

Preparation of Biodegradable Low Density Polyethylene by Starch – Urea Composition for Agricultural Applications

Torabi Angaji, Mahmood and Hagheeghatpadjoo, Hamid Reza**

Faculty of Engineering, Tehran University, P.O.Box 17665-351, Tehran, I.R. IRAN

ABSTRACT: It has been proven that polyolefins specially low density polyethylene (LDPE), are resistant against degradation and microorganism attacks; Thus, one of the most important properties of industrial plastics, is their environmental biodegradability. Since plastics are being widely used in agriculture, horticulture and packaging, meeting this requirement becomes increasingly difficult (specially in IRAN as one of the biggest manufacturers of polyethylene materials). So, attention is focussed on production of biodegradable polyethylene. In this study, some different formulations based on starch and urea for making polyethylenes which are biodegradable in soil and moist media, have been investigated. The compounds produced are injection molded, and tested under natural conditions and their biodegradability has been studied. It has been thus possible to produce a biodegradable low-density polyethylene which is environmentally biodegradable material that is suitable for agriculture and packaging applications.

KEY WORDS: Biodegradability, Starch, Polyethylene, Agriculture, Plastics.

INTRODUCTION

Since 1970s there has been a tendency to produce and apply biodegradable polyethylene (BDPE), which is not harmful to soil or the environment [2,3]. ASTM D883-93 shows that biodegradable plastic is a material, which under special conditions, its structure changed, so some proportions are lost in standard tests.

Since low density polyethylene is the most applied polyolefin in packaging, horticulture and agricultural utilizations, [6,7], its inherent resistance to environmental degradation is a global concern. In this paper, LDPE has been used as a matrix resin being mixed with compounds that can cause its biodegradation. All

polyethylene manufacturers add anti-oxidants to the resin because it's inherently unstable, especially when exposed on ultraviolet (UV) light and hard weathering [4,5,14]. The polymer chain is cleaved and oxidized via free radical formation due to the highly unsaturated carbon bonding in its molecules. So, it could be degraded in this way but usually the oxidant lasts as little as one year [5,16].

Hence, the low - density polyethylene (produced in Bandar Imam petrochemical complex), which is inherently strengthened against oxidation and biodegradability is chosen for investigation. Corn starch

* To whom correspondence should be addressed.

+ E-mail : h.hagheeghat@ikido.org

1021-9986/04/1/7

5/\$/2.50

and urea has been added to matrix resin and mechanical strength tested [8,9]. Meanwhile, optimal and economical production process for transferring this project in to industrial phase has been taken into consideration.

Theoretical Aspects

Biodegradation is the break down of materials by the action of microorganisms. The most popular organisms used on plastics are bacteria and fungi.

The break down caused by microorganism can be of three different types:

- 1) A biophysical effect, in which cell growth can cause mechanical damage,
- 2) A biochemical effect, in which substances from the microorganism can act on the polymer.
- 3) Direct enzymatic action, in which enzymes from the microorganisms attack components of the plastics product, lead to splitting or oxidative breaking down.

There are polymers such as polycaprolactone and polyhydroxybutyrate (PHB), which are degraded in enzymatic attack directly [2,3]. Due to cost and processing requirements, these materials are suitable only for special applications such as medical field. Therefore, preparing biodegradable plastics formulations by using the right additives is the most economic procedure. Degradation can be followed by measuring changes and deviations in physical properties of the product, by studying chemical changes in the film or assessing biological activity [5,11].

Degradable additives used here are starch based. These agents increase the susceptibility of the polymer to oxidation because they contain free radical initiators. Pro-oxidants or auto oxidants are compounds such as iron or manganese stearate, and photo-accelerators used are amines or peroxides. The free radical reactions involved, result in gradual reduction of the long polymer chain molecules into smaller, and lower molecular weight entities which are more suitable for microbial enzymatic attack. The degradative reactions are temperature dependent, thus they occur readily during extrusion process when the mixture is thoroughly being mixed and heated above 160 centigrade degrees. Therefore polyethylene thus proposed contains antioxidant, so firstly it should be consumed.

It is important to know that microbial action on pure polyethylene polymer is nil. However, the starch is

consumable by microbes and enzymes. So, the digestion of the starch leaves holes in the polymer matrix, increasing surface area which theoretically should increase the rate of oxidation of the polymer [9,13,14]. The rate and extent of degradation depends on the light, temperature, moisture and air exposure. Since landfills are designed to exclude air and moisture, they tend to be poor sites for degradation. The holes formed enhance the migration of potential reactants into the matrix. Then, the surface of the biodegradable resin, after removal of the starch is more hydrophilic and more easily wetted and leading to further enhanced transport properties [15,16].

As microorganisms consume the starch present in the matrix some physical damage occurs in the resin. In addition, the extra-cellular enzymes produced by the organism likely provide some direct attack on the resin and may be responsible for the fine cracking of the resin. The equations governing the process is called Michaelis-Menten, Lineweaver-Burk and Eadie-Hofstee. The most useful one for biodegradability of polyethylene resins is the Eadie-Hofstee equation:

$$V/[s] = 1/k_m (V_{\max} - V) \quad (1)$$

V = reaction Velocity

S = The concentration of substra

k_m = the constant of michaelis-menten

V_{\max} = maximum reaction velocity

MATERIALS AND METHODS

The matrix polyolefin resin used is low-density polyethylene (LDPE) from Bandar Imam petrochemical complex with properties listed in table 1; Biodegradable agent used is a mixture of corn starch and urea. The coupling agent which chemically bonds the starch and the matrix resin is polyacrylic acid and sodium polyacrylate. The radical initiator used is dicumyl peroxide (DCP) or benzoyl peroxide. For accelerating the oxidation of LDPE, an autoxidizing agent such as manganese stearate or ferrous stearate (II) should be used. A plasticizer such as dioctyl phthalate (DOP) and a Lewis acid catalyst like acetic acid, oxalic acid, p-toluene sulfonic acid or lactic acid are also utilized in a certain amount by mixing in a reactive twin screw extruder to lower the production cost through simplifying the process and minimizing the loss of physical properties of new material. The extruder was

APV model 2000 from Baker Perkins company (England) (BP). This way, (Polyethylene) PE, initiator, coupling agent, starch and catalyst are introduced concurrently and reactively-extruded at a temperature of 180-200 °C with a screw speed of 190-280 RPM to esterify the starch and interfere the starch-urea to polyethylene chains. The physical properties of produced new compound are found to be suitable. The compositions of BDPE formulations used are shown in table 2.

The biodegradable material incorporated is either wheat starch, corn starch or modified starch like starch acetate, starch phosphate or oxidized starch. The starch is dried in advance until the moisture content gets below 2.5 percent to avoid generating of bubbles or mocks in the formation of plastic film or part. (industrial starch contains a moisture content in the range of 10-16 %).

The biodegradable resin pellets can be prepared from the above formula, are mixed in a twin-screw extruder. Biodegradable films are prepared by making the pellets into compression molding films or blown film using a hot press and extruder. Mechanical properties such as tensile strength and elongation of biodegradable pellets were determined by the Instron and other standard instruments. The tensile and elongation test based on ASTM D638 has

been accomplished by Zwick and Instron equipments.

Fig. 1 confirms the occurrence of oxidation and formation of the starch holes, (scanning electronic microscopy SEM). As the starch component, provides a nutrient source for microorganisms, such as fungi and bacteria, which attack the granules until they are completely removed as illustrated in Fig.1. This, phenomena weakens the resin matrix, as well as greatly increase the surface area of the plastic material.

Biodegradation Studies

Approximately 5 x 5 cm pieces of each sample or prepared formulation were cut, weighed and washed with alcohol. The specimens were taken in to incubator along with prepared and given bacteria (*Aspergillus niger*) for 32 days (20 °C, 1 atm) in shaker by 150 rpm and 30 centigrade degrees. After this period, the samples were collected and air-dried for 5 days, then weighed and loss, if occurred, has been written.

Tensile specimens were tested at 23 centigrade degrees and 55% relative humidity by Instron Universal testing Machine (model 4201) using gate length of 10mm and speed of 25 mm/min.

For SEM studies specimens were fixed in 1 % wt.

Table 1: Properties of LDPE used as matrix resin.

Grade	Density (gr/cc)	MFI (gr /10min)	Tensile strength at break (kg/cm ²)	Dart impact (gr)
LF 020	0.92	2.0	MD 160 min	100 min

Table 2: Compositions formulations used for production of samples.

No.	Material	Grade/producer	Weight percent (%)
1	Polyethylene	Low density LF020	50-85
2	Wheat starch	Glukosan (90%) white	10-40
3	Sodium polyacrylate	D-302 PAAS DANDONG chemical plant CHINA	0.02-0.5
4	Polyacrylic acid	D-101(881) DANDONG chemical plant CHINA	0.05-0.5
5	Benzoyl peroxide	Purity 100% Merck	0.1-0.4
6	DOP	MERCK, 100%PURE	0.2-0.6
7	Manganese stearate	MERCK, 100%PURE	0.1-0.55
8	Acetic acid	Purity 100% Merck	0.5-2.5
9	Urea	Razi petrochemical complex (purity100%)	2-5

Fig. 1: Oxidation of biodegraded components and the emergence of cavities.

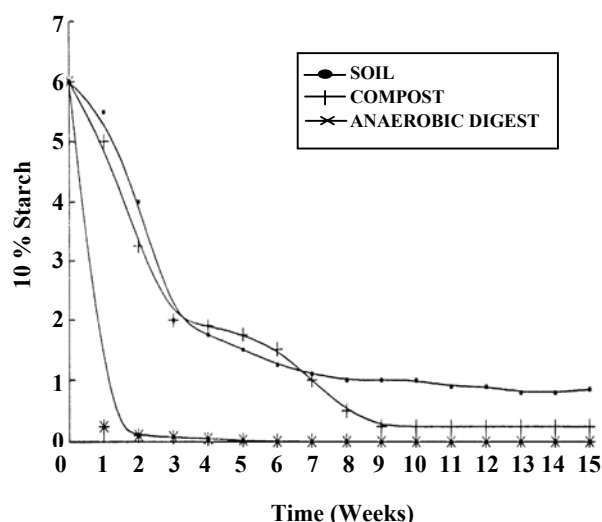


Fig. 2: Results of starch-urea removal from produced parts as given samples in table (3). Vertical axes is 10% starch used & horizontal axes is time.

Table 3: Mechanical strength of different samples containing starch and urea.

Sample NO.	Content of starch%-urea%	Tensile strength (kg/cm ²)
1	0-0	180
2	10-2.0	165
3	15-2.5	160
4	20-3.0	154
5	25-3.5	137
6	30-4.0	126
7	35-4.5	114
8	40-5.0	100

glutaraldehyde and dehydrated for 10 minutes each in 50, 60, 70, 80,90,100% ethanol and mounted on aluminum stubs. specimens were sputter coated with gold-palladium and visualized under a JOEL model 1200 Ex scanning electron microscope .

Specimens that went through biodegradation process, were inspected by SEM and their mechanical properties were tested. Their tensile strengths was measured by Instron and their biodegradability estimated in accordance via ASTM G 21-70 method.

RESULTS AND DISCUSSION

As the microorganisms utilize or remove the starch. Present in the polymer there would be some physical or mechanical damage on the specimen [12,14,16]. However, the extra cellular enzymes made by the organisms, also attack the resin and may be responsible for the fine cracking and tearing, which are observed in Fig. 1. The rate of removal or digestion of the starch particles, is dependent on the environment which the part or material is exposed to, Fig. 2. Specimens containing different percents of starch, were tested and the final results are given in table 3. Data show that these new polymer blends may be applied as agricultural plastics such as films, flower cases and bags, horticulture, packaging and related industries where rapid degradation is desirable.

Abbreviations

BDPE = Biodegradable Polyethylene
 BP = Baker Perkins
 DCP = Dicumyl Peroxide
 DOP = Dioctyl Phthalate
 LDPE = Low-Density Polyethylene
 MD = Machine Directory
 km = The constant of michaelis-menten
 V_{max} = The maximum reaction velocity
 PHB = Polyhydroxy Butyrate

Received: 18th June 2002 ; Accepted: 26th January 2003

REFERENCES

- [1] Cole. M. A, American chemical society, Washington, Agricultural of synthetic polymers; biodegradability of utilization, ACS sympium series no.433, (1990).
- [2] Dubios, R., Applied science publishers, Ltd, London,

- “Plastics in agriculture”, (1978).
- [3] G22 q 21, ASTM., Standard practice for Determining resistance of plastics to bacteria.
- [4] Krosh wilz, J.L., Encyclopedia of polymer science & technology, **2**, p. 1230 (1985).
- [5] wool, Rp., Cole, M.A., and peanasky, J.S., American chemical society, Toronto, June “Biodegradation & Biodisintegration of polymer-starch blends”, (1988).
- [6] Bastioli, C., Belloti, V., and lombi, R., PCT int, pat, “Expanded products of biodegradable plastics & a method for their production”, April (1991).
- [7] Manchester packaging company D-grad@degradable polyethylene (manchesterpkg.com)
- [8] Anderson et.al. US patents 6,231,970; Thermoplastic starch compositions incorporating a particulate filler, May (2001).
- [9] Yoo & yukong. Us patent 5,461,093 ; Biodegradable polyethylene composition chemically bonded with starch & a process for preparing thereof, (1995).
- [10] Akaranta, O., Oku. G.E., Carbohydrate polymers 34 “some properties of cassava mesocarp carbohydrates – LDPE blends”, p. 403, (1997).
- [11] Boembergen et al., Us patent 5, 462, 983; Biodegradable moldable products & films comprising blends of starch esters, Oct. (1995).
- [12] Austin, R.G., Us patent 5,281,681; Photodegradable & Biodegradable polyethylene, Oct. (1991).
- [13] Otera et al., Us patent 6,114,496 ; Biodegradable resin composition & preparation process thereof, Set. (2000).
- [14] Willett, J.L., Us patent 5,087, 650; Biodegradable plastics, Feb. (1992).
- [15] Loercks et al., Us patent 6, 235, 815; Biodegradable polymeric mixtures based on thermoplastic starch, May (2001).
- [16] D.M.Wiles et al., Biodegradable plastics '99 conference, Frankfurt, Germany. Biodegradable films from PE, April (1999).