Fully Bio-Based Nanocomposite: Formulations For Packaging Application

Adolfo Izzo Renzi
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II. Piazzale V.Tecchio, 80, 80125 Napoli, Italy
adolfo.izzo1@gmail.com

Anna Verdoliva
Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli Federico II. Piazzale V.Tecchio, 80, 80125 Napoli, Italy
annaverav@libero.it

Giovanni Filippone
Centro Regionale di Competenza (CRdC) Tecnologie, Università di Napoli Federico II, Via Nuova Agnano, 11, 80125 Napoli, Italy
giovanni.filippone@unina.it

Domenico Acierno
Centro Regionale di Competenza (CRdC) Tecnologie, Università di Napoli Federico II, Via Nuova Agnano, 11, 80125 Napoli, Italy
acierno@unina.it

INTRODUCTION

The world market of plastic films is dominated by petrochemical-based plastics such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA) because of their large availability at relatively low cost and good mechanical and barrier performances. Environmental concerns are driving the attention of plastic producers towards biopolymers, namely polymers obtained from renewable resources. Among others, poly(lactic acid) (PLA) is extensively studied because PLA closely resembles polystyrene in terms of high modulus and low elongation to break and poly(ethylene terephthalate) in terms of stiffness and tensile strength [1,2]. The main drawbacks of PLA are the brittleness and low heat deflection temperature (HDT), which essentially corresponds to the glass transition temperature T~55°C. To overcome these issues we propose a strategy that consists in blending PLA with polyamide 11 (PA11), a renewable resource extracted from the castor plant. PA11 is a high-performance, semi-crystalline polymer with low net CO_2 emission and global warming potential, when compared to petroleum based Nylons and other conventional plastics[2,3]. Some of the properties of PA11 include high impact and abrasion resistance, low specific gravity (about 1.03 g/cm^3), excellent chemical resistance, high thermal stability (melting point of about 180–190 °C), and ease of processing over a wide range of processing temperatures (130°C to 240°C). Since PA11 is not biodegradable and it is relatively expensive compared to other plastic materials including petroleum based Nylon-6, the aim is minimizing its content in the blend while maintaining it phase continuity, so as to provide the blend with a PA11 framework able to resist to high temperatures. This goal is pursued using small amounts of clay particles, which may simultaneously act as reinforcing nanofiller and promote the phase continuity of the PA11 phase.

EXPERIMENTAL SECTION

Materials and blend preparation

The PLA (2002D by Natureworks) has density ρ=l.24 g/cm³ at 25°C and melt flow index MFI=6 g/l0 min (2l0°C/2.l6 kg). The PA11 (Nylon 11 by Sigma Aldrich) has ρ = l.026 g/cm³ at 25°C, glass transition temperature Tg = 46°C and melting temperature Tm = l98°C. The filler is an montmorillonite (OMMT, Cloisite 30B from Southern Clay Products) modified by 90 meq/l00g of bis(2-hydroxylethyl) methyl tallow alkyl ammonium cations. The relatively low processing temperature of PAll allows to limit thermal degradation of PLA during melt blending. In addition, the onset of thermal decomposition of the organic modifier in Cloisite 30B is higher than temperature chosen for the melt compounding

To minimize hydrolysis phenomena during melt mixing, the polymers and the filler were dried at 80°C for 12 h in a vacuum oven. The blends were prepared using a Thermo-Haake twin screw extruder at T=210°C and screws speed ~80 rpm. The extruded materials were pelletized, dried again and film blown in a second step using a Collin film blowing line at T=215°C and screw speed ~20 rpm. The thickness of the films was typically ranging between 30 and 70 µm.

METHODS

Mechanical tests were performed according to ASTM D882 method using a dynamometer Tensometer 2020 by Alpha Technologies. Rectangular film specimens of 115 × 10mm were cut using a manual punch cutter. Tensile tests were performed at room temperature with a cross-head speed of 10mm/min for the first 5mm of elongation and after it was 50 mm/min until the end of the tests. Young modulus, tensile strength and elongation at break were evaluated in the extrusion direction on all film sample.

The oxygen permeability of the films (thickness: 30-60 µm) was estimated by using Totalperm Oxygen, Carbon Dioxide and Water Vapor Permeability Analyser provided by Extrasolution s.r.l., according to ASTM D3985 procedure. The temperature was set at 27°C and at Relative Humidity of 0%. The carrier flow was fixed at 12.3 ml/min and the sample surface was 2.01 cm² for each sample. An automatic barometric compensation was executed by the instrument to set the pressure to 1 atm.

Thermo gravimetric analysis was carried out on a TA Instruments Q500e. Each specimen was heated from 25°C to 700°C in air with a ramp rate of 20°C/min. The average initial mass of samples was approximately 8 mg.

Dynamic-mechanical analyzes (DMTA) were carried out using a Tritec 2000 DMA (Triton technology, UK). The dynamic moduli were measured as a function of temperature in tensile mode at a frequency ω=1 Hz and a strain amplitude of 0.005 mm. The samples were heated at 3°C/min from ~ -20°C to l20°C.

RESULTS AND DISCUSSION

The Young modulus, E, tensile strength, σ_R, and elongation at break, ε_R, of the films are shown in Figure 1.

Blending PLA with PA11 results in a decrease of E and σ_R with compared to neat PLA, which indicates poor interfacial adhesion between polymer phases. The addition of only 1%wt of OMMT brings about an enhancement of E and σ_R, which approach those of neat PLA, and a drastic increase of ε_R. The latter result suggests that the filler greatly improve the stress transfer across the polymer-polymer interface.

The oxygen permeability values are summarized in Table 2.

As far as the barrier properties are concerned, neither blending with PA11 nor the addition of OMMT alter appreciably the oxygen permeability, which remains comparable to that of pure PLA. The results of TGA analyses are summarized in Table 3, in which the

Fig.1. a) Young modulus, E and tensile strength, σ_R, and b) Elongation at break, ε_R of PLA, PLA/PA11 and PLA/PA11+OMMT respectively. The error bars represent the standard deviations over x independent measurements.
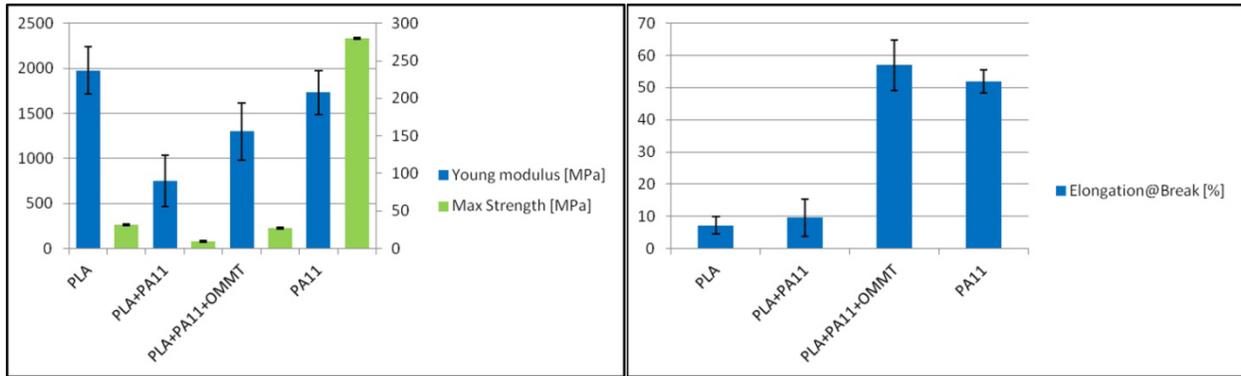

Table 2. Oxygen Permeability of PLA, PLA/PA11 and PLA/PA11+OMMT

Sample	P'O$_2$ x10^{-9} (cm^2/bar s)
PLA	3,79
PLA/PA11 70/30	3,56
PLA/PA11 70/30 + OMMT	3,80
PA11	2,58

Table 3. Thermogravimetric Parameters of all investigated materials

Sample	$T_{5\%wt}$	T_{peak}
PLA	324,3	365,2
PLA/PA11	337,5	365,6
PLA/PA11 + OMMT	338,8	363,1
PA11	416,3	445,8

Table 4. Dynamic-mechanical thermal analyses of PLA, PLA/PA11 and PLA/PA11+OMMT

Sample	E'$_{25°C}$ [MPa]	E'$_{60°C}$ [MPa]
PLA	793	40,8
PLA/PA11	755	62,2
PLA/PA11+OMMT	911	82,1
PA11	1080	550

temperature of incipient thermal degradation ($T_{5\%}$) and the temperature at which the rate of weight loss is the highest (T_{peak}) are reported.

The onset of thermal degradation of the unfilled and filled blends is 15°C higher than neat PLA. This improvement is likely due to the "labyrinth effect" of the PA11 phase, which acts as an insulating barrier able to the volatilization process of PLA. The clay does not promote significant improvements[5,6].

The results of DMTA analyses are summarized in Table 4. In particular, the storage moduli E'$_T$ at 25°C and 60°C are reported.

Adding the filler to the blend results in a slight enhancement of the glassy modulus in the sample PLA/PA11+OMMT at 25°C with respect the glassy modulus of unfilled blend. This supports the idea that the clay may exert improve the stress transfer across the interface[7]. This beneficial effect lasts up to T = 60°C, i.e. the glass transition temperature of PLA: the modulus of the filled blend is twice that of pure PLA.

CONCLUSION

Preliminary characterization of PLA/PA11 blends in the presence of OMMT have demonstrated that blending PLA with PA11 results in a decrease of E and σ_R compared to neat PLA, which indicates poor interfacial adhesion between two phases. The addition of only 1%wt of OMMT brings about an enhancement of E and σ_R, which approach those of neat PLA, and a drastic increase of ε_R. Neither blending with PA11 nor adding the OMMT cause appreciable alterations of the barrier properties of the films, which remains essentially the same as those of pure PLA blend is 15°C higher than of neat PLA. This improvement is probably due to the "labyrinth effect" of the PA11 phase. The clay does not promote significant improvements. Finally, the filler brings about a slight enhancement of the glassy modulus compared to the unfilled blend, which suggests that the clay may exert some compatibilizing action. Such a beneficial effect of the OMMT endures up to the glass transition of PLA.

Further morphological studies are currently in progress to clarify the origin of the improvements of the performances and possibly exploit the filler effect.

REFERENCES

[1]   Dorgan J.R., Lehermeier H., Mang M., 2000. " Thermal and rheological properties of commercial-grade poly (lactic acid) s". *Journal of Polymers and the Environment*, Springer, Vol. 8, Issue 1, pp 1-9.

[2]   Patel R., Ruehle D. A., Dorgan J. R., Halley P., Martin D., 2014. "Biorenewable blends of Polyammide-11 and Polylactide". *Polymer Engineering & Science*, Wiley, Vol. 54, Issue 7, pp 1523-1532.

[3]   Hu G.S., Wang B.B., Zhou X.M.,2005. " Compatibility of reactively compatibilized polyamide 11 (nylon 11)/polyethylene (PE) alloys". *Polymer International*, Wiley, Vol. 54, Issue 2, pp. 316-319.

[4]   Liu T., Lim K. P., Tjiu W. C., Pramoda K.P., Chen Z. K., 2003. "Preparation and characterization of nylon 11/organoclay nanocomposites". *Polymer*, Elsevier, Vol. 44, Issue 12, pp. 3529-3535.

[5]   Wu D., Wu L., Wu L., Zhang M., 2006."Rheology and thermal stability of polylactide/clay nanocomposites". *Polymer Degradation and Stability,* Elsevier, Volume 91, Issue 12, pp 3149-3155.

[6]   Russo P., Cammarano S., Bilotti E., Peijs T., Cerruti P., Acierno D., 2013. "Physical Properties of Poly Lactic Acid/ Clay Nanocomposite Films: Effect of Filler Content and Annealing Treatment". *Journal Of Applied Polymer Science,* Wile, Vol. 131, Issue 2, pp. 39798-39798.

[7]   [7]   Nuzzo A., Acierno D., Filippone G., 2012. "Clay-filled bio-based blends of poly(lactic acid) and polyamide 11". *AIP Conference Proceedings,* 10-14 June 2012, Ischia, Itala, ISBN: 978-0-7354-1061-9, Vol. 1459, pp 208-210.