



Halloysite nanotubes and thymol as photo protectors of biobased polyamide 11



Giuliana Gorrasi^a, Valeria Bugatti^a, Martina Ussia^{b, e}, Raniero Mendichi^c, Daniela Zampino^d, Concetto Puglisi^d, Sabrina Carola Carroccio^{d, e, *}

^a Dipartimento di Ingegneria Industriale, Università degli studi di Salerno, Via Giovanni Paolo II, 132, 84084, Fisciano, SA, Italy

^b Dipartimento di Fisica e Astronomia, Università degli studi di Catania, Via Santa Sofia, 64, 95123, Catania, Italy

^c Consiglio Nazionale delle Ricerche, CNR-ISMAR, Via A. Corti 12, 20133, Milano, Italy

^d Consiglio Nazionale delle Ricerche, CNR-IPC Catania, Via P. Gaifami 18, 95126, Italy

^e Consiglio Nazionale delle Ricerche, CNR-IMM Catania (Università), Via Santa Sofia, 64, 95123, Catania, Italy

ARTICLE INFO

Article history:

Received 27 December 2017

Received in revised form

7 March 2018

Accepted 21 March 2018

Available online 27 March 2018

Keywords:

PA11

Halloysite

Thymol

Nanocomposites

Ball milling

Photo-oxidation

UV irradiation

Mechanical properties

Degradation

Release

ABSTRACT

The formulation of cost-effectiveness sustainable materials is extensively growing and becoming an attractive approach for both industrial and academic fields. In this context, the bio-based aliphatic polyamide 11 (PA11) has acquired significant interest as environmentally friendly thermoplastic option. In addition, its formulation with selected natural antioxidant and/or reinforced compounds through green processing methods, might improve physical and mechanical properties without sacrificing the intrinsic bio-based nature of the matrix. In this work, we have investigated and compared the photo-oxidative degradation processes occurring on PA11 composites based on thymol and halloysite nanotubes prepared by using ball-milling method. In particular, halloysite nanotubes were used as green nano-container of a natural antioxidant molecule, and reinforced nano-filler as well. Molecular and structural information of photo-exposed samples were obtained by using size exclusion chromatography (SEC) and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS). Thermal and mechanical properties were also tested as well as thymol release. Data collected confirmed that PA11 filled with HNTs-Thymol nano-hybrid showed superior durability performance if compared to both pure PA11 and PA11 blend realized by simply adding thymol and HNTs to polymer matrix. Furthermore, we found that HNTs and thymol combined in the nano-hybrid form exhibited an active and synergic role to achieve a major photo stabilization of PA11 biocomposite, without sacrificing its mechanical properties.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Plastic materials derived from renewable resources for replacement of petroleum-based ones are gaining growing interest both in industry and in the scientific research community. Polyamide-11 (PA11) obtained from castor beans [1,2], is a promising material as “green” alternative in a variety of applications ranging from household devices to engineering materials. At the present, PA11 finds excellent placings in metal coatings, flexible pipes for automotive and offshore applications. PA11 exhibits in fact

outstanding mechanical properties (high fatigue resistance, low frictional coefficient, excellent creep resistance) and good chemical resistance. Furthermore, its potential ability in replacement traditional polymeric materials, especially where mechanical properties and flame resistance are required, could be enhanced by formulating it as nanocomposites [3,4]. From the degradation point of view, it is well known that polyamides (PAs) are not intrinsically stable in the presence of oxygen and/or humidity, especially at high temperature [5–11]. In particular, aliphatic polyamides undergo to degradation during processing and outdoor applications, involving a drastic drop in term of mechanical and physical properties [12]. Improvement in thermal stability of PA11 was observed by adding clays [13] and carbon nanotubes [14] whereas hydrolytic resistance was achieved by adding graphene [15]. Nevertheless, organic and inorganic fillers might affect in different ways the durability of

* Corresponding author. Consiglio Nazionale delle Ricerche, CNR-IMM Catania (Università), Via Santa Sofia, 64, 95123, Catania, Italy.

E-mail address: sabrinacarola.carroccio@cnr.it (S.C. Carroccio).

nanocomposites [16–18], especially in terms of photo and thermo-oxidative stability of polymer matrix [19,20].

Recently, a new class of green and naturally abundant fillers for polymers, halloysite nanotubes (HNTs), is attracting great interest for the peculiar chemical composition and physical shape. They are aluminosilicate sheets rolled into tiny tubes with general chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \times n\text{H}_2\text{O}$ [21,22]. The length of HNTs is about 1000 nm, the internal diameter ranges in 10–15 nm, and the external diameter is about 50–80 nm. Due to the tubular shape, HNTs can be dispersed in polymer matrices without exfoliation, as required for a good dispersion of layered clays. They have been widely used as filler for polymers as reservoirs of active molecules (drugs, antimicrobials, flame retardants, essential oils, self-healing agents, anticorrosion molecules, etc...) [23–30], imparting structural and functional properties to the materials. At the same time, HNTs are used for attaining advanced mechanical and/or thermal features [20,31,32]. Recently, a dramatic pro-degradant effects of HNTs on the photooxidation of PLA was reported by Therias et al. [20]. When this happens, the benefits deriving from the addition of fillers into the polymer matrix are counteracted, severely preventing the application of this material for outdoor exposure.

In this paper we investigated the accelerated photo-aging of a novel PA11 hybrid composite, formulated by using HNTs as nanocontainers of a light stabilizer. In view of packaging application, thymol (2-isopropyl-5-methylphenol), a phenolic antioxidant with high relevance in free radical scavenging processes [31,32], is tested as potential green additive for its harmlessness at low concentration.

The nano-hybrid was dispersed into the PA11 matrix using mechanical energy (high energy ball milling) at ambient temperature and in dry conditions. The molecular and structural data obtained from SEC and MALDI spectra of photo-exposed PA11 nano-hybrid composite are reported and discussed. Both thermal and mechanical properties as well as thymol release of the formulated PA11 samples were also tested and compared with referenced samples.

2. Experimental

2.1. Materials

PA11 ($\rho = 1.026 \text{ g cm}^{-3}$ at $T = 25^\circ\text{C}$, glass transition temperature $T_g = 46^\circ\text{C}$ and melting temperature $T_m = 198^\circ\text{C}$), 2-(4-hydroxyphenylazo)benzoic acid (HABA), hexafluoroisopropanol (HFIP), Halloysite nanoclay powders (CAS 1332-58-7) and thymol powders (CAS 89-83-8) were all supplied from Sigma Aldrich (Italy) and were used as received.

2.2. Preparation of HNTs/Thymol nanohybrid

3 g of Thymol were dissolved in 30 ml of distilled water at 50°C for 20 min. 3 g of HNTs were then mixed to the Thymol solution and ultrasonic processing was performed for 10 min to allow HNTs sufficiently dispersed. The solution was heated at 50°C for 2 min, then vacuum (0.085 MPa) was applied to remove the air between and within the hollow tubes. The vacuum was maintained for 15 min. The solution was then taken out from the vacuum and shaken for 5 min. Vacuum was re-applied, for 15 min, to remove the trapped air. The thymol loaded HNTs were dried in an oven for 72 h at 50°C to reach a constant weight. The content of Thymol (wt %) in the HNT-Thymol hybrid was calculated, using the TGA analysis, according to following equation:

$$\alpha_3 = w \cdot \alpha_1 + (1 - w) \cdot \alpha_2$$

where α_1 is the mass loss of Thymol at 800°C ; α_2 is the mass loss of HNTs at 800°C ; α_3 is the mass loss of HNTs-Thymol at 800°C (see Fig. 1). The content of Thymol (wt%) in HNTs-Thymol hybrid was estimated to be 55.5% and the HNTs content was 44.5%.

The incorporation of the HNTs-Thymol hybrid into PA11 was achieved using the High Energy Ball Milling (HEBM) technology. The powder mixture composed of PA11 and HNTs-Thymol (vacuum dried for 24 h) at 10 wt% was milled at room temperature in a Retsch (Germany) centrifugal ball mill (model S 100). The milling process occurred in a cylindrical steel jar of 50 cm^3 with 5 steel balls of 10 mm of diameter. The milling time was 60 min and the rotation speed was 580 r.p.m. Pure PA11 and PA11 with 5.55% of thymol, PA11 with 4.45% of HNTs and PA11 with 4.45% of HNTs and 5.55% of thymol formulations were milled in the same experimental conditions of the composite and taken as references.

2.3. Film preparation

Polymeric films were obtained by compression molding in a Carver laboratory press between two Teflon sheets, at 200°C , followed by cooling at ambient temperature. Their thickness was ca. $150 \pm 2 \mu\text{m}$.

2.4. Methods of analysis

The photo-oxidative degradation of PA11, PA11 formulations and composite films was carried out on a QUV PANEL apparatus at 60°C with continued exposure to UV radiation up to 7 days, in absence of water. At least two separate films were analyzed at each exposure time. The irradiance (0.68 W/m^2) of the UV lamps has a broad band with a maximum at 340 nm (UVA 340 lamps).

To perform Size Exclusion Chromatography (SEC) and Matrix Assisted Laser Desorption Ionization-Time of Flight Mass Spectrometry (MALDI-TOF MS) analyses, photo-oxidized films withdrawn at different degradation times, were solubilized in HFIP and filtered.

The molar mass distribution (MMD) of polymers was determined by a multi-detector SEC system using two on-line detectors: (i) a multi-angle light scattering (MALS); (ii) a differential refractometer (DRI) as concentration detector. The SEC-MALS system consists of an Alliance 2695 separation module from Waters with a

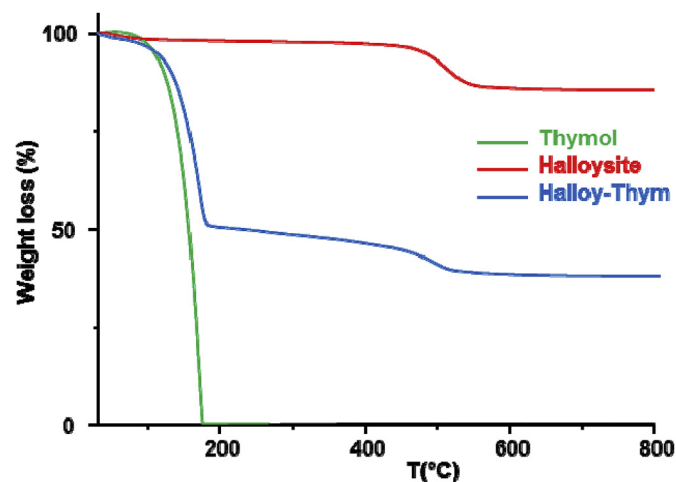


Fig. 1. Weight loss, measured by TGA at 800°C , of HNTs-Thymol nanohybrid, Thymol and HNTs.

Download English Version:

<https://daneshyari.com/en/article/7824020>

Download Persian Version:

<https://daneshyari.com/article/7824020>

[Daneshyari.com](https://daneshyari.com)