



Graft copolymerization of ethyl acrylate onto tamarind kernel powder, and evaluation of its biodegradability



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ABSTRACT

In the present study, tamarind kernel powder and ethyl acrylate were reacted by free radical polymerization to synthesize a grafted copolymer soluble in water. The grafted copolymer was analyzed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR); FTIR showed a shift of the vibration of R–CO–OR' from 1258 cm⁻¹ to 1253 cm⁻¹. This shift appeared because of the grafting copolymerization. Films were prepared to study the mechanical properties and the biodegradation of this material. The mechanical properties of the grafted copolymer were found to lie between those of the parent polymers, suitable for disposable products. The new grafted copolymer manifested a steady process of biodegradation under incubation with the bacterial strain *Alicyclophilus* sp. BQ1; this was proved by scanning electron microscopy (SEM) and near infrared spectroscopy (NIR).

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1. Introduction

The greater durability of synthetic polymeric materials compared to traditional, naturally-occurring materials causes serious environmental pollution due to discarded, undegraded polymers (Okada, 2002). In spite of recycling programs, most plastics still end up in municipal landfills, creating the problem of finding suitable landfill sites (Wu, 2012; Fang et al., 2005). Considerable effort has gone into developing biodegradable polymers that degrade more rapidly in the environment when discarded (Rutot, Duquese, Ydens, Degeé, & Dubois, 2001). One technique used is graft copolymerization of synthetic monomers to natural polymers.

Copolymerization, as a modifying chemical reaction, has been used to transform the properties of natural raw materials (Princia et al., 2005; Mishra & Bajpai, 2005; Nishioka, Minami, & Kosai, 1983; Ghosh, Sen, Jha, & Pal, 2010). Indeed, graft copolymerization has become an important resource for developing advanced materials, as it can improve the functional properties of polysaccharides (Chang, Hao, & Duan, 2008; Da Silva, De Paula, & Feitosa, 2007; Geresha et al., 2004), and has generated a new industry interested

in vanguard research in biopolymers to increase the use of agricultural materials and their by-products and so reduce consumption of unsustainable synthetic materials.

Many agricultural products can be used in copolymers through blending with one or more additional materials. The main components of these biopolymers are storage and structural polysaccharides. Storage polysaccharides include starch and glycogen, whereas structural polysaccharides include cellulose, chitin and glucan (these polysaccharides differ in the types of linkages between the monomers; Flieger, Kantorova, Prell, & Rezanka, 2003). Natural polymers that are currently being investigated are cellulose, chitin, and agricultural products like starch, wheat and soybean proteins, and milk, among others. Starch and cellulosic fibers are the most commonly-used polysaccharides from renewable resources (Kochumalayil, Sehaqui, Zhou, & Berglund, 2010).

Polysaccharides are unique raw materials since they are the most abundant natural polymers, inexpensive, widely available in many countries, renewable, stable, hydrophilic, and modifiable (Abo-Shosha, Ibrahim, Allam, & El-Zairy, 2008). Because starch is produced by plants it is susceptible to biodegradation (Bogaert & Coszach, 2000). Lignin is another polymer that has been explored in the search to prepare a novel polymer blended with starch (Vengal & Srikumar, 2000). However, by using materials like starch, the polymer industry might come into competition with food industries and cause problems in the future. Therefore, an alternative source of polysaccharides is required.

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The polysaccharide from the tamarind seed is an important by-product of tamarind processing, but in some countries (e.g. Mexico) it is considered waste. The tamarind seed polysaccharide is a natural polymer obtained from the endosperm of *Tamarindus indica* L. Compositional analysis of tamarind kernel powder (TKP) shows that it contains carbohydrates (61.5–72.2%) (Ishola, Agbaji, & Agbaji, 1990; Bhattacharya, Bal, & Mukherjee, 1993), protein (15–20.9%), moisture (11.4–22.7%), ether extract (3.9–8%), crude fiber (2.5–8.2%), and an ash content of 2.4–4.2%. In terms of its carbohydrate structure, hydroxyls constitute the main functional groups, and are considered reaction points that are available to improve the properties of this natural polymer. Seeds of the tamarind fruit (*T. indica*) contain a cell wall storage polysaccharide that is composed of a (1 → 4)-β-D-glucan backbone substituted with side chains of α-D-xylopyranose and β-D-galacto-pyranosyl (1 → 2)-α-D-xylopyranose linked (1 → 6) to glucose residues (Jana, Lakshman, Sen, & Basu, 2010). Recently, a polysaccharide derived from tamarind seed was envisaged as a high performance biopolymer in various applications (Kochumalayil et al., 2010; Mishra & Malhotra, 2009; Srinivasan, Ganta, Rajamanickam, Veerabhadraiah, & Varadharajan, 2011). This material has been used in the food industry and in medical applications, such as controlled drug release (Sumathi & Ray, 2002; Avachat, Guyar, & Wang, 2013; Sun, Shy, Xu, & Cao, 2013; Jana, Sen, & Basu, 2014), and recent studies have used the tamarind seed polysaccharide as a mucoadhesive. Ghosh, Sen, Jha & Bal (2010) developed a novel biodegradable polymeric flocculant based on the polyacrylamide-grafted tamarind kernel polysaccharide, while Abo-Shosha, Ibrahim, Allam, El-Zairy, and El-Zairy (2006) reported that tamarind gum/poly acrylic acid have applications as dyestuffs and textile substrates in textile printing.

Ethyl acrylate (EA), meanwhile, is an acrylic monomer used in the manufacture of a variety of polymers and copolymers as components of many commercially-important products. EA is used not only to improve the physical properties of synthetic polymers, but also to improve the properties of polymers from natural resources, such as wood pulp cellulose fibers and other renewable materials. Goñi, Gurruchaga, Vázquez, Valero, and Guzman (1994) studied the efficiency and conversion of the graft copolymerization of ethyl acrylate/alkyl methacrylate onto amylose. Gurruchaga, Goñi, Valero, and Guzman (1992) developed biocompatible materials by grafting hydroxyl methacrylates/ethyl acrylate onto amylopectin. Also, Singha and Rana (2012) functionalized cellulosic fibers by graft copolymerization of acrylonitrile/ethyl acrylate and studied moisture absorption behavior and chemical resistance in different environments.

Despite these studies and applications involving acrylates and polysaccharides, chemical reactions or physical mixtures of EA and the TKP polysaccharide have not been developed, and their subsequent degradation has not been studied.

Thus, the aim of this work focused on the chemical modification of a polysaccharide derived from a renewable resource, TKP, by grafting it with EA to synthesize a new copolymer in order to produce biodegradable films. Biodegradability of the grafted copolymer was evaluated by subjecting the material to cultures of the bacterial strain *Alicyclophilus* sp. BQ1, a dump-site insolated bacterium.

2. Experimental

2.1. Materials

Tamarind seeds were collected from waste industry in Mexico, separated manually from the pulp, and soaked in water at 90 °C before removing the testa. Next, the seeds were sun-dried for 4 h, in

which the moisture at the beginning was of 12% and at the final was controlled up to a 4% and subsequently dried in an oven (Scorpion Scientific A50980) at 35 °C for 4 h more. They were then ground and separated using a mesh sieve USA—no rigorous (mant inox) series 30, 40, 50, 60, 80 and pan, helped by a rot-tap (U.S. Standard model KH59986-60) with horizontal and vertical automatic stirrer. The separating procedure was done according to ASAE Standards (1995), where 100 g. of flour was separated during 12 min. with no-rigorous stirring. The solids passed by the mesh sieve 80 were used. The monomer of ethyl acrylate was distilled in a vacuum to remove the inhibitor. The ethyl acrylate and solvents (acetone, toluene, xylene, *n*-propanol, ethanol and methanol) used in the experiments were provided by Sigma-Aldrich.

2.2. Graft copolymerization

The copolymer was prepared via free radical polymerization, with EA as the synthetic monomer and TKP as the natural polymer in a mass concentration of 70:30 (P7:3). Synthesis was conducted in solution with azobisisobutyronitrile (AIBN) as the initiator. Before polymerization, nitrogen was bubbled through the reaction mixture to remove any dissolved oxygen.

2.3. Characterization

2.3.1. Infrared spectra

Infrared spectra were recorded with an ATR-FTIR Bruker Vector spectrometer on films of TKP, PEA and the P7:3 graft copolymer. All the films were vacuum-dried for 2 h at 2 kPa.

2.3.2. Nuclear magnetic resonance

NMR spectra was recorded in a Bruker Avance 400 spectrometer, solution (PEA) and HR-MAS (P7:3) probes (BBI 5 mm with Z gradient and HR-MAS 4 mm) were used; in both techniques ¹H proton spectra were taken. PEA was taken in CDCl₃ and P7:3 were swollen in D₂O. Each sample was put in a 4 mm zirconia rotor and spun at 5 kHz.

2.3.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to analyze the surface and cryogenic fracture microstructures on the films with a JEOL KSM-6060LV microscope with secondary electrons. The samples were coated with gold using a vacuum sputter-coater.

2.3.4. Thermal analysis

Thermal analysis data were measured by thermogravimetry (TGA, TA Q5000IR Instrument) and modulated differential scanning calorimetry (MDSC, Q100). All measurements were performed under a nitrogen atmosphere. The heating rate for TGA analysis was 10 °C/min, and the temperature ranged from 25 °C to 550 °C. During analyses, a platinum crucible was used. For MDSC analysis, the heating rate was 3 °C/min, and the temperature range was –70 °C to 270 °C. For this analysis, the sample was contained in an aluminum crucible.

2.3.5. Tensile test

For tensile tests, specimens were prepared by die-cut (from the films) according to the ASTM 1708 norm. Five specimens were tested for each sample. The surface of all the samples was free of visible imperfections. Before the samples were tested for tension, they were dried in a Thermo Scientific vacuum oven at 40 °C and 20 kPa. Tensile tests were conducted using an Instron 5500R machine at a testing speed of 10 mm/min.

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