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Plant polymer biodegradation in relation to global carbon management

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ABSTRACT

Natural polymers such as starch, protein, and algae are renewable and sustainable materials. They are used in many industrial applications such as polymeric blends for films, fibers, and injection molded articles. However, biodegradability of these materials in anaerobic sludge digestion is largely unreported.

Extensive laboratory results were acquired to elucidate biodegradability and biodegradation kinetics of the selected materials according to ASTM D5210. There was no remarkable difference in biodegradability of wheat, native corn, and modified corn starches. For the protein samples, wheat gluten biodegraded to a great extent than soy protein isolate. For the algal samples, *Spirulina* biodegraded to a great extent than *Nannochloropsis*. A first order kinetic equation was used to fit all experimental data.

A separate set of ^{14}C data examined if the carbon source, which is a building-block for all plant polymers, was bio-based (recent carbon) or fossil-based. The former is a part of global carbon cycle, and the latter is believed to cause adverse greenhouse gas effects resulting in global warming.

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1. Introduction

Utilization of natural polymers such as starch, protein, and algae for plastic manufacturing fits well within environmental sustainability strategy. The general susceptibility of almost all natural polymers to degrade in the environment would be advantageous if incorporated into non-durable products such as disposable diapers, wet wipes, tissues, sanitary napkins, feminine care pads, packaging films, and utensils due to their short product usage lifetimes. Polymers recommended for these applications must have inherent properties which facilitate fast biodegradability to meet waste disposal criteria. However, the degree of biodegradation and the kinetics of degradation for a particular polymer are often not available to facilitate the design of polymer articles or products that are intended for such a short period of usage and quick disposal.

Starches such as wheat, corn, rice and tapioca have been widely used in food industry and, in recent years, they have been extensively investigated for thermoplastic polymer blends for a number of applications with varying degrees of success. Initial use of starch as filler for polyethylene resulted in fragmentation of the blends in the environment, but not biodegradation (Kyrikou & Briassoulis, 2007). However, blending of thermoplastic starch with biodegradable polymers such as PLA, PCL, and Ecoflex® resulted in biodegradability consistent with biodegradation testing standards (Briassoultis, 2004). Chemical modification of starch to incorporate additional functional groups results in lower biodegradability of the product than the native counterpart (Tomasik & Schilling, 2004). Examples include carboxymethyl starch, hydroxypropyl starch, oxidized starch and cross-linked starch.

Plant proteins such as wheat gluten and soy protein are used extensively as raw materials for plastics manufacturing. Other natural protein materials such as zein and collagen have been investigated as well, but are less attractive due to high processing and isolation cost. The protein raw materials like wheat gluten and soy proteins contain other constituents, such as dietary fibers and carbohydrates. For example, soy protein isolate (SPI) contains greater than 90% protein, while wheat gluten contains about 75%. Kumar, Choudhary, Mishra, and Varma (2002) reported rapid biodegradation of an injection-molded soy protein article in both the soil and simulated marine environment. The biodegradation rate for the soy protein plastic was observed to be faster than the raw materials, although no explanations were offered for this difference.

The use of algae as a raw material source of biodegradable plastics manufacturing has increased in interest due to its recent applicability to large scale biofuel production. The US patents 2008/0155888 of Vick, Caspari, and Guido (2008) and 2008/0090284 of Hazlebeck and Dunlop (2008), detailed the processing steps to convert algae biomass into fuel. As a result, biomeal from algae biofuel refining processes is expected to be abundantly available, since the estimated quantity is about 0.77 kg for every kilogram of algae processed for biofuel. Therefore, effective utilization of such a waste material becomes an important business venture in the future, with plastic manufacturing being one of them (Skjanes, Lindblad, & Muller, 2007). Unfortunately, there is not much biodegradability information about algae biomass or biomeal in the open literature, to encourage research in this direction.

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One of the primary advantages of using bio-based polymers for products manufacturing is their relative impact on the balance of "old" versus "recent" carbon in the atmosphere (Noakes, Norton, Culp, Nigam, & Dvoracek, 2005). Carbon in plants such as corn and wheat is considered "recent" carbon as it is only fixed for one growing season and represents the natural carbon cycle. Such "recent" carbon would be the base material for biopolymer-based products. However, fossil-based carbon used for polyolefin production is considered "old" carbon as it has been fixed for thousands of years. Introduction of significant amounts of "old" carbon versus "recent" carbon into the atmosphere would further contribute to the causes of global warming.

In the context of "old" versus "recent" carbon, there has been some confusion around the advantages of oxydegradable polymers, or polyolefins incorporated with pro-oxidant additive which makes them photo and/or thermo-degradable upon exposure to sunlight (Scott, 2000; Wiles & Scott, 2006). Polymer fragmentation is observed with these materials over an extended period of time up to several years. However, these materials cannot be considered as biodegradable because the assimilation of oligomers or monomers by microorganisms is not yet substantiated. In addition, there would be little advantage to oxydegradable polymers being truly degradable, as such biodegradation would significantly contribute to the introduction of "old carbon" into the atmosphere and its associated disadvantages.

This technical paper summarizes experimental validation of biodegradation kinetics for some selected starch, protein, and algae samples in anaerobic sludge digestion. The anaerobic digestion is a series of processes in which microorganisms break down carbohydrate material in the absence of oxygen. For a broad application of these materials in personal care products, an understanding of anaerobic biodegradability is essential because the soiled products are usually disposed of in sanitary landfills, where biodegradability mechanisms are predominately in anaerobic conditions. This information is particularly useful for understanding the behavior of these important renewable and sustainable materials in the landfill environment and their utility for plastics manufacturing in non-durable products. In addition, a clear understanding of the relative proportions of "recent" versus "old" carbon comprising these materials will be beneficial for approaches to global carbon management.

2. Experimental

2.1. Materials

Native corn starch, Cargill Gum^{TM} 03460, was purchased from Cargill, Inc. (Minneapolis, MN). Native wheat starch, Midso 50, was purchased from MGP Ingredients, Inc. (Atchison, KS). The hydroxylpropyl modified corn starch, Glucosol 800 polymer, was purchased from Chemstar (Minneapolis, MN).

Vital wheat gluten purchased from ADM (Decatur, IL) is a cream-colored powder consisting of a minimum of 75% proteins, with the remainder being approximately 13% carbohydrate and 8% moisture. Soy protein isolate, PC4200, was purchased from DuPont Soy Polymers (Louisville, KY), containing a minimum of 90% proteins.

Blue-green algae such as *Nannochloropsis* and *Spirulina* were obtained from Seambiotic Ltd. (Tel Aviv, Israel) and Earthrise (Calipatria, CA), respectively. The former thrives in sea-water bodies, and the latter grows in warm, alkaline fresh-water bodies. They are a member of the class Eustigmatophyceae. The algae have both chlorophyll (green) and phycocyanin (blue) pigments in their cellular structure. Once harvested, they are in a form of fine powder with particle size at about 0.25 mm and a bulk density is 0.35–0.6 kg/l.

Digested sludge was collected from the Neenah-Menasha Regional Wastewater Treatment Facility (Neenah, WI) for the proposed investigation. Solids content in the digested sludge was 2.5% with a pH in the range of 7.4–7.8. The sludge color is black because of the presence of organic matter.

2.2. Methods

ASTM D5210 was used to assess plant polymer biodegradation in anaerobic conditions. The sample volume was 100 mL, and the incubation temperature was fixed at 35 °C throughout the experiments. The amount of each polymeric sample was about 0.2 g. The gas evolution data of a combination of carbon dioxide and methane generated during sample anaerobic digestion were averaged from at least three duplicates. The other detailed stepwise procedures were the same as those specified in ASTM D5210 and are not repeated here for the sake of brevity.

For an initial understanding of the carbon source used in plant biomass photosynthesis, a native corn starch and algal sample (*Nannochloropsis*) were sent to the University of Georgia Center for Applied Isotope Studies for ^{14}C determination of the percent bio-based carbon. The detailed testing procedures to determine "old" and "recent" carbon in polymeric samples were those of ASTM D6866.

2.3. Calculations

Biodegradability of the carbohydrate polymers such as starch, wheat gluten, and algae can be estimated according to Eq. (1) shown below:

$$\text{Biodegradability (\%)} = \frac{\sum V_{\text{Sample}} - \sum V_{\text{Blank}}}{V_{\text{Theoretical}}} \times 100 \qquad (1)$$

ΣV_{Sample} is the total CO_2 and CH_4 volume measured from the sample vessel under standard conditions in milliliters. ΣV_{Blank} is the CO_2 and CH_4 volume measured from the blank vessel under standard conditions in milliliters. $V_{\text{Theoretical}}$ is the maximum theoretical volume of the biogas (CO_2 and CH_4) evolved after complete biodegradation of the test material under standard conditions in milliliters. There are residue by-products and biomass formed by microorganisms during the anaerobic sludge digestion, in addition to gaseous products, which is not accounted according to ASTM D5210.

Cellulose is normally used as the reference material so that biodegradation of carbohydrate samples can be compared. $V_{\text{Theoretical}}$ of the 0.2 g cellulose $[(C_6H_{10}O_5)_n]$ was calculated to be 166 mL. The evolved ($CO_2 + CH_4$) volume is dependent on only the carbon amount regardless of the CO_2 and CH_4 ratio (Itavaara & Vikman, 1996; Gartiser, Wallrabenstein, & Stiene, 1998). For samples, actual carbon content (%) was analytically determined and used for $V_{\text{Theoretical}}$ estimates.

3. Results and discussion

3.1. Polymer biodegradation

Anaerobic sludge digestion experiments were carried out to test plant polymer anaerobic biodegradation at a constant temperature of 35 °C with cellulose powder as the reference for the study. Fig. 1 presents the results for all of the starch samples with the accumulated methane and carbon dioxide gases expressed as net amounts following subtraction of the blank samples. The blank sample is defined as digested sludge without the presence of the carbohydrate polymer samples. The points on the graph represent experimental data and solid lines are model fitting results, which will be discussed in Section 3.2.

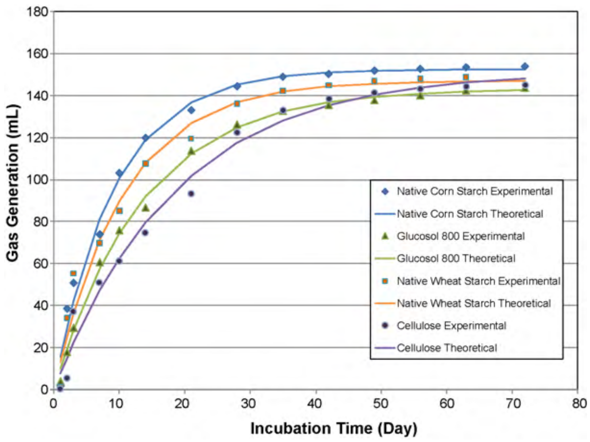

Fig. 1. Anaerobic biodegradation of native wheat, corn and modified starches.

As data in Fig. 1 indicates, all samples achieved 80–90% biodegradation in little over one month as estimated using Eq. (1). The degree and rate of native corn starch biodegradation are faster and more complete than the modified corn starch (Glucosol 800), likely due to the impact of the hydroxylpropyl modification of the latter toward microbial availability. The rate of wheat starch biodegradation lies between those for both native and modified corn starches. The ultimate degree of starch biodegradation is closer to that of cellulose except for the modified corn starch (Glucosol 800), which is slightly lower than the others.

Fig. 2 shows anaerobic biodegradation of two protein samples at 35 °C. Wheat gluten anaerobic biodegradation is accelerated in the earlier stage relative to cellulose but ends with similar percentage of biodegradation. On the other hand, soy protein isolate only achieved about 62% mineralization within 70 days of anaerobic digestion. The results seem to indicate that the protein aggregates are less accessible by microorganisms.

Fig. 3 displays two algae sample biodegradation results. In comparison to cellulose, *Nannochloropsis* showed a lower 40% of biodegradation, likely due to the high amount of lipid content, ca. 37%. On the other hand, *Spirulina* achieved about 70% biodegradation, which is comparable to cellulose. Kinetically, algae biodegradation is slower than the reference cellulose material.

3.2. Kinetic model

U.S. Environmental Protection Agency (1993) uses the LandGEM model to describe annual methane generation from landfills. However, this model cannot be directly used for this study because the gas generation expressed in all figures is calculated on the basis of the accumulated methane and carbon dioxide over the incubation time. A slight modification/rearrangement of the EPA model can be written as below:

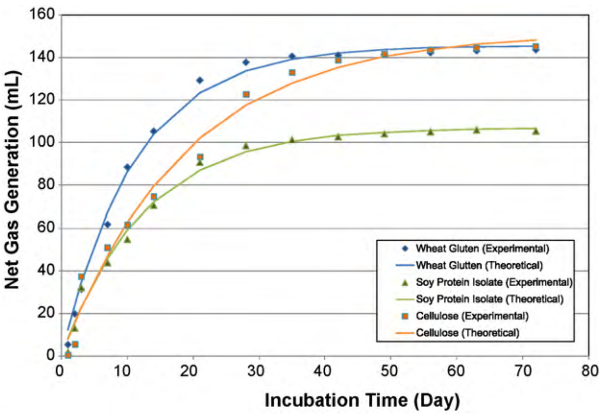

Fig. 2. Anaerobic biodegradation of wheat gluten and soy protein isolate.

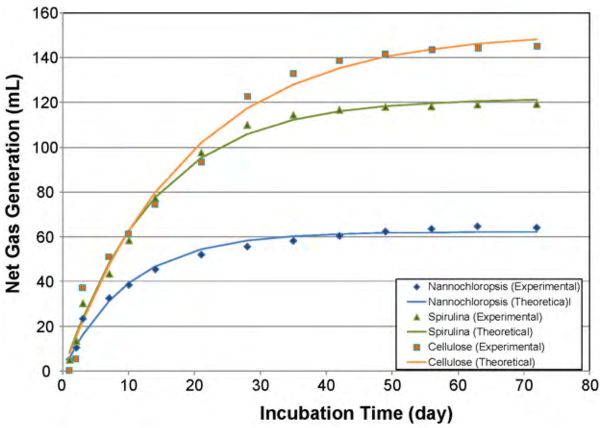

Fig. 3. Anaerobic biodegradation of *Spirulina* and *Nannochloropsis*.

$$q = Q_{\max}(1 - e^{-Kt}) \tag{2}$$

Q_{max} is the total gases generated during the material biodegradation, which can be viewed as an overall parameter, and K is the first order reaction-rate constant. Using the experimental data, these parameters were obtained by non-linear curve fitting to Eq. (2). A good fit was obtained and plotted in the solid lines shown in Figs. 1–3. The key fitting parameters such as Q_{max} and K are listed in Table 1 with the associated root-mean-square-error (RMSE) to illustrate the predictability of the model.

3.3. Bio-based products

In an ideal case, the global carbon cycle is carbon neutral, which means that for every ton of carbon that is produced, it should be locked up in a “carbon sink” at an equivalent amount. Examples of carbon sink are trees and plants. The CO_2 released by animal and human respirations, material decay, burning, etc. is a part of the carbon cycle, and does not contribute to the cause of global warming. Rather, it is the release of CO_2-derived from fossil fuels or “old” carbon due to the operation of automobile and power plants that distorts the carbon balance. Therefore, an effective sequestration of fossil-based carbon becomes important for protection of the environment and the ecosystem.

Fig. 4 shows the distribution of bio-based versus fossil-based carbon for native corn starch (left) and algae-*Nannochloropsis* (right), respectively, according to ^{14}C determinations. The results indicate that the starch contained 96% bio-based carbon from recent/new carbon sources. Thus when such starch-based products complete their service life, their biodegradation will enter the normal global carbon cycle without contributing to adverse greenhouse gas effects. In contrast, the algae (*Nannochloropsis*) sample contained only 11% bio-based carbon, with the remaining 89% carbon coming from fossil or petroleum sources.

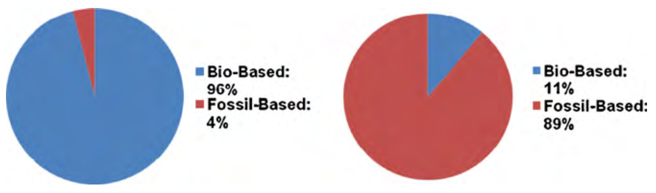

Fig. 4. Mean ^{14}carbon results for native corn starch (left) and Algae-*Nannochloropsis* (right).

Table 1
Biodegradation kinetic parameters obtained using non-linear regression.

Biopolymer samples		Q_{max} (mL)	K (day^{-1})	Goodness of fit (RMSE)
Starch	Glucosol 800	143.5	0.073	2.74
	Native wheat starch	147.4	0.094	7.52
	Native corn starch	152.5	0.108	2.43
Protein	Wheat gluten	145.5	0.090	3.98
	Soy protein isolate	107.1	0.080	3.92
Algae	*Spirulina*	122.0	0.072	3.43
	Nannochloropsis	62.12	0.100	2.77
Reference	Cellulose	151.4	0.053	6.86

The distribution of bio-based carbon and fossil-based carbon content in algae is largely depending on algae cultivation methods. For example, algae need nutrients such as phosphorus (P), nitrogen (N) and CO_2 during their growth stage. If CO_2 is supplied from a power or cement plant and used to feed into an algae cultivation system, algae biomass will contain a high percentage of "old" carbon. The biodegradation data shown in Fig. 4 implies a release of "old" carbon back to atmosphere during anaerobic sludge digestion. Therefore, any methods to store or fix gaseous CO_2 must be carefully examined.

Chiellini, Cinelli, Ilieva, & Martera (2008) used biodegradable polyvinyl alcohol (PVOH) to create composites comprising algae such as *Ulva* armoricana. Consequently, a release of the CO_2 that was sequestrated by algae back into the atmosphere is expected because PVOH and algae composites are biodegradable. However, Zhang, Endo, Kitagawa, Kabeya, & Hirotsu (2000) and Otsuki, Zhang, Kabeya, & Histosu (2004) made a novel composite of *Chorella* and polyethylene, which would permanently fix CO_2 because polyethylene is not biodegradable. Thus, unlike starch or protein-based products, algae-based products will contribute to the global warming if "old" carbon is photosynthesized and when products based on such an algae biomass are biodegraded. This argument is also applicable to other CO_2-derived polymers such as alkyl polycarbonates if CO_2 is not from "recent" carbon sources. Biodegradable blends containing CO_2-based polymers will render the CO_2 sequestration efforts to nil because of the material degradation at the end of its life cycle. Therefore, it is important to use a proper method to permanently store and fix fossil-based CO_2, which can be discussed separately.

The factors that result in global warming are complicated. Many instances such as plant species, nutrients and growing environments can affect the ratio of "recent" carbon/"old" carbon in plants. This paper shows two examples that may stimulate additional research activities in the future.

4. Conclusions

For the starch and protein polymers studied, there are some differences in terms of anaerobic biodegradation rate and percentage of biodegradation. In general, they conform to cellulose biodegradation behavior. Modified starch biodegrades slower than native starch. Algae such as *Nannochloropsis* does not biodegrade as much as *Spirulina*. Studies in different media other than anaerobically digested sludge may be needed to confirm these observations.

The first order kinetics model works well and is useful to predict complete material biodegradation when soiled personal care products are disposed of in the areas such as landfills.

The elucidated bio-based carbon is an important concept to proper global carbon management and for judicious utilization of the renewable and sustainable materials studied in this paper. It is also important to current trends in developing bio-based products. Additional fixation of algae biomass will be another subject of technical discussion. The information presented here will help product life cycle analysis and assessment of the fate of the plant polymers in the environment.

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