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Comparison of kinetic biodegradation of potato starch based and corn starch based low density polyethylene compound in aerated sludge

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ABSTRACT

The biodegradability rates of two different kinds of polyethylene bonded with corn and potato starch are studied in this paper. While it is usual to use soil as the environment for biodegradation, an aerated sludge tank was used in this study which offers a richer microbial medium and increases the rate of biodegradation. The biodegradability is determined by two ways: first, comparing differences in the weight change of two samples, one placed inside distilled water and the other placed in aerated sludge tank. Second test for biodegradation is by examination of FTIR spectroscopy. Through FTIR spectroscopy, the biodegradability rate and reduction in some of the existing bonds in polymer before and after placing the samples inside aerated sludge tank is exhibited and the consumption of polymer by microorganisms is also revealed. Kinetic correlations for both samples are presented which shows that the kinetic rate closely follows limiting first order reactions.

KEYWORDS

Starch;
Biodegradation;
Kinetic;
Low density polyethylene;
FTIR.

INTRODUCTION

In recent years, biodegradable polymers have attracted special attention of researchers with respect to reducing the volume of solid wastes[1,2]. Biodegradable polymers are materials that could be converted to natural compounds such as water, CO2, methane and other biological components by means of microorganisms such as fungi, bacteria, algae and other natural agents[3,4,5].Most of the biodegradable polymers were developed by blending petroleum based polymers such as Low Density Polyethylene (LDPE) with natural biodegradable materials. This method not only conserves the environment, petroleum reservoirs and landscapes, but also decreases CO2 production and presents a green solution in a sustainable development[5].

Study on starch-based synthetic polymers began in 1970s when environmental issues attracted attention[6].Starch is an abundant, biodegradable, capable of recycling and inexpensive natural polymer which is obtainable from many botanical sources[7]. Starch is composed of two parts: amylose and amylopectin whose percentages are different in various kinds. On the contrary to amylose, amylopectin is branched and forms the water soluble part of the starch[8]. The proportion of amylose to amylopectin affects the manufacturing process and properties of the final product[8].

Low density polyethylene is employed in packaging industry, in production of bags, bottles and many other items as well as being used in composites with other materials[9,10,11]. On the other hand, starch is an attractive biopolymer for packaging material and the existence of amylose in starch gives rise to stronger films. However, biodegradable products based on starch, possess weaknesses, mainly attributed to the water solubility, brittle nature of starch films and poor mechanical properties. One of the effective measures to overcome the poor mechanical properties, while preserving the biodegradability of the materials, is to associate starch with chitosan derived from renewable resources to obtain biocomposites[12,13]

Kinetic studies on biodegradability of low density polyethylene bonded with corn and potato starch and blended with Chitosan were studied in this paper using weight loss and FTIR spectroscopy.

Weight loss is a common method to measure the rate of biodegradation. Due to the long time required for a polymer sample to degrade in soil, weight loss in an aerated sludge tank, rich in microorganisms is considered as an accelerated method for studying the biodegradability of the samples[16]. Moreover, FTIR spectroscopy of the samples reveals the rate of degradation of the existing bonds of the compound after exposure to aerated sludge environment[14].

Experimental part

For this study two samples were prepared and used in the experimentations: Low density polyethylene blended with corn starch (20% weight) called as compound A, and low density polyethylene mixed with potato starch (20%weight) and hereinafter named as compound B. The compounds were produced in form of 0.4 mm thick pressurized sheets.

The aerated sludge system consisted of semi-batch tanks equipped with aeration devises supplying dissolved oxygen to a suspension of microorganisms in water. The volume of first tank was 9 liters, half filled with settled urban sewage and half filled with normal tap water. A second tank was filled with distilled water and maintained under the same laboratory conditions in order to verify the effect of rich microbial environment. Two samples from compounds A and B were cut in 4 cm×1.5 cm and weighed accurately. One of them was placed inside the aerated sludge and the other inside distilled water tank. Nutrients such as a carbon source (sugar), nitrogen (urea) and phosphorus (ammonium phosphate) were added to the aerated sludge tank to ensure microorganism growth. Furthermore, to control the nutrient and dissolved oxygen content and the growth of the microorganisms, volatile suspended solids (VSS) tests were employed regularly. The PH and temperature of the tanks were held in the range of 7.5± 1 and 26± 1 æ%C, respectively. To compensate for water evaporation during the experiments, tap water was added on a regular basic to hold the system volume at 9 liters. The supplied air ensured adequate mixing and prevented the formation of a two phase mixture due to settlement of the solids.

Water absorption rate of the samples, was carried out at seven days interval for a total period of 49 days (7 weeks). A sample of compounds A and B were placed in a distilled water tank and similarly in aerated sludge tank. After a certain time interval, each sample was taken out of the tank, dried with a piece of cloth and weighed for determination of the amount of absorbed water. After weight measurement, the samples were returned back to the distilled or aerated sludge tank accordingly, immediately.

In order to confirm the sample biodegradability in aerated sludge tank, FTIR tests were performed on each sample before and after placing it in the aerated sludge tank. The tests were performed using equinox 55 made by Bruker at 23 degrees centigrade. The tests were run according to ASTM E 1252-07 and the samples were scanned at 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

In Figures 1 and 2 the FTIR spectra for sample A containing low density polyethylene, corn starch and chitosan, and sample B containing low density polyethylene, potato starch and chitosan are shown respectively, before and after degradation in aerated sludge. As can be seen, the peak which falls in the range of 1400-1550 confirms the existence of C-H groups. On the other hand in all 4 spectra the peak which falls in the range of 1730-1750 confirms the existence of Carbonyl groups. The different peak which falls around 1465cm-1 appears for both samples and is related to C= H bonds. The reduction of this peak after exposure to aerated sludge suggests carbon consumption by microorganisms[15] has taken place. The reduction in the peaks of the range 1730-1740 also shows the reduction of Carbonyl groups of chitosan or amine groups. Amine and O-H groups are derived from chitosan and starch, respectively. Any reduction in this range suggests biodegradation of starch and chitosan which means these materials have been consumed by microorganisms present in aerated sludge tank.

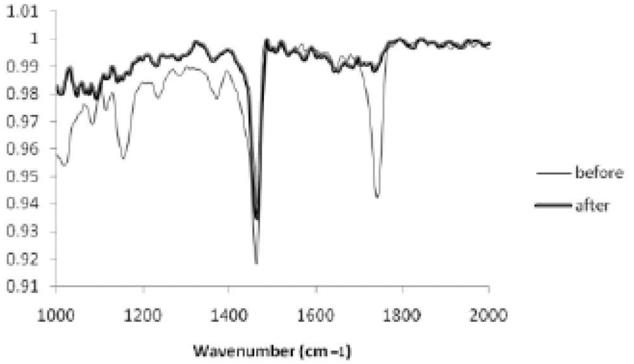

Figure 1: FTIR spectra of corn starch based LDPE compound before and after exposure to aerated sludge.

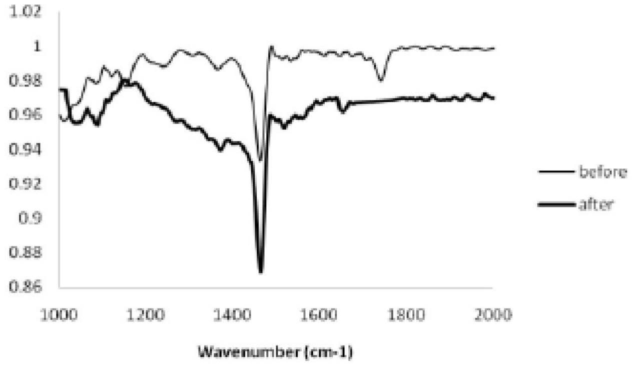

Figure 2 : FTIR spectra of samples potato starch based LDPE compound before and after exposure to aerated sludge.

According to Figure 3, increasing the exposure time for samples in distilled water, obviously increases their weight and amount of water absorbed. The rate of water absorption was found to be higher for sample A, containing corn starch in comparison with sample B, and containing potato starch. The rate of water absorption was found at its highest level, during the first 5 to 10 days. For both samples, the rate of water absorption was higher than the rate of hydrolysis, which suggests the hydrophilic property of starch. The hydroxyl groups of starch can establish Hydrogen bonds with water molecules. Chitosan is also a hydrophilic polymer trapping water molecules by NH2 groups. The water absorption rate for samples exposed to aerated sludge was lower than samples exposed to distilled water due to the consumption of starch by microorganisms.

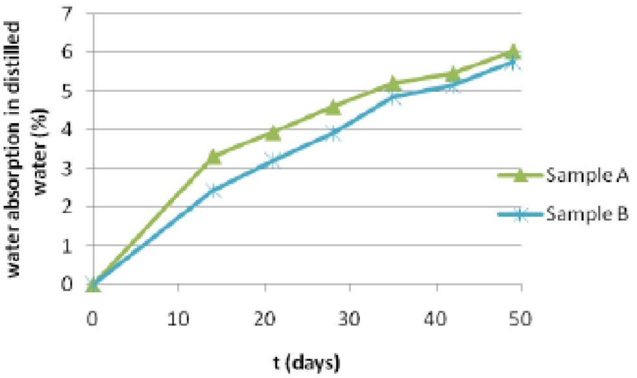

Figure 3 : Increase in sample weight soaked in distilled water.

In Figure 4, the relative data of weight measurements for samples in aerated sludge are shown. Like previous test the more exposure time, the more water absorption and for both samples, the rate of water absorption is higher than the rate of hydrolysis and biodegradation by microorganisms. On the contrary to distilled water, sample A in aerated sludge shows lower weight gain in comparison with sample B. Lower weight gain in aerated sludge means higher degradability of sample A containing corn starch in comparison to sample B containing potato starch. This difference becomes more significant with passing time.

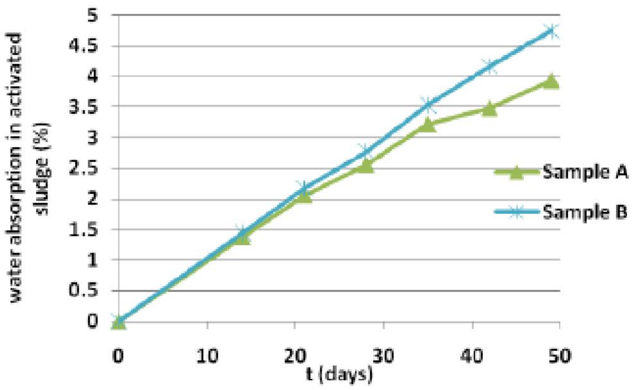

Figure 4 : Increase in sample weight soaked in aerated sludge.

The weight loss of the samples during a specific exposure time is expressed as the following relationship and is considered as the benchmark of their biodegradability[14]:

[Percentage of Sample's weight loss]= [percentage of sample's water absorption in distilled water] – [percentage of sample's water absorption in aerated sludge] (1)

According to Figure 5, the percentage of absolute weight loss for sample A containing corn starch is higher than that of sample B containing potato starch confirming the higher biodegradability of corn starch.

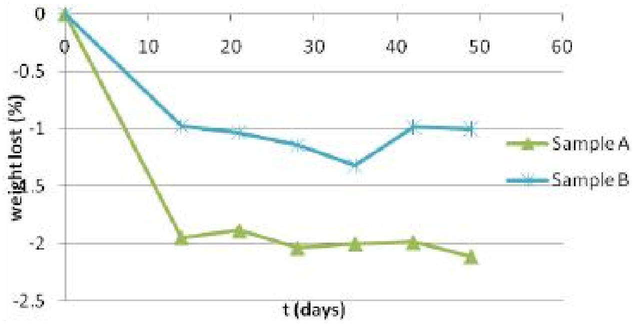

Figure 5 : Percentage of Sample's absolute weight loss in accordance with equation (1)

If a reversible kinetic model is presumed for the weight change of each sample in either distilled water or aerated sludge with first order forward and reverse reactions, then equation (2) can be presented. In this reaction, M is the solid biodegradable plastic sample which is made up of LDPE, starch and chitosan molecules. It absorbs water and in the absence or presence of microorganisms dissolves in aqueous environment. R represents the product of this reaction that constitutes the water soluble or interactive-with-microorganism part of A that may be re-absorbed by the solid plastic sample. Forward and reverse rate constants of equation (2) are called as Kf and Kr, respectively. Therefore:

$$M \Longleftrightarrow R \qquad (2)$$

$$\frac{-dm_M}{dt} = K_f.m_M - K_r.m_R \qquad (3)$$

Where t is the exposure time, mM and mR are the instantaneous weight of the sample and product respectively.

The fractional conversion of M is defined as follows:

$$X \equiv \frac{m_{M_0} - m_M}{m_{M_0}} \qquad (4)$$

In which m_{M_0} is the original weight of the sample. In Figures 3 and 4, experimental data of "100×X" against exposure time was plotted for each sample.

Using X other relationships are presented as:

$$m_R = X.m_{M_0} \qquad (5)$$

$$m_M = m_{M_0}(1-X) \qquad (6)$$

$$m_{M_0}.\frac{dX}{dt} = K_f.m_{M_0}(1-X) - K_r.X.m_{M_0} \qquad (7)$$

Solving the above differential equation the following results obtained:

$$X = \left(\frac{K_f}{K_f + K_r}\right).[1-\exp(-(K_f + K_r).t)] \qquad (8)$$

The equilibrium fractional conversion of A is obtained:

$$X_e \equiv \lim_{t\to\infty} X = \frac{K_f}{K_f + K_r} \qquad (9\text{-}1)$$

If K is set equal to the sum of forward and reverse rate constants:

$$K \equiv K_f + K_r \qquad (9\text{-}2)$$

Therefore:

$$X = X_e.(1-\exp(-k.t)) \qquad (9\text{-}3)$$

In a similar way and through similar assumptions, a kinetic correlation is also attained for weight change of each sample in aerated sludge environment:

$$Y = Y_e.(1-\exp(-k'.t)) \qquad (10\text{-}1)$$

Where:

$$Y_e \equiv \lim_{t\to\infty} Y = \frac{K'_f}{K'_f + K'_r} \qquad (10\text{-}2)$$

$$K' \equiv K'_f + K'_r \qquad (10\text{-}3)$$

Therefore, the overall kinetic correlation for the rate of sample's weight loss could be calculated as follows which can be counted as a benchmark for biodegradability rate:

$$Z \equiv Y - X \qquad (11\text{-}1)$$

In Figure 5, experimental data of "100×Z" versus exposure time were plotted for each sample.

Substituting equations (9-3) and (10-1) into equation (11-1) results:

$$Z = Y_e.(1-\exp(-k^{'}.t)) - X_e.(1-\exp(-k.t)) \quad \textbf{(11-2)}$$

The Taylor series for the exponential function”e^t”in neighbourhood of zero is as follows:

$$e^t = 1 + \frac{t^1}{1!} + \frac{t^2}{2!} + \frac{t^3}{3!} + \ldots \quad \textbf{(12)}$$

In which if “t” takes small enough values, terms with higher order than 2 can be neglected from the Taylor expansion, thus:

$$e^t \cong 1 + t + \frac{t^2}{2} \quad \text{(if t is small enough)} \quad \textbf{(13)}$$

Substituting equation (13) into equation (11-2) results:

$$Z \cong Y_e - Y_e.(1 - k^{'}.t + \frac{(k^{'}.t)^2}{2}) - X_e + X_e.(1 - k.t + \frac{(k.t)^2}{2}) \quad \textbf{(14-1)}$$

$$Z \cong (Y_e k^{'} - X_e k)t + (X_e k^2 - Y_e k^{'2})\frac{t^2}{2} \quad \textbf{(14-2)}$$

On the other hand, if we assume a kinetic correlation similar to those used for the fractional conversion in distilled water (X) or aerated sludge (Y), also apply to the overall fractional conversion (Z):

$$Z = Z_e.(1-\exp(-k''.t)) \quad \textbf{(15-1)}$$

In which,

$$Z_e \equiv \lim_{t\to\infty} Z = \frac{K''_f}{K''_f + K''_r} \quad \textbf{(15-2)}$$

$$K'' \equiv K''_f + K''_r \quad \textbf{(15-3)}$$

Substituting equation (13) into equation (15-1) results:

$$Z = Z_e - Z_e.(1 - k^{"}.t + \frac{(k^{"}.t)^2}{2}) \quad \textbf{(16-1)}$$

$$Z = Z_e k^{"}.t - Z_e k^{"2}\frac{t^2}{2} \quad \textbf{(16-2)}$$

Comparing equations (14-2) and (16-2) concludes:

$$k^{"} = \frac{Y_e k^{'2} - X_e k^2}{Y_e k^{'} - X_e k} \quad \textbf{(17-1)}$$

$$Z_e = \frac{\left(Y_e k^{'} - X_e k\right)^2}{Y_e k^{'2} - X_e k^2} \quad \textbf{(17-2)}$$

In the performed experiments, the compounds were exposed to distilled water or aerated sludge environment around 50 days which can be considered a relatively short time for complete biodegradation of the plastic samples. Therefore, the approximation of omitting higher order terms of the Taylor expansion is reasonable, and the absolute weight loss or biodegradability of the samples is indicated as follows:

$$Z = \left(\frac{\left(Y_e k^{'} - X_e k\right)^2}{Y_e k^{'2} - X_e k^2}\right)\left(1 - \exp\left(-\left(\frac{Y_e k^{'2} - X_e k^2}{Y_e k^{'} - X_e k}\right)t\right)\right) \quad \textbf{(18)}$$

Figures 6 and 7 in addition to TABLES 1 and 2 demonstrate the results from curve fitting of experimental data with the above suggested kinetic correlations. The reported R-squared values in TABLES 1 and 2, indicate that the assumption of reversible kinetic model with first order forward and reverse reactions for the weight change of samples in distilled water and in aerated sludge is acceptable. Besides, the approximation used for obtaining the overall fractional conversion (Z) in a similar way to those used for the fractional conversion in distilled water (X) or aerated sludge (Y), is also justified . Special attention should be paid to the reported values of fractional conversions (Xe, Ye) in these TABLES which are negative originating from the fact that the samples gain weight in both distilled water and aerated sludge. However, since the values of overall sample weight change are negative, the fractional conversions (Ze) are expected to be positive.

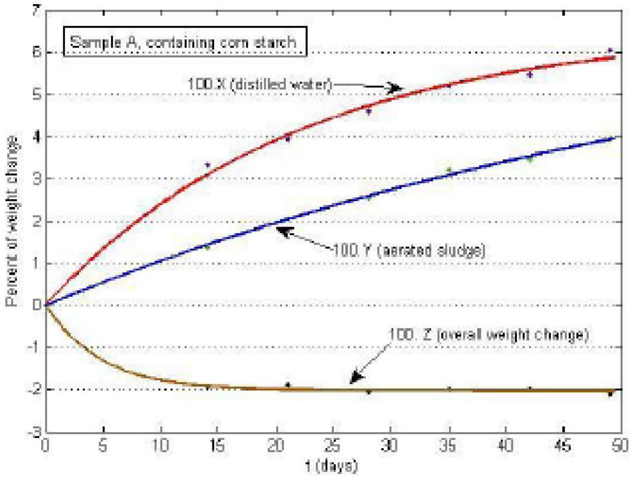

Figure 6 : Curve fitting of experimental data relative to sample A’s rate of water absorption in distilled water (equations (9-3)), water absorption in aerated sludge (equation (10-1)) and overall weight loss (equation (15-1)).

On the basis of Ze values reported in TABLES 1 and 2, it can be concluded that Sample A containing corn starch is more biodegradable than Sample B containing potato starch.

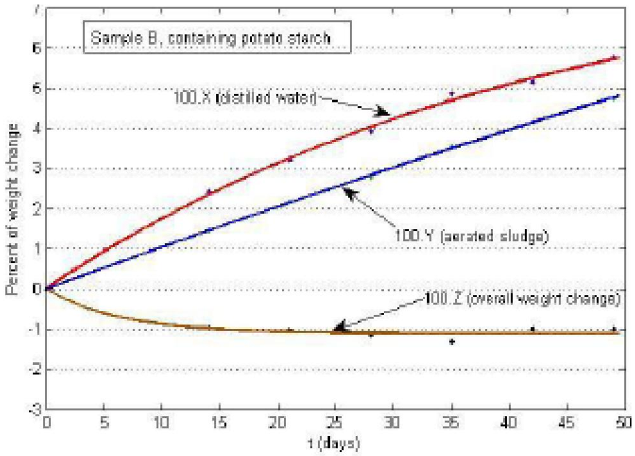

Figure 7 : Curve fitting of experimental data relative to sample B's rate of water absorption in distilled water (equations (9-3)), water absorption in aerated sludge (equation (10-1)) and overall weight loss (equation (15-1)).

TABLE 1 : Parameters of the suggested kinetic correlations for sample A.

Equation (9-3)			Equation (10-1)			Equation (15-1)		
$100.X_e$	k	R^2	$100.Y_e$	k'	R^2	$100.Z_e$	k''	R^2
-6.565	0.04536	0.9948	-7.616	0.01485	0.9977	2.017	o.2107	0.9931

TABLE 2 : Parameters of the suggested kinetic correlations for sample B.

Equation (9-3)			Equation (10-1)			Equation (15-1)		
$100.X_e$	k	R^2	$100.Y_e$	k'	R^2	$100.Z_e$	k''	R^2
-6.565	0.04536	0.9948	-7.616	0.01485	0.9977	2.017	o.2107	0.9931

CONCLUSION

In this study, the biodegradability of polyethylene mixed with corn and potato starch was studied by placing them inside an aerated sludge environment. It is concluded that aerated sludge environment is a suitable medium for biodegradability measurement of polymer samples. While similar studies using soil as medium takes more than 24 weeks, the aerated sludge environment reduced this time to 6-7 weeks.

By comparing the rate of weight change of the samples in distilled water and in aerated sludge, a kinetic model for each is proposed. The biodegradation studies indicated that the biodegradability of sample containing low density polyethylene bonded with corn starch is higher than sample containing low density polyethylene bonded with potato starch when exposing to aerated sludge. The examination of their FTIR spectra also confirms this issue.

Limiting or reversed first order kinetics was proposed for biodegradation rates and results show the assumed kinetics closely follows experimental data. Derived equations can well be used in prediction of degradation time of these types of bio-plastics.

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