Carbohydrate Polymers 137 (2016) 127–138

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Utilization of starch films plasticized with urea as fertilizer for improvement of plant growth

Piotr Rychter[a,*], Marta Kot[a], Krzysztof Bajer[b], Diana Rogacz[a], Alena Šišková[c], Janusz Kapuśniak[a]

[a] *Jan Długosz University in Częstochowa, Faculty of the Mathematics and Natural Sciences, Institute of Chemistry, Environmental Protection and Biotechnology, 13/15 Armii Krajowej Av., 42-200 Częstochowa, Poland*
[b] *Institute for Engineering of Polymer Materials & Dyes, 55 M. Skłodowskiej-Curie Av., 87-100 Toruń, Poland*
[c] *Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava 45, Slovak Republic*

ARTICLE INFO

Article history:
Received 29 July 2015
Received in revised form
21 September 2015
Accepted 14 October 2015
Available online 19 October 2015

Keywords:
Urea
Fertilizer
Starch-based polymers
Slow release of agrochemicals
Waste management
Biodegradable mulching films

ABSTRACT

The utilization of starch films, obtained by extrusion of potato starch with urea as plasticizer, for the fertilization of plants has been undertaken. Release rate of urea from the starch films was conducted in water conditions. The molecular weight distribution, surface erosion and weight loss of the starch samples have been determined. The evaluation of efficiency of urea as a fertilizer in the process of release from the starch films was performed under laboratory conditions based on the plant growth test proposed by OECD 208 Guideline and the PN-ISO International Standard using oat and common radish.

Although among extruded starch-based films, those that contain the highest amount of fertilizer hold the most promise for a delayed release system, the time of release of fertilizer from obtained films in undertaken study was not satisfactory. All the same, in the present study effort has been made to utilize extruded samples as a fertilizer for agriculture or horticulture purposes. Urea-plasticized starch was successfully used as a fertilizer. Plant growth assessment, including determination of such parameters as fresh and dry matter of plants and their visual evaluation, has proved the stimulating effect of using extruded films on the growth and development of cultivated plants.

1. Introduction

Currently, Europe is facing tremendous environmental challenges. Plastic products have become one of the most used materials in all the major branches of industry. Conventional polymers are utilized in more and more applications, such as packaging, building and construction, automotive, agriculture, machinery engineering or household appliances. But, the growing use of these nondegradable materials and their additives is inevitably connected with the increasing number of landfill sites, resulting in a negative impact on the environment through water or land pollution (Lithner, 2011; Swift & Wiles, 2002). Recently, biodegradable polymers have been intensively studied as an alternative to the more conventional, slow-degrading synthetic polymers that have a negative effect on the living organisms (Adams, Biddinger, Robillard, & Gorsuch, 1995; Seretoudi, Bikiaris, & Panayiotou, 2002).

Among the commercially available biodegradable polymers, the polyhydroxyalkanoates (PHAs), polylactide (PLA), polybutyleneadipate-co-terepthalate (PBAT) or starch-based polymers are more and more popular, finding acceptance among consumers (Auras, Lim, Selke, & Tsuji, 2011; Sabu, Kuruvilla, Malhotra, Goda, & Sreekala, 2014; Urtuvia, Villegas, González, & Seeger, 2014).

The main advantage of using these materials is no toxicological impact of degradation products after disposal, but it must be noted that only very few publications deal with the eco-toxicity of degradation products of bio-based polymers (Fritz, Sandhofer, Stacher, & Braun, 2003; Rychter et al., 2006; Rychter, Kawalec, Sobota, Kurcok, & Kowalczuk, 2010; Tuominen et al., 2002).

Among them, starch – a cheap, easily available and biodegradable natural polymer – arouses interest. It has been widely accepted as a bio-based component in plastic formulations in packaging and agricultural fields, in particular in blends with other biodegradable or low toxic, biocompatible polymers such as polylactide, polycaprolactone, polyurethanes or poly(ethylene oxide) (Peelman et al., 2013; Yu, Prashantha, Soulestin, Lacrampe, & Krawczak, 2013; Zia, Zia, Zuber, Kamal, & Aslam, 2015).

* Corresponding author.
E-mail address: p.rychter@ajd.czest.pl (P. Rychter).

http://dx.doi.org/10.1016/j.carbpol.2015.10.051

Various attempts have been carried out to produce biodegradable thermoplastic materials based on starch using natural plasticizers and commercial fibers by extrusion, injection molding and solution casting techniques (Avérous, 2014; Nafchi, Moradpour, Saeidi, & Alias, 2013; Theubaud et al., 1997; Wang, Cheng, & Zhu, 2014). Nevertheless, the constantly growing application of starch-based products has kindled the concern about their management after usage. Recently, organic recycling, known as the composting process, has been attracting interest as one of the methods of treating waste from starch materials (Ganjyal, Weber, & Hanna, 2007; Iovino, Zullo, Rao, Cassar, & Gianfreda, 2008). On the other hand, starch-based polymers have also been widely investigated in controlled release technology of active agents such as medicines, pesticides or fertilizer. Sustainable agriculture has been attracting interest to produce abundant food without depleting the earth's resources or polluting its environment. However, maximizing food production is intrinsically connected with the increasing application of pesticides to prevent crop failure and fertilizers to provide the nutritional substances for the intensive growth of plants. Unfortunately, if these active substances mingle with the runoff, it can have a devastating effect on non-target organisms as well (Asada, Kondo, Sasaki, & Nakamura, 2010; Casida, 2009; Innes, 2013; Kolenbrander, 2013). Thus, there is an urgent need to develop new methods to lower the amount of agrochemicals that enter into the environment, thereby help to maintain biological activity at an appropriately desirable level. In this respect the control release systems (CRS) of active substances may represent one of the main future trends in agricultural practice. These systems offer a delayed gradual release of the active contents of pesticides/fertilizers just at the level sufficient for the target, thereby minimizing the pollution of ground and water associated with overdosage (Ades, Kesselman, Ungar, & Shimoni, 2012; El-Mohdy, Hegazy, El-Nesr, & El-Wahab, 2011; Gonzalez et al., 2015; Han, Chen, & Hu, 2009; Niu & Li, 2012).

It is known that controlled release formulation of agrochemicals using native starch (without chemical or physical modification) does not provide satisfying results because of the lack of its appropriate thermoplastic properties. However, in the presence of plasticizers, elevated temperature and shear, native starch starts to exhibit thermoplastic properties like most conventional synthetic thermoplastic polymers; properties required for its application as an extruding, injection molding or blowing material (Gomes, Ribeiro, Malafaya, Reis, & Cunha, 2001; Thymi, Krokida, Pappa, & Maroulis, 2005; Xie et al., 2014).

Besides pesticides, fertilizers are another important factor responsible for increased agricultural productivity. Since nitrogen is a key nutrient that manipulates plant growth, urea is referred to as one of the major nitrogenous fertilizers. The versatility of urea faces this substance, on the other hand as a crucial factor for plant growth (Meessen, 2012), from the other hand is also one of the most popular, natural plasticizers used for chemical modification of starch (Wang et al., 2014). Urea as a fertilizer may be successfully applied in controlled release systems for agricultural purposes (Azeem, KuShaari, Man, Basit, & Thanh, 2014; Gao, Li, Zhang, Wang, & Vhen, 2015).

Table 1
Composition and mechanical properties of plasticized starch films. The values of elongation at break (*E*) and tensile strength (TS) are the mean of five measurements and are given with standard deviation (SD).

Samples	Starch/glycerol %	Urea wt. %	TS (MPa)	*E* (%)
M0	100	0	3.8 ± 0.4	148 ± 7
M1	99	1	6.3 ± 0.5	212 ± 11
M5	95	5	1.6 ± 0.2	242 ± 9
M10	90	10	1.7 ± 0.2	254 ± 13
			$LSD_{0.05}$ = 0.5	$LSD_{0.05}$ = 15

Many approaches have been previously undertaken to obtain starch films modified with urea. But to our knowledge, this study is the first to present the results of the application of urea as a potential plasticizer and fertilizer.

The aim of the present study was evaluation of the possibility of applying starch plasticized with urea as a fertilizer for improving plant growth.

2. Materials and methods

2.1. Materials

The potato starch (superior standard, no. of certificate quality ZN-2005/PPZ SA-1) in was purchased from PPZ S.A. Niechlow, Poland. According to certificate: humidity 18%, content of SO_2 max. 10 mg kg of starch, ash in dry matter <0.35%, harmful metals like Ar, Cd, Pb and Hg: 0.1, 0.1, 0.2 and 0.1 mg/kg of starch respectively. Technical glycerol (Rafineria Trzebinia S.A., Poland) and urea (ZAK S.A. Poland) have been used in this work.

Seeds of oat *Avena Sativa* was purchased in Manufacturing and Trading Company Nieznanice, Malopolska Cultivation of Plants. Seeds of common radish (*Raphanus sativus* L. subvar. radicula Pers.) was purchased in agriculture shop.

2.2. Preparation of films of plasticized starch (PS)

The starch-based material has been prepared as follows: 75% of starch was mixed with 25% glycerol (w/w), and then suitable amount of urea, as given in Table 1, was added. All components were mixed for 10 min by mixer MJI 30 (IMPiB Institute, Poland). The extrusion of resin was processed in single-screw (diameter 45 mm, L/D = 27) extruder provided with six heating zones. The screw rotation speed was maintained at 50–60 rpm. The temperature profile along the extruder was 60°, 115°, 130°, 110°, 110° and 100° from feed zone to die. The value of torque and melt pressure at the screw tip was 80–100 Nm and 25–30 Ba. Obtained pellets with average diameter 3–4 mm have been used for extrusion of flat films using laboratory single-screw extruder PLV 151 (Brabender, Germany). The parameters were as follows: screw with L/D = 25, 4 heating zones, flat die head sheet mold regulated between 0.1–1 mm. The pellets were fed into the extruder and the screw rotation speed was maintained at 60 rpm. The extrusion temperature profile starting from feed zone was 80°, 90°, 100° and 110° (die head). Films of 1 mm thickness and 100 mm width were obtained.

2.3. Mechanical properties of PS

The mechanical properties, including tensile strength (TS) and elongation at break (*E*), of the obtained films were analyzed following PN-EN ISO 527-1-3 by TIRA test (PN-EN ISO 527-1-3, 2012). This standard is typical for the evaluation of tensile properties of plastics films or sheets less than 1 mm thick. The samples were cut from extruded film in machine direction to dumbbell shape type 5. Before analysis, the samples were stored for 24 h in measurement conditions (standard conditions). The results are average of 5 measurements of every sample.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of extruded potato/urea starch films were determined by Fourier transform infrared (Shimadzu IRAffinity-1 Spectrophotometer with MIRacle Attenuated Total Reflectance Attachment). Each film sample was scanned 50 times at a