

Photoprotective effect of starch/montmorillonite composites on ultraviolet-induced degradation of herbicides



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ABSTRACT

Despite the extensive research about polymer/clay composites and nanocomposites, there have been few investigations devoted to the resistance of these hybrids against ultraviolet radiation. This property is especially of interest for materials based on biodegradable polymers since they could be applied for slow release of light-degradable molecules, such as herbicides. This paper describes the photoprotective effect of starch/montmorillonite composites on the ultraviolet-induced degradation of ametryne, a commercial herbicide. The starch/montmorillonite composites highly loaded with ametryne (50% by weight), and different contents of clay were produced by the starch gelatinization method. The results showed that encapsulation of ametryne by starch/montmorillonite composites is simple and possible to be done as a one-step procedure. It was shown that the main photodegradation mechanism involves herbicide volatilization, which was significantly reduced due to formation of composites with starch and montmorillonite. The composite presented a synergistic photoprotective effect between components. ¹³C solid-state nuclear magnetic resonance (¹³C-NMR) and FTIR spectroscopy indicated that the photoprotective effect is based on absorption of ultraviolet radiation by starch/montmorillonite composites, and not due to herbicide interaction with the hybrid structure. The novel composites for controlled or slow delivery of herbicides exhibited a promising efficiency in protecting active inputs against solar light degradation in field.

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1. Introduction

Herbicides have a singular importance in agricultural productivity due to their role in eliminating weeds in crops, which compete with plants for water, light, nutrients and space [1]. An ideal herbicide is one that remains active in the environment for a period of time sufficiently long to control the target weed, but not long enough to cause injuries to crops and environment [1,2]. The susceptibility or resistance of an herbicide against environmental degradation usually determines its residence time in a given culture, and thus its effectiveness in specific plantations [3]. The photostability of herbicides beneath ultraviolet (UV-C) radiation, for instance, is a key property to be controlled, and plays an important role in avoiding excessive and unnecessary application of herbicides in agriculture. Photodegradation is one of the most common degradation processes of pesticides [4]. The sunlight that reaches the surface of the earth contains UV-C rays (290–400 nm) which can degrade pesticides by direct photolysis and indirect photolysis [5–7]. In direct photolysis, the high-energy UV rays are directly absorbed by organic compounds, causing a chemical reaction. In indirect photolysis,

the radiation is absorbed by photosensitizers solutes, resulting in the formation of reactive intermediates that react with the organic compounds [6]. As a result, the effect of pesticides on a target pest is diminished, and harmful photodegradation products might be formed and released to the environment [5,6].

Photodegradation of polymers (chain scission and/or crosslinking) is likely caused by activation of polymer macromolecules as a result of photon absorption. The control of this chemical phenomenon is of particular interest, since photodegradation has the potential of facilitating biodegradation by reducing molecular weight and introducing oxygen groups on polymer chain, which also facilitate further chemical degradation [3–10]. In this context, the use of biopolymers as protective agents – where they could serve as a matrix that encapsulates the active compound – has attracted much scientific attention [11–16]. The protective effect of biopolymers is mostly attributed to a sacrificial behavior, i.e., the material blocks ultraviolet radiation by suffering degradation, thereby decreasing the exposure of the active compound. This effect is thus limited, and may demand a large amount of biopolymer in order to achieve a proper final efficiency. On the other hand, inorganic materials may act as photoprotective agents by pathways involving reflection of incident radiation or excitation/decay of electronic levels [17]. Generally, a well-dispersed inorganic phase may reduce ultraviolet-induced

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reactions by absorbing part of the spectrum, avoiding transference of energy to the active compound. This effect may also be particularly useful in biopolymers, since the production of nanocomposites using inorganic phases (for instance, exfoliated clays) has been extensively reported in the last few decades [18,19]. However, to the best of our knowledge there are only few studies devoted to the photoprotective effect of dispersed clays on biopolymers and, specifically, their shielding effect when applied as a host matrix for light-degradable compounds, such as herbicides.

In this study starch/montmorillonite composites were prepared by the starch gelatinization method without the use of plasticizers, with the aim of serving as a host matrix to improve the photostability of ametryne, a commercial herbicide. Starch was chosen because it is an abundant, renewable, and biodegradable polymer obtained from many agricultural sources, thereby being convenient for scaled up applications [11,21–25]. Furthermore starch is a hydrophilic biopolymer, and montmorillonite readily suffers exfoliation in aqueous medium, then compatibilization between starch and montmorillonite was expected to occur spontaneously, without the use of compatibilizers [27,28]. Different factors affecting the photostability of the starch/montmorillonite/ametryne composites were examined. The discussion was based on structural, thermal, and spectroscopic characterizations of the composites before and after exposure to UV-C radiation.

2. Experimental

2.1. Materials

Ametryne (aqueous solution, Metrimex 500 SC) was supplied by Nufarm. Montmorillonite (Mt) (Bentonite, Drescon S/A) was purchased from Drilling Products, and regular corn starch (St) (Amidex 3001, 30% amylose and 70% amylopectin) was kindly supplied by Corn Products Brazil. All these materials were used as received.

2.2. Preparation of ametryne-loaded composites

Starch/montmorillonite composites were obtained by starch (St) gelatinization following the procedure described by Giroto et al. [26]. Briefly, starch was first dispersed into distilled water (5 wt.%) using mechanical stirring for 15 min, and then heating the dispersion to approximately 90 °C for 30 min until formation of a sticky starch gel. The temperature was then decreased to 70 °C and montmorillonite (Mt) was added to the gelatinized starch gel. Since Mt is dispersible in water, its compatibilization with starch gel was done by vigorous shaking in a similar manner as proposed by Valadares et al. [27] and Bragança et al. [28] for natural rubber nanocomposites. Ametryne (Amet) was added at a concentration of 50 wt.% (with basis on the total mass of the composite) to the starch gel simultaneously with Mt in order to accomplish encapsulation of the herbicide into the St/Mt composite structure. The gelatinized formulation was then stored at 50 °C into an air circulating oven for at least 72 h to obtain a dried solid material. All samples were prepared using the same procedure. The different ratios of St and Mt ($w \cdot w^{-1}$ basis) are listed in Table 1. All samples were dried at 50 °C and stored in dry boxes prior to characterizations. The final water content in the composites was approximately 4%.

Table 1
Mix design used in the production of composites.

Samples	Amount (g)			
Starch (St)	15	15	15	15
Montmorillonite (Mt)	0	15	30	60
Ametryne (Amet)	15	30	45	75
Designation	St/Amet 1:1	1:1:2 Amet	1:2:3 Amet	1:4:5 Amet

2.3. Experiments of degradation induced by UV-C radiation

Composites samples were exposed to UV-C radiation in a chamber (40 cm × 60 cm) set at constant temperature of 25 °C and relative humidity of 65%. Eight parallel tube lamps (16 W each) were positioned at the top of the chamber at a distance of 22 cm to the sample surface. The samples were irradiated continuously for 8 days [29] and the weight loss was monitored using an analytical scale. Afterwards, the samples were removed from the chamber, and characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and solid state ^{13}C NMR spectroscopy (NMR). The parameters used for each technique are described hereafter. All irradiated samples were designated with the acronym (irr).

2.4. Characterizations

The morphology and relative element concentration of the samples were assessed by scanning electron microscopy (SEM) using a JSM 6510 microscope (JEOL) equipped with an EDX analysis system (Thermo Scientific NSS coupled or linked). Samples were previously fixed onto carbon tapes, and coated with thin layer of gold in an ionization chamber (BALTEC Med. 020). The imaging by SEM was carried out using the secondary electron mode. X-ray diffraction patterns were obtained on a Shimadzu XRD 6000 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405$ nm). The measurements were performed using a scanning speed of $1^\circ \cdot \text{min}^{-1}$ in the 2θ range of 3–40°. The X-ray tube was excited with a voltage of 30 kV and current of 30 mA. Thermal degradation of samples was evaluated in the range 25 °C–600 °C using a Q500 analyzer (TA Instruments, New Castle, DE, USA) under the following conditions: sample size of 10.0 ± 0.5 mg, synthetic air atmosphere (80% N_2 and 20% O_2) with flow of $60 \text{ mL} \cdot \text{min}^{-1}$, and heating rate of $10^\circ \text{C} \cdot \text{min}^{-1}$. The vibrational spectra were obtained with a Shimadzu FTIR-8300 spectrometer in the range 4000–400 cm^{-1} . KBr pellets were prepared by mixing 5 mg of sample with 200 mg of anhydrous KBr. Structural analyses were conducted by solid state ^{13}C NMR spectroscopy using a spectrometer Varian Inova 400 model (9.4 T). The ^{13}C -NMR spectra were obtained at ^{13}C core with the CPMAS technique and high-power decoupling under the following conditions: pulse of $\pi/2$ of 4 μs , contact time of 1 ms, 16,384 points, and repetition time of 3 s. Samples were measured in a 5 mm ZrO rotor, rotation in magic angle of 10 kHz, 2048 transients and $\text{lb} = 20$. The chemical shift values were calibrated using hexamethyl benzene (HMB) at 17.2 ppm.

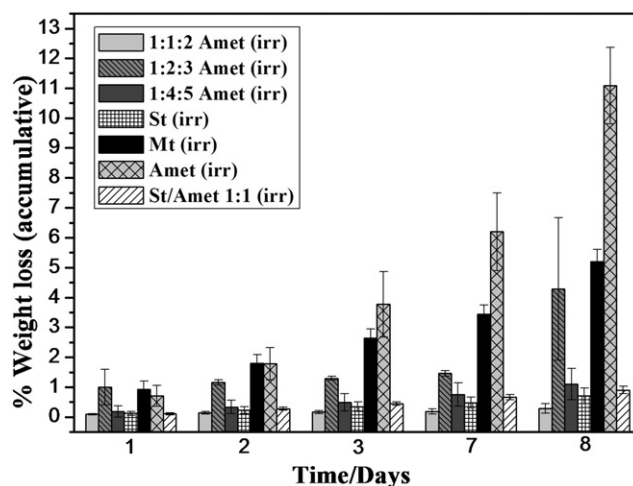


Fig. 1. Percentage of accumulative weight loss of samples exposed to ultraviolet (UV-C) radiation.

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