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Radiation-induced graft polymerization of chitosan onto poly(3-hydroxybutyrate)

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ABSTRACT

Chitosan is among the most studied biopolymers and offers important advantages, such as biodegradability, biocompatibility and nontoxicity. In this study, this polysaccharide was grafted onto poly(3-hydroxybutyrate) using the simultaneous gamma-irradiation-initiated polymerization method. The polyester was immersed in diverse solvents, which allowed the preparation of graft copolymers with different yields and crystallinities. A successful synthesis and the estimation of the degree of crystallinity were verified by spectroscopic and calorimetric techniques. The most suitable method was found to be the thermoanalytical approach because it displayed a linear relationship between the degree of crystallinity and the increasing degree of grafting. The results also indicated that the lowest degree of grafting was seen for acetic acid (14.27%), while the highest degree corresponded to ethyl acetate (32.11%). The mechanism of grafting was proposed on the basis of the experimental results.

1. Introduction

Polymeric carbohydrate molecules and polyesters, such as chitosan (CS) and poly(3-hydroxybutyric acid) (P(3HB)), have aroused considerable interest because of their great biodegradability and biocompatibility (Thakur, Thakur, Raghavan, & Kessler, 2014b). However, they have some important drawbacks that significantly restrict their application. The poly(3-hydroxybutyrates) suffer from rigidity and brittleness because of their high degree of crystallinity, hydrophobicity and lack of functional groups. These have strongly influenced and limited their physical properties and consequently have hampered their applications as biomaterials (Hazer, Kiliçay, & Hazer, 2012). In addition, CS is known to be an insoluble polymer that can also be considered a shortcoming (Jayakumar, Prabaharan, Reis, & Mano, 2005). Therefore, there has been increasing interest in the structural research of P(3HB) (Meng et al., 2014) and CS (Thakur, Thakur, Raghavan, 2014b) to overcome these limitations (Ding, Lian, Samuels, & Polk, 2002). Considerable attention has been paid to the reduction of the degree of crystallinity of these materials with the introduction of new functional groups (Bahari et al., 1998; Hsieh et al., 2009; Sudesh et al., 2000; Wada et al., 2007). On the other hand, many studies regarding the modification of CS have been reported on the extension of its application (Alves & Mano, 2008; Mourya & Inamdar, 2008; Thakur & Thakur, 2014c). The use of chitosan derivatives as renewable polymer-based materials also has become attractive because of their advantages, such as environmental friendliness, nontoxicity, biodegradability, and biocompatibility, which makes CS one of the most commercially meaningful carbohydrate polymers (Thakur & Thakur, 2014c; Thakur, Thakur, & Gupta, 2013a; Thakur, Thakur, &

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Gupta, 2013b; Thakur, Thakur, & Gupta, 2014a). These polymers, which are obtained from bio-renewable resources, are usually referred in the literature as bio-based polymers and have been the subject of extensive research efforts (Thakur, Thakur, & Gupta, 2014a; Thakur, Thakur, & Gupta, 2013a; Thakur, Thakur, & Gupta, 2013c).

In addition, it is noteworthy that many techniques and methods have been used recently to modify the P(3HB) and P(3HB-co-HV) structures. Some approaches have attracted widening interest, such as blends (Furukawa et al., 2006; Murakami, Sato, Dybal, Iwata, & Ozaki, 2007); plasma-initiated polymerization (Pompe et al., 2007; Zhang, Kasuya, Takemura, Isogai, & Iwata, 2013); block copolymers (Li et al., 2006); ozone-treated grafting reactions; and ultraviolet and gamma-radiation-induced graft polymerization (Luk, Rondeau, Trau, Cooper-White, & Grøndahl, 2011; Wada et al., 2006). From this perspective, the gamma-radiation-induced method seems to be a more controlled and stable technique to modify the surface and bulk substrate all at once, with radiation doses of at most 10 kGy (Keen et al., 2006; Nasef & Hegazy, 2004; Torres et al., 2014; Yang & Liu, 2004).

Marchessault et al. previously succeeded in the graft polymerization of P(3HB) and chitosan. However, the reaction was carried out by using chemical methods, leading to a conjugate polysaccharide (PS) family (Introduction & Phb, 1991; Yu, Morin, Nobes, & Marchessault, 1999); therefore, the gamma-irradiation method has not been reported to any extent.

Herein, with the purpose of reducing the excessive crystallinity of P(3HB) and widening its processability window, we report on the synthesis of poly(3-hydroxybutyrate) grafted with chitosan by a new method. We have used the simultaneous irradiation method that involves the irradiation of the poly(3-hydroxybutyrate) mixed with another component (in this case a polysaccharide) in the same reaction. This method has the advantages of the easy processability of the samples, obtaining of pure grafted P(3HB) and simplicity of operation. There are some minor disadvantages, such as collateral and undesired homo-polymerization (Li et al., 2006). A simple one-step procedure is developed to irradiate P(3HB) in the presence of chitosan and the selected solvent to investigate the changes in the degree of grafting and crystallinity with variations of the reaction conditions. It is expected that P(3HB)-g-CS will show new properties, which will be investigated by typical spectroscopic and calorimetric techniques.

Vibrational spectroscopy (Fourier-transform infrared (FTIR) and Raman spectroscopy) has shown to be an attractive approach in the understanding of the relationship of molecular dynamics with the conformation of polyhydroxyalkanoates (PHAs) and their derivatives, as well as the study of their structure, as they affect dispersibility and crystallinity (Furukawa et al., 2005, 2006, 2007; Izumi & Temperini, 2010; Kister, Cassanas, & Vert, 1998; Murakami et al., 2007; Suttiwijitpukdee, Sato, Unger, & Ozaki, 2012; Torres et al., 2015a; Unger, Sato, Ozaki, & Siesler, 2011; Xu et al., 2002). Recently, we conducted a detailed investigation of the crystalline characteristics of poly(2-amino ethyl methacrylate hydrochloride) grafted onto P(3HB) by gamma-radiation-induced polymerization (Torres et al., 2015b).

To the best of our knowledge, a successful method of grafting chitosan onto P(3HB) and a study of the degree of crystallinity of P(3HB)-g-CS has not yet been reported. This research is aimed at employing the ^{60}Co gamma radiation-induced-graft polymerization method for the synthesis of grafted P(3HB) with Chitosan. The evaluation of grafting was performed by ^{1}H NMR/Raman spectroscopy. The degree of crystallinity was further determined by using three different methods based on: (a) FTIR, (b) differential scanning calorimetry (DSC), (c) thermogravimetric analysis (TGA), (d) and wide-angle X-ray diffraction (WAXD) techniques.

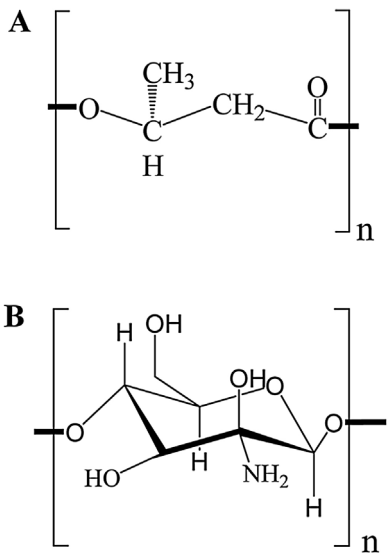

Fig. 1. The chemical structures of: (A) poly(3-hydroxybutyrate) (P(3HB) and (B) Chitosan (CS).

2. Experimental

2.1. Materials and methods

P(3HB) and chitosan, as well as the solvents, were purchased from Sigma/Aldrich Co. and used as received. Typical solvents were employed, such as ethyl acetate, hexane, ethanol, acetone, chloroform and acetic acid. These solvents were named S3, S2, S1, S5, S4 and S6, and the name of the samples was assigned in the following way: the variable P1 was attributed to the reacted P(3HB); correspondingly, Q1 was assigned to the modified chitosan. For example, P1Q1S1 stands for P(3HB)-g-CS carried out in ethanol. All the experiments mentioned here were performed in triplicate to ensure reproducibility (Fig. 1).

2.2. Synthesis of poly(3-hydroxybutyrate) grafted with chitosan

The synthesis of P(3HB)-g-CS was achieved through the simultaneous irradiation method, which is a straightforward irradiation method where both polymers, P(3HB) and CS, were subjected to the same source of ^{60}Co-γ-radiation in air (Gamma Beam 651 PT, Nordion International), which has a dose of 12 kGy and a dose rate of approximately 2 kGy/h (measured with a Fricke dosimeter). In accordance with this, the experiment involved approximately 6 h of exposure time to high-energy radiation. The synthesis procedure uses glass ampoules under vacuum, which were appropriately sealed while containing approximately 100 mg of each polymer and 2 mL of solvent. The synthesized grafting copolymer was washed with chloroform to partially eliminate the un-grafted P(3HB), and the final product was dried to constant weight at 50 °C in a vacuum oven.

2.3. Degree of grafting

The degree of grafting Y (%) was estimated by gravimetric analysis using an FA2204B Digital Analytical Balance that permitted the determination of the mass increase ratio of the graft copolymer compared to the initial mass of the sample:

$$Y(\%) = [(m_{P(3HB)-g-Chitosan} - m_{P(3HB)})/m_{P(3HB)}] * 100 \quad (1)$$