Effect of TiO_2 and ZnO on PLA degradation in various media

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INTRODUCTION

The study of degradation of polymer nanocomposites is an extremely important area from the scientific and industrial point of view. Therefore, the material usefulness depends on its durability in a particular environment in which materials are used or their interaction with environmental factors [1]. The study of durability/degradability of polymers-nanoparticulate systems under environmental conditions will give an insight to their applications as well as limitations. Today the largest contributor to the plastic waste is the packaging (63%) [2], the use of bio-polymers represents a way to reduce the environmental impact, from 2013 to 2020 the use of bio-polymers in different market segment is increasing from 14% to 40% [3]. The aim of this study is to investigate the influence of a different metal oxide particles (TiO_2 and ZnO) on hydrolytic, enzimatic and UV degradation.

EXPERIMENTAL MATERIALS

MATERIALS

1. Polylactic Acid

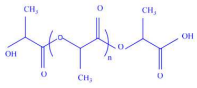
Material	PLA 4032D
Producer	Nature Works®
Mn (g/mol)*	1.3 x 10^5
Mw (g/mol)*	2.1 x 10^5
Mn/Mw	1.56
Tm (°C)	160
Tg (°C) (measured by DSC)	58
Density (g/cm^3)	1.24

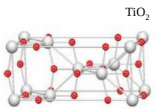
*The Value of Mn e Mw was calculated by GPC analysis at IPCB-CNR of Pozzuoli

2. TiO_2 and ZnO particles

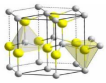
Material	TiO_2[a]	ZnO[b]
Producer	Degussa	PYLOTE
Average particle diameter (dry) (nm)	25	100-500
Purity	99.5%	100%

a : TiO_2not modified and modified particles with fluorocarbon film by plasma reactor, University of Texas in Arlington.
b: ZnO particles produced by spray pilolysis


PLA


Anatase


Rutile

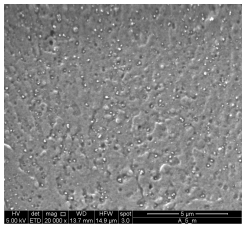

Rocksalt

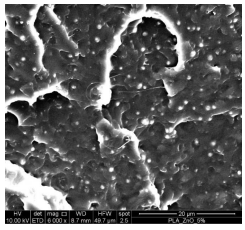
PROCESSING CONDITIONS

1) PLA was mixed with the powder of TiO_2 using a Barbender Plastograph EC mixer. Two formulations were prepared by using both modified and unmodified TiO_2 nanoparticles: 2% in wt and 5% in wt. The films were prepared by compression moulding.

2) To improve the dispersion of ZnO in PLA a masterbatch with composition PLA 80% and ZnO 20% was prepared by mixing the components in a twin-screw extruder, Collin ZK 25.The masterbatch was diluted in PLA to obtain the desired composition(1,3 and5% wt of ZnO). The films were produced by calender.

MORPHOLOGICAL ANALYSIS


PLA/5% TiO_2
Particles (modified and not) embedded in the matrix


PLA/5% ZnO
Particles fairly distributed with some agglomerates

Homogeneous dispersion and distribution

REFERENCES

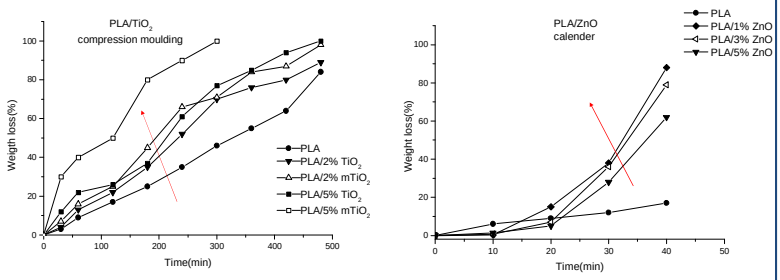
1)N. Touati, M. Kaci, S. Bruzaud and Y. Grohens, Polym. Degrad. Stab., 96 (2011) 1064.
2)PlasticsEurope, EuPC, EuPR, EPRO and Consultic (2009) The Compelling Facts about Plastics - An analysis of European plastics production, demand and recovery for 2008.
3)Nova-institute 2015.

ACKNOWLEDGMENTS

The research leading to these results has received support from FP7 Eranet Susfood-Cereal "Improved and resource efficiency throughout the post harvest chain of fresh cut fruits and vegetables", Erasmus+: "Cooperation and Innovation for Good Practices Joint innovative training and teaching/learning program in enhancing development and transfer knowledge of application of ionizing radiation in materials processing", Health Ministry and Italian Ministry of Foreign Affair (Bilateral Project Italy/Quebec 2014-2016 "Sviluppo di nanomateriali ecosostenibili per l'Imballaggio alimentare adatti alla sterilizzazione per radiazione").
Professor Richard B. Timmons of University of Texas, Arlington, USA is thanked for supplying fluorocarbon TiO_2 nanoparticles functionalized by plasma treatment
Dr. J. Dexpert-Ghys, M., Verelst, from CEMES-CNRS, Toulouse and S. Augier from Pylote SAS, Toulouse, are kindly thanked for supplying ZnO particles obtained by spray-pyrolysis.

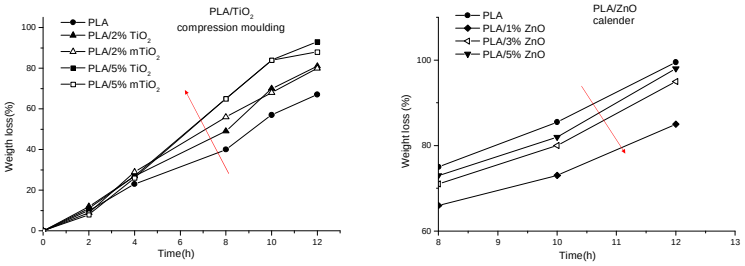
DEGRADATION

HYDROLYTIC: in 1N NaOH films (10mm x10 mm) at 37°C



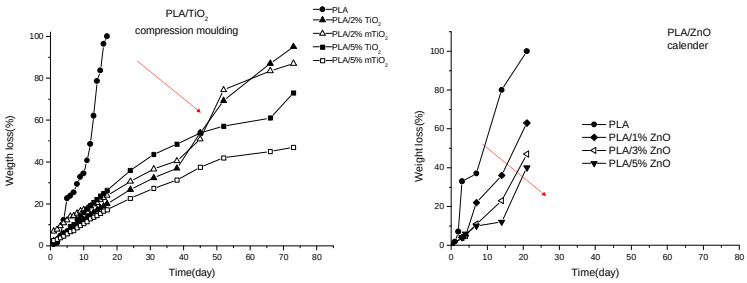
✓PLA/TiO_2 and PLA/ZnO films exhibit degradation faster than PLA.

ENZYMATIC: in Proteinase K solution films (2.5cm x 1.0cm) in 5mL of Tris-HCl buffer (pH 8.6)+1mg of proteinase K+1mg of sodium azide in distilled water



✓Proteinase K degrades L-lactyl units;
✓In all the systems the weight loss is function of the filler amount.

UV: monochromatic light at λ= 365 nm, 40°C and 25% RH



✓The neat PLA degrades faster than PLA loaded with TiO_2 and ZnO.

CONCLUSIONS

The degradation study has shown that the composites degrade in different times respect to neat PLA as a function of kind of particles, composition and degradation media.

Hydrolitic deg.: **PLA**<PLA/TiO_2<$PLA/mTiO_2$
Enzymatic deg.: **PLA**<PLA/TiO_2<$PLA/mTiO_2$
UV deg.: **PLA**>PLA/TiO_2>$PLA/mTiO_2$

Hydrolitic deg.: **PLA**<PLA/ZnO
Enzymatic deg.: **PLA**>PLA/ZnO
UV deg.: **PLA**>PLA/ZnO