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Material properties

Gamma irradiation effects on morphology and properties of PHBV/PLA blends in presence of compatibilizer and Cloisite 30B

Idris Zembouai [a], Mustapha Kaci [a], Stéphane Bruzaud [b, *], Loic Dumazert [c],
Alain Bourmaud [b], Mohamed Mahlous [d], José Marie Lopez-Cuesta [c], Yves Grohens [b]

[a] Laboratoire des Matériaux Polymères Avancés (LMPA), Faculté de Technologie, Université de Bejaia, 06000, Algeria
[b] Laboratoire d'Ingénierie des Matériaux de Bretagne (LIMATB), Université de Bretagne-Sud, Rue de Saint Maudé, 56321 Lorient Cedex, France
[c] Centre des Matériaux des Mines d'Alès (C2MA), Ecole des Mines d'Alès, 6 avenue de Clavières, 30319 Alès Cedex, France
[d] Centre de Recherche Nucléaire d'Alger (CRNA), 2 Boulevard Frantz Fanon, Alger 16000, Algeria

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ABSTRACT

The effects of gamma irradiation on the morphology and physical properties of various blends based on poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) and polylactide (PLA): 50/50 w/w were studied with and without PHBV-g-MA and organomodified montmorillonite used as the compatibilizer and reinforcement agent, respectively. The different blend compositions prepared by melt compounding were compression molded to thin films of an average thickness of 150 μm, and subjected to 25, 50 and 100 kGy at room temperature; the dose rate being 1.0 Gy/h. Infrared spectra analysis indicated the occurrence of some chemical modifications in the irradiated samples, in particular an absorbed dose of 100 kGy resulted in the formation of a large absorption band in the carbonyl region. Size exclusion chromatography (SEC) data showed a decrease in the average molecular weight for all irradiated samples with increasing absorbed dose due to chain scission. Nanoindentation tests showed that γ-irradiation significantly decreased both modulus and hardness of neat PHBV and neat PLA after 100 kGy, whereas no noticeable changes were observed for PHBV/PLA blends. Thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC) tests revealed that the organomodified clay can act as a compatibilizer and compensate for the effect of irradiation on both thermal stability and fire retardancy of PHBV/PLA blends.

1. Introduction

Plastics packaging is one of the biggest sectors of the polymer processing industry, with the food sector being its principal customer [1]. However, most synthetic polymers used for this application often have short service life, so they end up mostly in landfills. The non-biodegradability of such commercial plastics has caused many environmental problems associated with their disposal [2,3]. Due to their biodegradability and biocompatibility through non toxic intermediates, PHBV and PLA are considered as ideal candidates to replace non biodegradable polymeric materials for packaging applications [4]. Further, they can be processed in equipment commonly used for synthetic polymers. On the other hand, there has been significant interest in the gamma sterilization of polymers being used in some technological fields such as biomedical and food packaging to guarantee microbiological safety [5,6]. However, it is known that γ-irradiation may cause some undesirable effects on polymers [7]. Therefore, it becomes necessary to study the chemical and physical effects that are induced by the transfer of energy to the polymer [8]. Often, the occurrence of these effects makes the irradiated materials unsuitable for some applications. Indeed, several papers [9–12] reported that γ-irradiation of polymers generally produces simultaneous scission and cross-linking of the polymeric chains. The latter causes the formation of a macroscopic network, which reduces gas permeability and improves mechanical properties, whereas the former decreases mechanical properties, but increases the biodegradation rate. In this respect, considerable work has been published on oxidative degradation of PHBV or PLA under gamma irradiation at both higher and lower doses [13–18]. One of the significant conclusions that can be drawn from these publications is, in particular, the decrease in molecular weight of the irradiated polymers below

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* Corresponding author.
E-mail address: stephane.bruzaud@univ-ubs.fr (S. Bruzaud).

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100 kGy due to chain scission, which occurs in the amorphous region and continues further to crystalline regions at higher doses. Melting point (T_m) and glass transition temperature (T_g) are reduced with increasing radiation dose, while the degree of crystallinity increases. The values of the surface potential of the irradiated biopolymers were higher in comparison with the non-irradiated samples. However, to the best of our knowledge, literature data dealing with γ-irradiation effects on polymer blends, in particular those based on PHBV/PLA, are rather scarce.

In this work, which is a continuation of previous ones devoted to the characterization properties of PHBV/PLA blends, and the methods for improving their compatibility and recycling [19–22], the assigned objective was to study the effects of γ-irradiation up to 100 kGy on the chemical structure, morphology and physical properties of blends based on PHBV/PLA: 50/50 w/w. Furthermore, the changes induced by γ-irradiation on the morphology and properties of PHBV/PLA blends were evaluated in the presence of 5 wt.% of PHBV-g-MA and 3 wt.% of Cloisite 30B used as compatibilizer and filler, respectively.

2. Experimental part

2.1. Materials used

PLA was supplied in pellets form by NatureWorks under the trade name 7001D. The polymer is semi crystalline having the following properties: density = 1.25 g/cm^3, MFI = 6 g/10 min (210 °C, 2.16 kg), $T_g = 60$ °C and $T_m = 160$ °C.

PHBV was manufactured by Tianan Biological Materials Co. Ltd. (China) and commercialized in pellets form under the trade name ENMAT Y1000P. According to the manufacturer, PHBV has the following properties: density = 1.25 g/cm^3, $T_g = 8$ °C and $T_m = 165$ °C. This grade has been comprehensively characterized in a recent paper [23].

Cloisite 30B (C30B) is an organically modified montmorillonite, which is commercially available and supplied by Southern Clay Products (Texas). C30B is a montmorillonite modified with bis-(2-hydroxyethyl)methyl tallow alkyl ammonium cations. C30B was dried under vacuum at 60 °C for at least 24 h before any use.

Maleic anhydride (MA) and dicumyl peroxide (DCP) were obtained from Sigma–Aldrich and used as received.

PHBV-g-MA was prepared by reactive extrusion in the laboratory according to the process previously described in the literature [21]. The MA content was 0.29 wt.%.

2.2. Sample preparation

Prior to use, all materials were dried under vacuum at 60 °C for 24 h. Drying was necessary in order to minimize the hydrolytic degradation of the polymers during melt processing. The samples of various blend compositions shown in Table 1 were prepared in an internal mixer according to the procedure previously described [21]. The mixing temperature, screw speed and residence time were set at 180 °C, 50 rpm and 8 min, respectively. The resulting materials were ground into pellets. Prior to compression molding, the pellets were dried under vacuum at 60 °C and compression molded in a Carver® hydraulic press at 180 °C under a pressure of 10 metric tons for 3 min to obtain films of about 150 μm of thickness.

2.3. Gamma irradiation test

Gamma irradiation was carried out on circular film samples of almost 20 cm diameter, placed in the ^{60}Co pilot irradiator at the Nuclear Research Center of Algiers (CRNA), Algeria. The samples were exposed to 25, 50 and 100 kGy at a dose rate of 1 Gy h^{-1} in the presence of air at room temperature.

2.4. Technical characterization

2.4.1. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of various film samples were recorded by an FT-IR spectrometer (Shimadzu 8400 M) using 4 cm^{-1} resolution and 40 scans. All spectra were recorded in the absorbance mode in the 4000–400 cm^{-1} region.

2.4.2. Molecular weight measurements by SEC

Size exclusion chromatography (SEC) was used to determine the evolution of molecular weight. The apparatus was equipped with a set of three columns: two ResiPore and one PLgel Mixed C (Polymer Labs.). The detection system was composed by a refractometer and a UV detector. Chloroform was used as an eluant with a flow rate of 0.8 mL/min. The elution profiles were analyzed by the Empower SEC module software (Waters). Calculations were based on calibration curves obtained from polystyrene standards ranging from 200 g/mol up to 6×10^6. The weight-average molecular weight $\overline{M}_w$ and number-average molecular weight $\overline{M}_n$ were obtained from the SEC analysis. The polydispersity index (PDI) was calculated as the ratio of $\overline{M}_w/\overline{M}_n$.

2.4.3. Differential scanning calorimetry (DSC)

DSC analyzes were performed on weighted samples of about 10 mg, using a Mettler-Toledo DSC-882 equipment. The samples were subjected to two heating and cooling ramps starting from −40 °C up to +200 °C and down to −40 °C with a scanning rate of 10 °C min^{-1} under nitrogen atmosphere. In the first run, the samples were heated from −40 to +200 °C at a rate of 10 °C/min. After keeping the temperature at 200 °C for 2 min, the samples were rapidly quenched to −40 °C. In the second run, they were heated at a rate of 10 °C/min to +200 °C. From DSC thermograms, thermal characteristics, i.e. crystallization temperature (T_c), cold crystallization temperature (T_{cc}), crystallization enthalpy (ΔH_c), cold crystallization enthalpy (ΔH_{cc}), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined.

2.4.4. Thermogravimetric analysis (TGA)

TGA experiments were carried out in a thermal analyzer (Setaram TG/DTA 92-10) using a heating rate of 10 °C min^{-1} under nitrogen atmosphere, between 20 and 600 °C. The average sample mass was almost 10 mg.

2.4.5. Nanoindentation test

Nanoindentation testing involves the contact of an indenter on a material surface and its penetration into it to a specified load or depth. In this study, a flattened conical indenter was used. This geometry is well suitable to nanocomposites due to the high contact surface, generally inducing results with a low spread. Both the nanoindentation principle and method used to determine hardness and elastic modulus were described in previous work [24].

2.4.6. Scanning electron microscopy (SEM)

Morphological changes were observed using a Jeol JSM-6031 scanning electron microscope (SEM) to examine the fracture surface of the film samples. The neck region for the broken specimens fractured in liquid nitrogen is parallel to the draw direction in order to reveal the internal morphology. Prior to observation, the fracture surface was coated with a thin gold layer by means of a polaron sputtering apparatus.

2.4.7. Pyrolysis combustion flow calorimeter (PCFC)

Pyrolysis combustion flow calorimeter apparatus from FTT (UK)