jatomea, M.; Rodriguez-Felix, F.; Herrera-Franco, P. Preparation of extruded polyethylene/chitosan blends compatibilized with polyethylene-graft-maleic anhydride. *J App Polym Sci* **2014,** *101*, 1094-100 *10.1016/j.carbpol.2013.10.052*
18. Djellali, S.; Haddaoui, N.; Saoun, T.; Bergeret, A.; Grohens, Y. 18. Structural, morphological and mechanical characteristics of polyethylene, poly(lactic acid) and poly(ethylene-co-glycidyl methacrylate) blends, *Iran Polym J* **2013,** *22*, 245-257, 10.1007/s13726-013-0126-6
19. Thurber C.M.; Xu Y.; Myers J.C.; Lodge T.P.; W. Macosko C.W.; Accelerating reactive compatibilization of PE/PLA blends by an interfacially localized catalyst, ACS *Macro Lett.*, **2015,** *4*, 30–33. 10.1021/mz500770y
20. Gregorova, A. Application of Differential Scanning Calorimetry to the characterization of Biopolymers. In: World ' s largest Science , Technology & Medicine Open Access book publisher A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope. InTech; p. 3–20.
21. Anstey, A.; Codou, A.; Misra, M.; Mohanty, A.K. Novel Compatibilized Nylon-Based Ternary Blends with Polypropylene and Poly(lactic acid): Fractionated Crystallization Phenomena and Mechanical Performance, *ACS Omega*, **2018,** *3*, 2845-2854, 10.1021/acsomega.7b01569
22. Madhu, G.; Mandal, D.K.; Bhunia, H.; Bajpai, P.K. Thermal degradation kinetics and lifetime of high-density polyethylene/poly(L-lactic acid) blends, *J Thermoplast Compos*, **2017**, 30(6), 773-793, 10.1177/0892705715610411
23. Salzano de Luna, M.; Filippone, G.; Effects of nanoparticles on the morphology of immiscible polymer blends – Challenges and opportunities, *Eur Polym J*, **2016**, *16, 10.1016/j.eurpolymj.2016.02.023*