

VARIOUS TECHNOLOGICAL
PROCESSES

Photocatalytic Degradation of Polyhydroxybutyrate Films Using Titanium Dioxide Nanoparticles as a Photocatalyst¹

Zainab Hussain^a, Gamal A. El-Hiti^{b*}, Ahmed Ahmed^c, Nadia Altaee^d,
and Emad Yousif^{e**}

^a Department of Chemistry, College of Science, Misan University, Misan 62001, Iraq

^b Cornea Research Chair, Department of Optometry, College of Applied Medical Sciences, King Saud University,
P.O. Box 10219, Riyadh 11433, Saudi Arabia
*e-mail: gelhiti@ksu.edu.sa

^c Polymer Research Unit, College of Science, Al-Mustansiriyah University, Baghdad, Iraq

^d Department of Horticulture and Garden Engineering, College of Agriculture,
Al-Qasim Green University, 51002 Babil, Iraq

^e Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq
**e-mail: emadayousif@gmail.com

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Abstract—Photocatalytic degradation of polyhydroxybutyrate (PHB) polymeric films (30 μm thickness) containing different concentrations of titanium dioxide (TiO_2) nanoparticles under ultraviolet (UV) irradiation ($\lambda_{\text{max}} = 313 \text{ nm}$) has been studied. The activity of TiO_2 (0.001–0.005%) as a photocatalyst was determined by monitoring various functional group indices, weight loss in polymeric films and photodegradation rate constant (k_d) with irradiation time. Photodegradation was found to be highly dependent on the TiO_2 nanoparticles concentration and the UV irradiation time. The rate of PHB sample photodegradation was highest when the concentration of TiO_2 was 0.005% (by weight) and lowest when its concentration was 0.001%.

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INTRODUCTION

Degradation of pollutants in the presence of a photocatalyst (e.g., semiconductor metal oxides) has sparked a great interest in the scientific community recently. It has been proposed that semiconductor metal oxide nanoparticles have unique characteristics including catalytic, mechanical, thermal, electronic, magnetic, and optical properties [1–4]. In addition, they have the potential to be used in photo-electronic and gas-sensor devices [1–4]. Titanium dioxide (TiO_2) and zinc oxide (ZnO) are the most commonly used semiconducting metal oxides as they are highly stable and exhibit effective catalytic properties [5]. The use of such metal oxides and in particular TiO_2 as photocatalysts can be very useful at solving numerous environmental problems. For example, they can be used in air

and water purification systems [6] as they have the ability to trap and photocatalyze undesirable organic materials including acids, aldehydes, alcohols, amines, and herbicides. Therefore, carrying out these purification processes could help reduce or even eliminate the hazards associated with the presence of undesirable organic compounds in water and/or air systems [6]. This is achieved as they are converted to carbon dioxide, water, and simple organics [7–9]. Due to the electronic structure of semiconductors, they become valuable scientific tools to allow the investigation of photochemical reactions. They are particularly useful in light induced redox reactions which can be portrayed by empty conduction bands and filled valence bands. The energy difference between these two bands is referred to as a band gap (i.e., threshold energy).

Semiconductor photocatalysts can absorb impacting photons that have energies equal to or higher than its

¹ The text was submitted by the authors in English.

band gap. Each photon with a certain wavelength (i.e., possessing the required energy) can hit an electron in the occupied valence band exciting it to the unoccupied conduction band. As a result, positive valence band holes and excited state conduction band electrons will be obtained [10–12]. Such process initiates the photodegradation reaction of organic materials in the presence of semiconductor metals.

Polyhydroxybutyrate (PHB) is water insoluble thermoplastic. It decomposes using acids and bases. PHB can be degraded at temperatures higher than its melting point, 175°C [13]. The biodegradation of PHB produces carbon dioxide, water and methane [14]. Biodegradation of PHB can be achieved using microorganisms in soil [15] and could be accelerated using plasticizers [16]. In this paper, the degradation of PHB produced from *Rhodococcus equi* cells grown on crude oil [17] was investigated as part of our containing research in the area of polymeric materials [18–23].

EXPERIMENTAL

General

A Shimadzu UV-Vis 160A-Ultraviolet Spectrophotometer (Shimadzu Cooperation, Kyoto, Japan) was used to record the ultraviolet-visible (UV-Vis; 200–1100 nm) spectra. The Fourier transform Infrared (FT-IR; 400–4000 cm^{-1}) were recorded on FTIR-8300 Shimadzu Spectrophotometer (Shimadzu, Tokyo, Japan).

Pure PHB

Pure PHB (Fig. 1) was extracted with chloroform from *Rhodococcus equi* in the presence of crude palm kernel oil (CPKO; 1%) which served as a carbon source [17,24]. The purity of PHB has been checked using gas chromatography (GC) and its structure was confirmed by various spectroscopic techniques. The weight average was measured using gel permeation chromatography and was found to 642 kDa, while, the average mass was 373 kDa. The nuclear magnetic resonance (NMR) spectral data were found to be consistent with those already published [23]. ^1H NMR (500 MHz, CDCl_3) δ , ppm: 5.28 (sextet, $J = 5.5$ Hz, 1H, CH), 2.61 (d.d, $J = 15.0, 7.5$ Hz, 1H, 1H of CH_2), 2.50 (d.d, $J = 15.0, 5.5$ Hz, 1H, 1H of CH_2), 1.29 (d, $J = 6.5$ Hz, 3H, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ , ppm: 169.2 (s, C=O), 67.6 (d, CH), 40.8 (t, CH_2), 19.8 (q, CH_3).

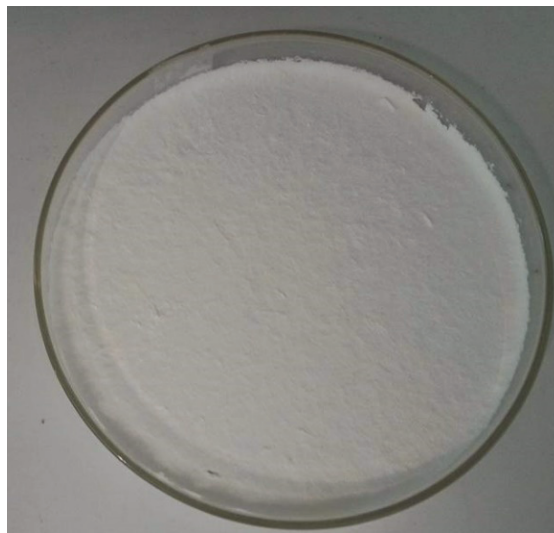


Fig. 1. Pure PHB extracted from *R. equi* cells in the presence of CPKO.

Film Preparation

The PHB films (30 μm thickness) were prepared with a micrometer (Digital Vernier Caliper 2610A; Vogel GmbH, Kevlaer, Germany). Aluminum plate stands (Q-Panel Company, Homestead, FL, USA) were used to fix the PHB films [25].

Accelerated Testing Technique

Accelerated weather-meter QUV tester (Q-Panel Company; Homestead, FL, USA) was used to irradiate the PHB in air at 6.02×10^{-9} $\text{ein dm}^{-2} \text{ s}^{-1}$ as light absorption intensity. The tester is composed of a stainless steel plate with three holes (two in the front side and one at the back). It is also equipped with two UV-B 313 fluorescent ultraviolet lamps (one at each side; 40 W). The maximum wavelength was fixed at 313 nm and the spectrum range was 290–360 nm. The PHB samples were fixed vertically and parallel to the lamps. To ensure that the incident light intensity is consistent, samples were occasionally rotated [26,27].

Photodegradation Measuring Methods

Measurement of PHB photodegradation rate using IR spectrophotometry. The progression of photodegradation of PHB films was followed by FTIR spectra (400–4000 cm^{-1}). The changes in absorption bands for carbonyl (1720 cm^{-1}), polyene (1631 cm^{-1}) and hydroxyl (3400 cm^{-1}) were monitored *versus* irradiation time. The polyene (I_{PO}), carbonyl (I_{CO}) and hydroxyl (I_{OH}) indices were calculated by the comparison between reference