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A combined study based on experimental analyses and theoretical calculations on properties of poly (lactic acid) under annealing treatment

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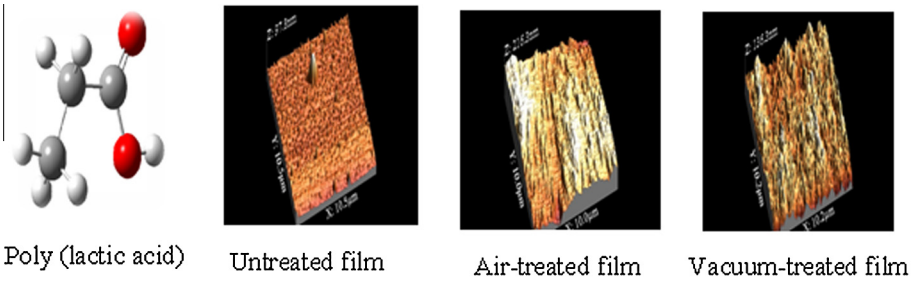
HIGHLIGHTS

- Effects of annealing temperature and environment on surface characteristic of PLA films.
- Density Functional theory (DFT).
- HOMO–LUMO energies and quantum chemical parameters were calculated.
- Thermodynamic properties were studied.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the significance of annealing, in two different atmospheres (air and vacuum), on the surface characteristics of poly (lactic acid) (PLA) films was investigated. X-ray diffraction (XRD) measurements correlated to atomic force microscopy (AFM) observations of the cast PLA films show that thermal treatment under air atmosphere is responsible for a significant increase of crystallinity with the increase of temperature. However, band gap energy of the title compound is slightly affected by annealing at different temperatures. As for the untreated PLA, the molecular geometry was optimized using density functional theory (DFT/B3LYP) method with 6-31g (d) basis set in ground state. From the optimized geometry, HOMO and LUMO energies and quantum chemical parameters were performed at B3LYP/6-31g (d). The theoretical results, applied to simulated optical spectra of the compound, were compared to the observed ones. On the basis of theoretical vibrational analyses, the thermodynamic properties were calculated at different temperatures, revealing the correlation between internal energy (U), enthalpy (H), entropy (S), Free energy (G) and temperatures.

Introduction

Aliphatic polyesters such as poly (lactic acid) (PLA), poly (glycolic acid) (PGA) and their copolymer poly (lactide-co-glycolide) (PLGA) are the most promising biopolymers with a large market potential [1]. Among bio-based polymers, PLA has attracted much attention because of its numerous interesting properties [2]. Its biodegradability and its biocompatibility [3] had made it a suitable material for biomedical and pharmaceutical applications (e.g., sutures, surgical implants, artificial skin, drug delivery systems, biosensors, materials for orthopedics) [4]. Moreover, the PLA good mechanical properties, transparency and compostability [5] have made it more competitive for commercial applications such as packaging, table wares, electronic housing, and automobile interiors [6]. This polymer, which is derived from renewable plant sources (e.g., corn, cassava and sugarcane) [7], can be produced by ring-opening polymerization or by direct condensation [8]. Thus, it

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has the potential to replace conventional petrochemical-based polymers [9]. The building block of PLA, lactic acid (2-hydroxy-propionic acid) [10], can exist in optically active D-or L-enantiomers. Furthermore, the term "poly-lactic acid" refers to a family of polymers: pure poly-L-lactic acid (PLLA), pure poly-Dlactic acid (PDLA), and poly-D,L-lactic acid (PDLLA) [11]. Depending on the proportion of the enantiomers, PLA properties could be modified [12]. Poly (lactic acid) could be amorphous or semicrystalline, but in general, it is semicrystalline [13]. Polymer degradation is affected by simple hydrolysis of the ester bonds and does not require the presence of enzymes [14]. However, enzymatic degradation rate can be reduced by more than 7 times for highly crystalline PLA compared to the amorphous samples [15]. Besides, PLA properties could be improved by the PLA crystallization. In most studies, however, the virgin PLA effect of processing is often neglected [16]. The present work is focused on the effect of annealing treatments on the crystallinity of PLA by varying annealing temperature and atmosphere. The experimental obtained results were completed by theoretical calculations based on density functional theory (DFT) method. In fact, different parameters such as: molecular structure, quantum chemical parameters and HOMO–LUMO energies were performed. We hope from this experimental analyses combined with theoretical calculations to predict the correlation structure–properties of PLA in order firstly, to study if this biopolymer could be exploited as an active layer in biomedical displays. Secondly, we think to study its properties when it is grafted to another biopolymer or organic polymer. The UV–Visible and the simulated spectra of PLA were compared and the thermodynamic properties for different temperature were also studied.

Experimental

Poly (lactic acid) (PLA), with a number average molecular weight (Mw) of 60.000 g/mol, was purchased in pellet form from Sigma–Aldrich (France). Chloroform ($CHCl_3$) as solvent was received from the same company. The PLA (0.1 g) was added to $CHCl_3$ (20 ml). The mixture was reacted under magnetic stirring for few minutes at room temperature. Thus a homogeneous solution of PLA was obtained. After casting some drops on the silica substrate, a solid film was formed for optical and structural measurements. The prepared films were then heated at 45 °C, 105 °C and 195 °C in air and vacuum oven.

Siemens D5000 "PSD" diffractometer (Cu Kα radiation λ = 1.54 Å, generator voltage = 40 kV and generator current = 40 μA) was used to evaluate the crystallinity of the PLA powder and PLA films obtained before and after annealing. The detector was placed on goniometer scanning from 4° to 55°.

Nanoscale characteristics of surface morphology of PLA films have been visualized by atomic force microscopy (AFM). Surface imaging of films was performed in tapping mode (TM-AFM) under ambient conditions on a Multimode SPM Microscope (Nanoscape IIIa, Veeco, France).

Shimadzu spectrophotometer double beam were used to record the optical absorption spectra of PLA films and PLA solution varying from 200 nm to 800 nm.

Theoretical

In this work, DFT with the B3LYP (Becke three-parameter Lee–Yang–Parr) hybrid functional and the 6-31g (d) basis set were used to optimize the geometric structures of polylactic acid (PLA). Optical absorption spectra were calculated using the time-dependent density functional theory (TD-DFT) method based on optimized ground state geometries and were fitted to Gaussian curves within Swizard program. These calculations were performed in the gas phase by the Gaussian 03 package. The HOMO–LUMO energies and the quantum chemical parameters for PLA oligomers were also investigated from calculations. Finally, the thermodynamic properties of the optimized structures were obtained theoretically from the harmonic vibrational frequencies.

Results and discussion

Surface characteristics

In the annealing studies, the effect of the annealing time was evaluated under ambient atmosphere by fixing the annealing temperature at above its glass transition point (105 °C) while varying the annealing time (5, 30 and 60 min). It can be seen from Fig. 1 that, under air annealing at 105 °C, the different time periods are enough to appear a significant peak at around 16.66° for 5 min as annealing time and this peak also shifted to 16.82 for 60 min. In this work, during the annealing process, 5 min as annealing time was adopted for all experiments.

Fig. 2a shows the X-ray spectrum of PLA powder. An important peak at 2θ = 16.78° was observed. The interplanar spacing d and diffraction angle θ is related through Bragg's relation

$$n\lambda = 2d\sin\theta \quad (1)$$

where λ is the X-ray wavelength and n is an integer (in the experiments, λ = 1.54 Å and n = 1 were used) [17]. By using, the above relation, interplanar spacing was evaluated to be 5.26 Å. Other less intense peaks also appeared at 12.50, 14.80, 19.10 and 22.40°, indicating a crystalline structure of PLA. According to the experimental test, this PLA, which is highly crystalline, is not miscible in water as a solvent. This is due to the impermeability of the crystalline region [18]. Actually, it is well known that polymers with high crystallinity are usually less permeable due to their ordered structure [19]. Depending on the stereochemistry, PLA could be either amorphous or semicrystalline. PLA polymers with an L-content greater than 93% tend to be crystalline while those with 50–93% L-lactic acid are strictly amorphous [20]. For a commercial PLA, a blend of a higher amount of L-lactide and a lower amount of D-lactide is used [21]. From these data, we could explain the crystalline structure of the polymer. Based on the differential scanning calorimetry (Fig. 3), PLA (powder) could crystallize in the α-form which is the more stable structure [22] and has a melting temperature T_m about 188 °C. To study the effects of air and vacuum annealing on structural properties and to quantify the crystallinity changes as a function

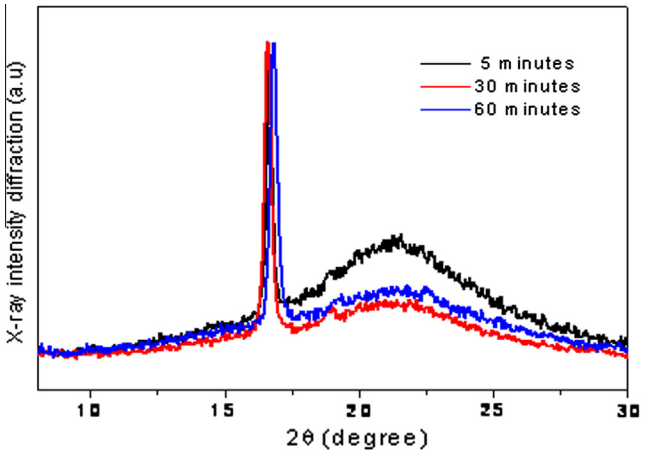

Fig. 1. XRD patterns of PLA films after air annealing at 105 °C for 5, 30 and 60 min as annealing time.