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Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications: Part 1

Ioannis Arvanitoyannis[a,*], Costas G. Biliaderis[a], Hiromasa Ogawa[b], Norioki Kawasaki[b]

[a]*Laboratory of Food Chemistry and Biochemistry, School of Agriculture, Aristotle University of Thessaloniki, Box 265, 54006 Thessaloniki, Greece*
[b]*Osaka National Research Institute AIST, 1-8-31 Midorigaoka, Ikeda, 563 Osaka, Japan*

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Abstract

Blends of LDPE and rice or potato starch were extruded in the presence of varying amounts of water, hot pressed and studied with regard to their mechanical properties and their gas/water permeability and biodegradability before and after storage. The presence of high starch contents (> 30%, w/w) had an adverse effect on the mechanical properties of LDPE/starch blends. Gas permeability and water vapour transmission rate increased proportionally to the starch content in the blend. Several theoretical and semiempirical calculations for mechanical properties and gas permeability were carried out and possible interpretations were provided for the occasionally observed deviations between the experimental and the theoretical values. The biodegradability rate of the blends was enhanced when the starch content exceeded 10% (w/w). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Food packaging; Starch; Biodegradable; LDPE (polyethylene)

1. Introduction

Most widely used polymeric materials developed in the past 50–60 years are durable and inert in the presence of microbes thus leading to a long term performance. However, in view of the current emphasis on environmental pollution problems and in conjunction with the land shortage problems for solid waste management and pending legislation, the need for environmentally degradable and 'environmentally friendly' polymers has arisen (Schnabel, 1981; Kumar, 1987; Albertsson, 1993; Satyaranayana and Chatterji, 1993; Albertsson and Karlsson, 1995; Wool, 1995). The two major applications of synthetic polymers fall in the field of food packaging (wrapping materials) and other uses (i.e. mulch films, seedling pots and binding twine) (Wool and Cole, 1988). LDPE is an 'omnipresent' polymer having already found numerous applications. Although both low and high density polyethylene have been rather extensively used in packaging and agricultural applications, their degradability was questioned on several occasions mainly because of lacking documentation either with regard to the properties of the tested polymer or in relationship to the degradation procedure employed (Scott, 1994). For the purpose of the present study, biodegradation is defined as the conversion by microorganisms of a material to CO_2, H_2O and trace inorganic products under aerobic conditions or to CH_4, CO_2 and inorganic products under anaerobic conditions (Krupp and Jewell, 1992). Furthermore, it should be pointed out that though fragmentability of the polymer and loss of elongation (95% is defined as the embrittlement point) should constitute inherent characteristics of degradable polymers (Scott, 1994), several additional features are required if the polymers are to be acceptable from the ecological point of view (Kumar, 1987; Albertsson, 1993; ASTM, 1993; Satyaranayana and Chatterji, 1993; Scott, 1994): (i) a predetermined service time (induction time) during which no properties change whatsoever; (ii) the end of induction period should be followed by an accelerated fragmentation stage; (iii) a final, total and innocuous assimilation of the fragmentary products by the ecosystem.

The aim of this study was to prepare a series of LDPE/rice or potato starch, varying in starch and water content, and to investigate their performance both before and after their biodegradation. The latter was evaluated by means of mass and percentage elongation changes after burial in soil and exposure to bioreactor and by determining the biochemical oxygen demand (BOD).

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[*] To whom all correspondence should be addressed. Tel.: +30 31 998785; fax: +30 31 998789

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2. Materials and methods

2.1. Materials

Rice and potato starch was purchased by Wako (Japan) and LDPE was a gift from Asahi Chemicals (Japan).

2.2. Extrusion: preparation of samples

LDPE and granular rice or potato starch, after having been thoroughly mixed, were extruded, in the presence of 15–20% water content, using a twin-screw extruder (Ikegai Co. Ltd. PCM-30, Japan). The extrusion conditions were as follows: temperatures 120, 120, 120, 110°C (slot die); *L/D*, 500/30; feed motor and mix motor, 2.0 and 50 rpm, respectively. Preparation of films of LDPE with rice or potato starch for permeability measurements was carried out by pressing the extrudates at temperatures 110–120°C for 15 min, 35 kN (Arvanitoyannis and Blanshard, 1993; Arvanitoyannis et al., 1994).

2.3. Wide-angle X-ray diffraction (WAXD)

X-ray diffraction measurements of LDPE/rice or potato starch blends at various moisture contents were carried out using a Shimadzu (Japan) diffractometer from 5 to 40 2Θ. The crystallinity was determined as previously reported (Marsh, 1986).

2.4. Measurements of permeability

The measurements of gas permeability were carried out using a Davenport apparatus connected to an IBM/PC in accordance with ASTM (D1434-66) (ASTM, 1966). Film thickness was measured with a micrometer at five or six locations of the film.

Assuming that a unidirectional diffusion through a flat membrane occurs, then diffusion can be expressed as follows:

$$J_i = D_{i(ci)}\frac{dc_i}{dx} \qquad (1)$$

where J is the flux, $D_{i(ci)}$ signifies that the diffusion coefficient is dependent on the composition of the penetrant and c refers to the local gas or penetrant concentration.

The formula for the determination of the diffusion constant is as follows:

$$D = d^2/6\theta \qquad (2)$$

where d is the thickness of the film and θ is the time lag of the permeation. The lag is related to the time required by the gas to establish an equilibrium in an originally gas-free film. The extrapolation of the pressure increase–time curve to the zero axis will produce the time lag (θ) (Amerongen, 1947; Amerongen, 1949). The quantity of gas (Q) that will then pass through the film is directly proportional to the difference in the pressure exerted by the gas on each face of the film ($p_1 - p_2$) and is inversely proportional to thickness (x). It is also directly proportional to the area exposed (A) and the time (t) for which permeation occurs according to the following relationship:

$$Q = \frac{PAt(p_1 - p_2)}{x} \qquad (3)$$

where P has a constant value for a specific combination of gas and polymer at a given temperature, known as the 'transmission factor' or 'permeability factor/constant/coefficient' (van Krevelen, 1990). The water vapour transmission rate (WVTR) measurements were carried out as previously reported (Martin-Polo et al., 1992).

2.5. Mechanical properties

2.5.1. Tensile strength and percentage elongation

Tensile strength and percentage elongation were measured on dumbbells using an Instron Universal Testing Instrument (model 1122) operated according to ASTM (D828-88) (ASTM, 1989). Measurement conditions and calculations of tensile strength and percentage elongation were made as previously described (Arvanitoyannis and Psomiadou, 1994).

2.5.2. Three-point bending test

All samples were cut with a scalpel, scissors or sawn into bars ~150 × 10 × 2.40 mm and stored in laminated polyethylene bags until testing. Three-point bend tests were carried out at room temperature using an Instron Texturometer at a cross head speed of 1 mm min^{-1}. The load range and the support span were 5000 N and 60 mm, respectively. The initial slope of the force/distance graph and the sample dimensions were used for determining the flexural modulus which was calculated with three different methods (chord (mod-1), secant (mod-2) and least-square (mod-3)), as shown in Fig. 1. The peak force was also recorded.

2.6. Scanning electron microscopy

A scanning electron microscope (JEOL, JSM 5200 Scanning Microscope, Japan) was used, at an accelerating voltage of 10 kV with a beam directed normal to the edge or at a 45° angle, for taking micrographs of specimens before and after their fracture.

2.7. Biodegradability experiments

2.7.1. Bioreactors

The bioreactors composed of cylindrical glass tanks, fitted with gas-tight covers, were aerobically semicontinuously mixed and fed microbial reactors. The bioreactor was fed a substrate composed of a 1:1 (volatile solid basis) mixture of α-cellulose and dried, milled sorghum twice a week at a loading rate of 1.42 g of volatile solids (VS)/kg of total reactor contents. The compound formula used for the substrate mixture was $C_6H_{9.6}O_{4.1}N_{0.07}$, and its maximum biodegradability was measured to be approximately 86% as previously reported (Krupp and Jewell, 1992). Both aerobic and anaerobic reactors were in function for 180 days at

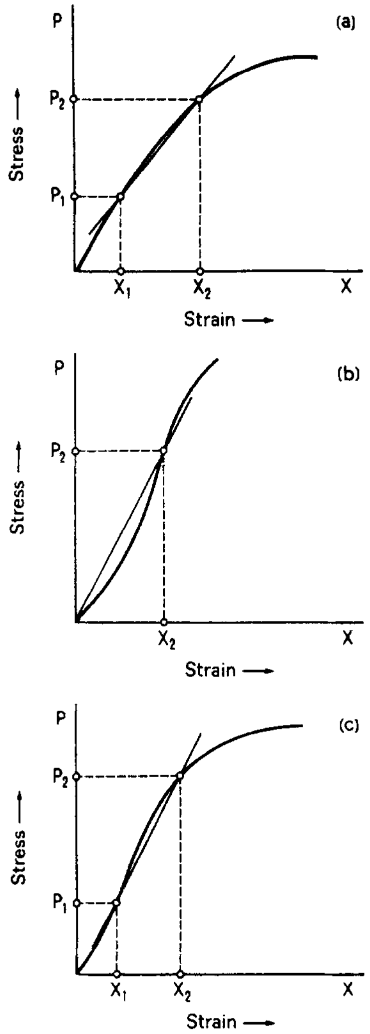


Fig. 1. Calculation modes of flexural modulus determined from three-point bend test; (a) chord, (b) secant and (c) least-squares

30 kg of total reactor contents and 37°C. The wet air supply to the aerobic reactor was approximately 1/27 m^3/h to adequate oxygen transfer. Analyses for temperature, pH, total and volatile solids, ammonia nitrogen, alkalinity, volatile fatty acids (VFA, anaerobic reactor) and dissolved oxygen (aerobic reactor) were carried out twice per week. Whenever needed, additions of trace nutrients, nitrogen and pH adjustment were made and the efficiency of substrate biodegradation of each reactor was periodically assessed as elsewhere reported (Krupp and Jewell, 1992).

2.7.2. Mass changes

A Sartorious balance was used for measuring, to 0.01 mg accuracy, the film masses. The films were weighed both prior to and after exposure. In the latter case the films were first rinsed with distilled water after removal from the burial site (burial time, up to 360 days) and then dried at 60°C for 48 h prior to their weighing.

2.7.3. Determination of biochemical oxygen demand (BOD)

The oxygen demand of waste water is measured in most cases by using the standard 5-day BOD method. Although the method on its own does not constitute a direct way of biodegradability evaluation, through exposure time prolongation the measurement of bioavailable materials can be ensured. BOD measurements were taken for 90 days at 22 ± 1°C. Dilution water contained 2 ml of raw settled sewage and 10 mg of 2-chloro-6-(trichloromethyl)pyridine (TCMP), which acts as a nitrification inhibitor, per litre. Five replicate bottles were run per film sample per trial and 10 blank bottles per trial. Dissolved oxygen concentration in each bottle was measured every 5 days using an electrochemical BOD stirring probe connected to a dissolved oxygen meter. Bottle contents were completely exposed to the atmosphere for 30 s. The milligrams of oxygen consumed per milligram of plastic film added to the BOD bottle (mg O_2/mg PE) express the BOD. The required soluble fractions of films for BOD testing were prepared as follows: first 25 ml of distilled water were autoclaved in a BOD bottle followed by the addition of a known mass of the testing material. After having stoppered the bottle, the sample was incubated at 60°C for solubilization over the required time (Krupp and Jewell, 1992). The solid film sample was removed and the BOD test was carried out. Apart from sample addition, the blanks were prepared similarly to the above described procedure.

2.7.4. Theoretical BOD calculation

By applying the general equation for aerobic biodegradation (Sawyer and McCarthy, 1978) the theoretical BOD values were calculated as follows:

$$(C_nH_aO_bN_c) + (n + a/4 - b/2 - 3c/4)\,O_2 \rightarrow nCO_2 + (a/2 - 3c/2)\,H_2O + cNH_3 \qquad (4)$$

Therefore, from Eq. (4) it can be deduced that 1 mol of the organic compound $C_nH_aO_bN_c$ would require for its complete oxidation $(n + a/4 - b/2 - 3c/4)$ mol of O_2. Division of this number by the compound molecular weight, the oxygen consumption in BOD units (mg O_2/mg LDPE) can be determined. The theoretical BODs for starch and LDPE are 1.07 and 3.08, respectively. An experimental protocol similar to the one previously reported (Krupp and Jewell, 1992) was adopted. A minimum of five replicates were tested per sample and the films were exposed to aerobic reactor and hot bath. In an attempt to study the effect of prolonged exposure, films remained in the reactor for up to 180 days. Non-exposed films were also tested for BOD for comparison purposes.

3. Results and discussion

3.1. Mechanical properties

3.1.1. Tensile strength, modulus and percentage elongation

It is evident that the LPDE/rice starch blend, because of its inherent polymer incompatibility, has four separate

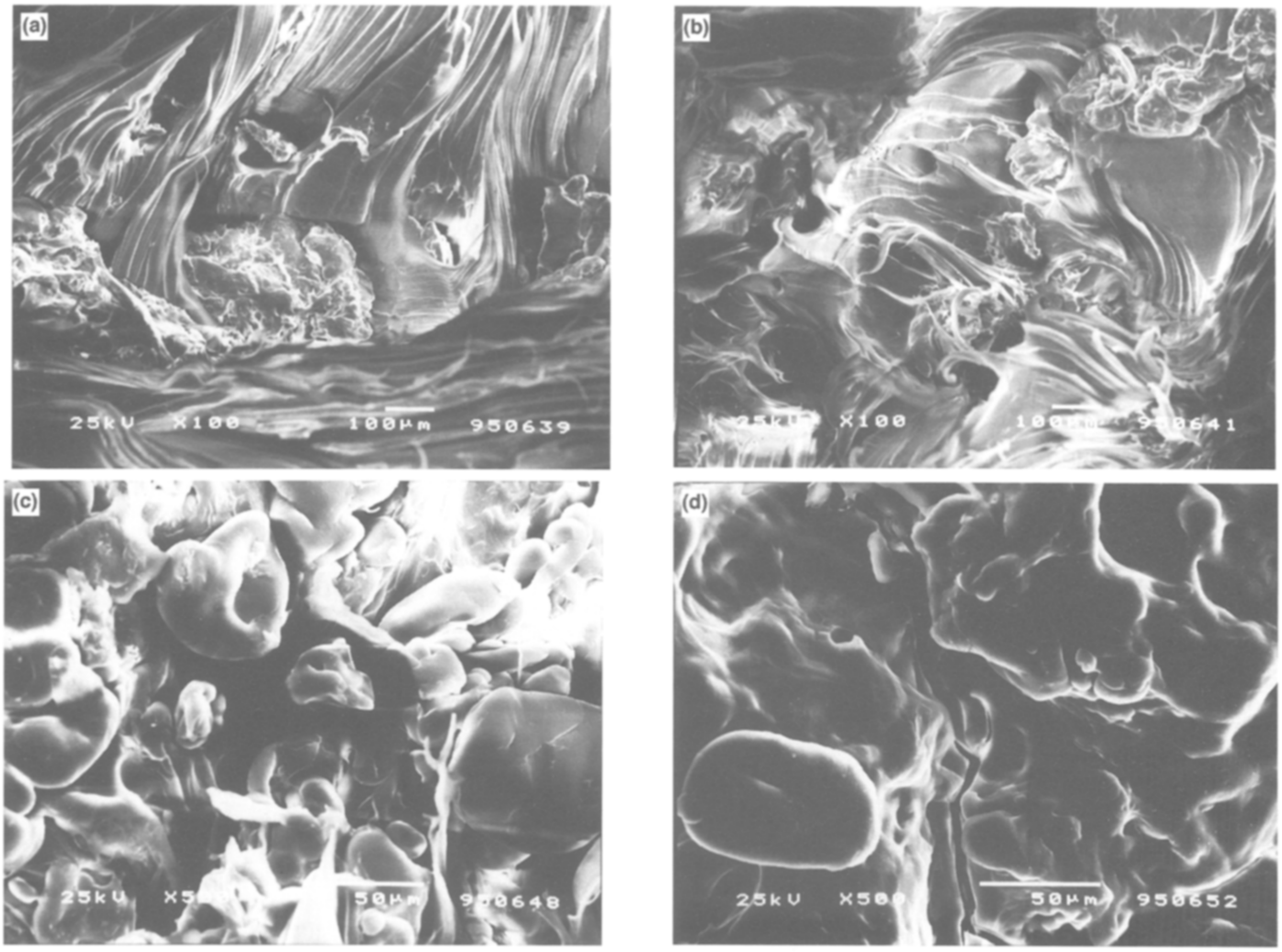


Fig. 2. SEM micrographs of various LDPE/potato starch blends after their fracture; (a) 95/5, (b) 90/10, (c) 80/20, (d) 70/30

phases, two crystalline and two amorphous, thus complicating considerably the mechanical modeling. A rather simplified approach might be to start by taking into account exclusively the LPDE and the rice starch as the main blocks and to ignore, at least for the time being, the existence of two phases for each component. The retaining of separate crystalline domains and the morphological features of the composite (SEM, Fig. 2) could be advocated in favour of this approach (Gallagher et al., 1991).

Bearing in mind the phase separation between the blend components, the values of the experimentally obtained Young's modulus were compared to those calculated from the corresponding homopolymers according to the following equations (Eqs. (5) and (6)), which were originally proposed for composite materials (Ashby and Jones, 1985):

$$E_{\mathrm{blend}} = V_{\mathrm{starch}}E_{\mathrm{starch}} + (1 - V_{\mathrm{starch}})E_{\mathrm{LDPE}} \tag{5}$$

$$E_{\mathrm{blend}} = \frac{1}{\dfrac{V_{\mathrm{starch}}}{E_{\mathrm{starch}}} + \dfrac{1 - V_{\mathrm{starch}}}{E_{\mathrm{LDPE}}}} \tag{6}$$

If we apply Eq. (5) and Eq. (6) for the LDPE/potato starch (70/30) blend, using the weight ratios of LPDE and starch for V_{starch} and V_{LDPE}, respectively, and the corresponding tensile moduli of the pure components ($P_{\mathrm{LDPE}} = 195$ MPa (Table 1) and $P_{\mathrm{Potato\ starch}} = 23.1$ MPa (Lourdin et al., 1995)), the calculated tensile moduli for the blend are 143.43 and 60.3 MPa, respectively. These values are somewhat higher or lower than the one experimentally found (103 MPa, Table 1), which is almost the average of the former two.

Table 1 summarizes the tensile strength, tensile modulus and percentage elongation of LDPE/rice starch blends. The results show that, although the incorporation of starch in the LDPE leads to lower tensile strength and modulus, the blends are still operational provided that the starch content does not exceed 20%. The tensile strength and percentage elongation measurements are in close agreement with those obtained by other researchers for blends of similar composition (Griffin, 1994; Kim and Pometto, 1994). Micrographs taken with SEM after fracture, indicated clearly the heterogeneous morphology of the blend where deformed starch particles (filler) are interspersed in the LDPE continuous matrix (Fig. 2).

The failure modes of polyethylene (PE) have been extensively investigated (Brown and Wang, 1988; Wang et al.,

Table 1
Tensile strength, tensile modulus and percentage elongation of LDPE/rice starch blends with various water contents

LDPE/rice starch	Moisture content[a]	Tensile strength (MPa)	Tensile modulus (MPa)	Percentage elongation (%)
100/0	0	8.34 ± 0.72	195 ± 17	627 ± 40
95/5	0	7.89 ± 0.51	176 ± 18	490 ± 29
	3	6.30 ± 0.21	141 ± 12	530 ± 35
	6	5.12 ± 0.18	104 ± 9	562 ± 40
90/10	0	7.52 ± 0.48	160 ± 19	340 ± 23
	4	6.01 ± 0.39	125 ± 12	450 ± 33
	9	4.83 ± 0.44	89 ± 7	509 ± 38
80/20	0	6.88 ± 0.38	132 ± 11	160 ± 13
	9	4.65 ± 0.29	85 ± 7	300 ± 21
	15	5.20 ± 0.32	62 ± 5	395 ± 35
70/30	0	5.76 ± 0.29	103 ± 9	110 ± 12
	8	4.29 ± 0.33	68 ± 6	205 ± 18
	12	3.90 ± 0.25	59 ± 7	278 ± 25
	17	3.32 ± 0.30	48 ± 6	340 ± 30
60/40	0	4.96 ± 0.27	85 ± 6	55 ± 6
	5	4.17 ± 0.28	64 ± 5	123 ± 11
	12	3.52 ± 0.31	51 ± 4	210 ± 18
	20	3.04 ± 0.29	35 ± 4	290 ± 25

[a] Moisture as percent of initial feed blend composition (on a wet basis)

1989; Huang and Brown, 1990; Lu and Brown, 1991; Stojmirovic et al., 1992; Kadota et al., 1993; Chudnovsky et al., 1995) since PE is involved in many applications. Two different modes of failure, brittle and ductile, have been suggested depending on the deformation features and the crack growth. The brittle failure mode is closely related to the slow crack growth induced by a catastrophic failure, whereas the occurrence of the ductile mode is considered as a result of macroscopic shear rupture. The capability of chain defects (in the form of branches, unsaturation and comonomer units) to become incorporated into the crystal lattice of LDPE as interstitial imperfections has been a topic of considerable controversy (Kadota et al., 1993; Chudnovsky et al., 1995). Although it was previously suggested that the presence of any defects should be excluded from the lattice, it was later proved that the accommodation of chain defects within the lattice of LDPE through formation of conformational chain isomers such as interstitial (kinks) and/or substitution sites (jogs) is feasible (Balta-Calleja et al., 1978).

In the case of LDPE/rice starch blends the brittle mode is favoured, at least when the samples contain low amounts of water, because of the occurring disruption of LDPE network continuity by the occluded filler particles (starch). However, plasticization of LDPE/rice starch blends with increasing amounts of water, should result in penetration of the

Table 2
Flexural strength and flexural moduli-1, -2 and -3 of LDPE/rice starch blends with various water contents

LDPE/rice starch	Moisture content[a]	Flexural strength (MPa)	Modulus-1 (MPa)	Modulus-2 (MPa)	Modulus-3 (MPa)
95/5	0	13.0 ± 1.2	196.5 ± 11.6	[—]	186.2 ± 15.0
	3	9.4 ± 0.7	187.0 ± 14.5	[—]	170.0 ± 13.4
	6	6.6 ± 0.4	165.5 ± 10.7	[—]	156.4 ± 11.0
90/10	0	14.5 ± 1.1	203.0 ± 17.5	229.3 ± 16.0	188.5 ± 15.6
	4	9.2 ± 0.6	184.6 ± 14.6	203.0 ± 17.8	170.7 ± 13.8
	9	6.5 ± 0.3	160.1 ± 11.8	155.2 ± 12.2	141.5 ± 12.0
80/20	0	15.7 ± 1.3	222.4 ± 16.5	246.3 ± 18.2	213.0 ± 17.0
	9	7.0 ± 0.5	170.0 ± 13.4	192.5 ± 14.6	159.3 ± 11.5
	15	5.3 ± 0.3	131.9 ± 10.2	154.0 ± 13.8	120.4 ± 10.4
70/30	0	16.8 ± 1.4	250.6 ± 18.6	275.2 ± 16.3	231.5 ± 20.0
	8	10.6 ± 0.8	212.0 ± 19.3	243.4 ± 17.5	187.6 ± 13.0
	12	8.8 ± 0.9	175.7 ± 14.0	190.2 ± 14.6	143.3 ± 12.4
	17	5.2 ± 0.4	130.9 ± 11.2	157.0 ± 13.0	121.5 ± 10.1
60/40	0	19.2 ± 1.5	287.5 ± 23.6	351.0 ± 22.3	243.6 ± 13.5
	5	11.9 ± 1.0	221.4 ± 16.8	283.4 ± 23.0	205.7 ± 16.2
	12	10.1 ± 0.9	187.0 ± 14.0	210.9 ± 16.5	160.0 ± 11.4
	20	6.4 ± 0.5	141.2 ± 11.5	167.5 ± 12.7	128.3 ± 10.5

[a] Moisture as percent of initial feed blend composition (on a wet basis)

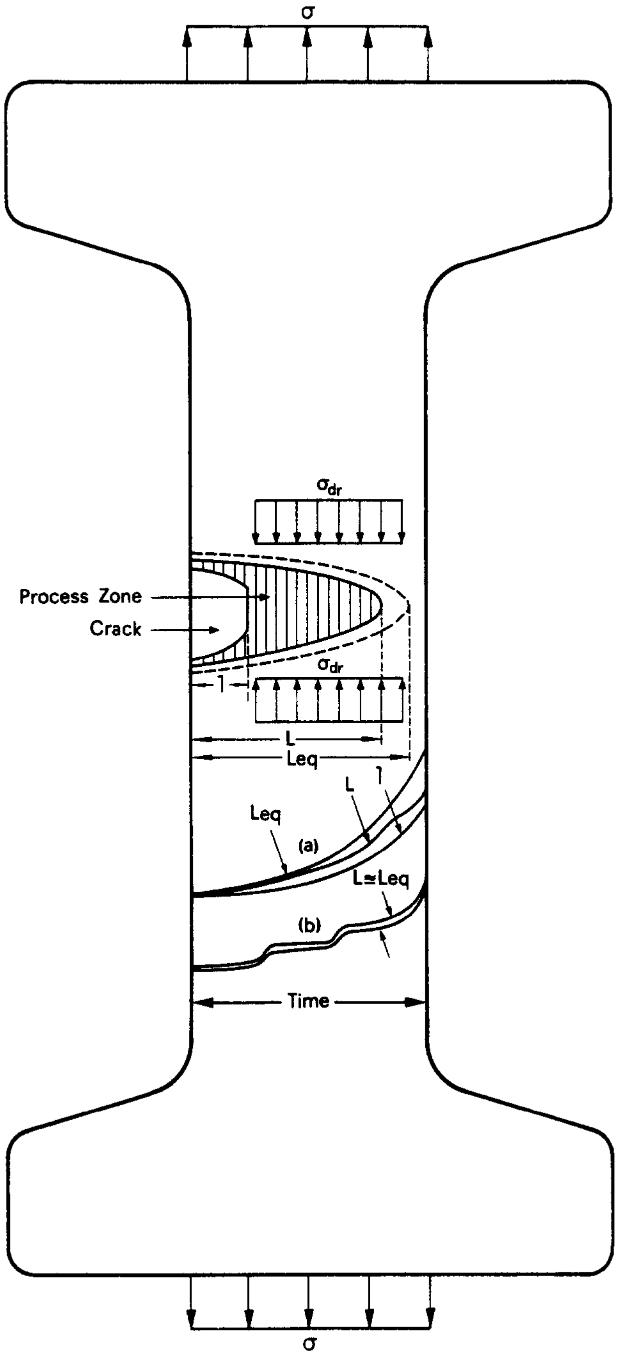


Fig. 3. Schematic representation of crack layer growth mechanism in LDPE/rice starch blends where: l is crack length; L is crack layer length; L_{eq} is the length at which the process zone is in a stable state; σ is remote stress; σ_{dr} is drawing stress; (*a*) and (*b*) modes stand for smooth and stepwise crack layer growth, respectively

plasticizer in the composite network leading to 'filling' of the voids and thus reducing considerably the number of existing defects. The process of crack propagation of LDPE/rice starch blends can be visualized as shown in Fig. 3. The crack layer (CL) consists of a closely coupled crack and the process zone (PZ) (Kim and Pometto, 1994). The earlier developed (Chudnovsky et al., 1995) model of the crack layer is described by two parameters, the crack length (l) and the crack layer length (L). The crack layer growth can be either (a) smooth or (b) discontinuous (stepwise) depending, to great extent, on the plasticization of the matrix. In particular, plasticization of the blends, as can be seen from the traces (Fig. 4), results in a smoother crack layer growth, whereas dry starch-rich blends ($>$ 20%) follow a discontinuous crack layer growth (van Krevelen, 1990).

Among the many reasons that should be probably quoted for the occasionally recorded high standard deviation of tensile strength and percentage elongation of some LDPE/rice or potato starch blends, the following should be mentioned: variation of the true strain rate with time, occurrence of softening at the early stages of the large deformation process, which results in stress localization, and nonuniform extension because of 'necking' (Balta-Calleja et al., 1978). Furthermore, another inherent problem usually encountered with LDPE/rice or potato starch blends is that some of the starch particles are bound to protrude thus affecting the uniform size of the produced sheet (Fig. 5) and the ensuing measurements of the mechanical properties (Griffin, 1994).

3.1.2. Three-point bend test

Tables 2 and 3 show that the flexural modulus increases proportionally to the starch content in the blend. In fact, the presence of starch islets does not contribute to the matrix plasticization, as is the case with low molecular weight plasticizers (Kirby et al., 1991, 1993), but rather to the formation of a more strengthened composite. However, a higher moisture content in the blends imparted some flexibility to the three-point bend specimens (Tables 2 and 3). The occasionally observed variability in measurements of some specimens should be rather attributed to the nonuniform distribution of water throughout the blend matrix. Any initially available microcavities or 'holes' are nonuniformly filled by water and this phenomenon is further promoted by the creation of a greater number of microcavities during the mechanical treatment of the blends. The samples with low water contents exhibited brittle behaviour similar in some aspects to that of pure synthetic polymers in the glassy state.

3.2. Water vapour transmission rate (WVTR)

Table 4 shows that, since LDPE does not absorb a great quantity of water, the higher the starch contents in the LDPE/rice or potato starch blends the higher the WVTR. This increase in WVTR is due to the pronounced hydrophilic character of starch. We should bear in mind that, even in dry starch, the starch chains are insufficiently packed, compared to the other semicrystalline synthetic polymers and they have small voids within which accommodation of water molecules usually occurs. For example, it has been noted that water removal from granular starch causes a high degree of strain on crystallites which is evidenced by losses

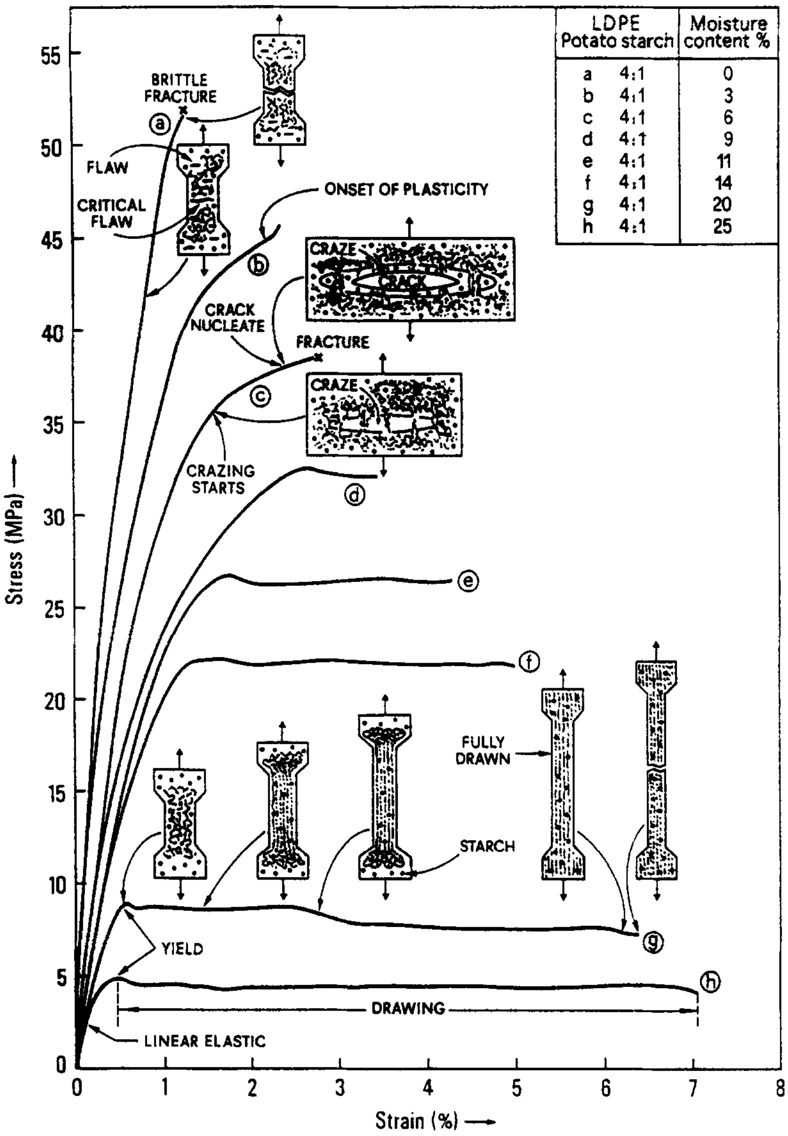


Fig. 4. Stress–strain curves for 80/20 LDPE/potato starch blend with various water contents

in intensity and sharpness of its WAXD pattern (French, 1984). The observed significant increase of WVTR at high starch contents > 15% (Table 4) in the LDPE/rice or potato starch blends could reflect the disruption of the polyethylene matrix by the starch particles.

3.3. Gas permeability (GP): percentage crystallinity (%Xc) from WAXD patterns

Although the gas permeability of polyethylene has attracted the interest and has been the subject of many investigations (Michaels and Bixler, 1961; Zollandz and Fleming, 1992; Stern et al., 1983), to provide a better insight of the gas permeability of LDPE/starch blends it is imperative to consider in more detail the morphology of LDPE which, in our case, acts as a matrix. The crystallites in LDPE can be visualized as ribbonlike lamellae of 70–1500 Å thickness. We should bear in mind that the crystallites obtained from the melt are not completely perfect but rather consist of both amorphous imperfections and crystalline parts which can be increased depending on the heat treatment and the thermal history of the sample. Despite the rather constant values for gas permeability rates reported for LDPE, it should be recognized that these values truly reflect the average behavior of three distinct amorphous regions of LDPE: intralamellar, interlamellar and interspherulitic amorphous material (Michaels and Bixler, 1961). The incorporation of starch particles in the LDPE matrix complicates the issue even more, mainly because of the hydrophilicity of starch. Rice or potato starches can sorb water which, either strongly bound (0–12%) or as capillary moisture (12–30% on a starch basis), can further influence the gas permeability of the blends as can be seen from Tables 5, 6 and Fig. 6. The GP modelling of LDPE/rice starch blends using the Salame's

Table 3
Flexural strength and flexural moduli-1, -2 and -3 of LDPE/potato starch blends

LDPE/potato starch	Moisture content[a]	Flexural strength (MPa)	Modulus-1 (MPa)	Modulus-2 (MPa)	Modulus-3 (MPa)
100/0	0	12.1 ± 0.9	181.6 ± 13.5	—	—
95/5	0	12.8 ± 0.8	190.5 ± 14.0	—	178.0 ± 11.7
	4	8.9 ± 0.6	175.9 ± 8.5	—	162.3 ± 6.8
	6	7.0 ± 0.5	154.3 ± 9.2	—	140.8 ± 8.3
90/10	0	15.1 ± 1.3	206.0 ± 16.2	271.9 ± 14.3	193.0 ± 14.4
	5	12.7 ± 1.4	188.5 ± 11.8	194.8 ± 12.9	171.8 ± 11.2
	9	8.1 ± 0.7	152.4 ± 10.3	163.0 ± 11.5	138.7 ± 10.6
80/20	0	16.3 ± 1.5	217.3 ± 11.6	221.9 ± 14.0	208.4 ± 16.5
	8	11.2 ± 1.0	161.5 ± 13.2	177.7 ± 12.3	147.9 ± 12.1
	15	7.5 ± 0.6	123.4 ± 8.4	136.5 ± 8.8	111.3 ± 8.5
70/30	0	17.1 ± 1.6	230.5 ± 22.1	242.8 ± 16.4	221.6 ± 18.0
	8	12.9 ± 1.0	191.7 ± 12.4	205.5 ± 13.6	171.4 ± 13.5
	13	9.5 ± 0.8	143.4 ± 11.2	162.4 ± 12.5	128.5 ± 10.2
	19	6.2 ± 0.7	119.3 ± 8.7	131.5 ± 9.4	104.8 ± 8.7
	25	3.0 ± 0.2	90.8 ± 7.4	103.4 ± 7.2	72.3 ± 5.6
60/40	0	18.9 ± 1.5	240.9 ± 19.5	280.5 ± 14.6	227.8 ± 15.5
	6	14.5 ± 1.1	207.5 ± 13.3	218.6 ± 20.5	191.2 ± 13.0
	12	11.6 ± 1.3	160.0 ± 12.6	184.5 ± 16.0	142.9 ± 11.5
	22	7.2 ± 0.7	118.9 ± 10.4	130.0 ± 11.2	106.5 ± 7.8
	33	2.8 ± 0.2	77.7 ± 8.2	91.0 ± 6.7	63.8 ± 5.0

[a] Moisture as percent of initial feed blend composition (on a wet basis)

equation (Salame, 1986) occurs according to the following procedure:

$$N \times \pi = \Pi = \Sigma(N_i \times \pi_i) \quad (7)$$

where Π is an additive molar function of permeability, N is the number of characteristic groups per structural unit and i is the increment of the group i.

The numerical value of polymer permachor, π, being known, the permeability at ambient temperature can be estimated from

$$P_{(298)} = P^{*}_{(298)} \exp(-S\pi) \quad (8)$$

where $P_{(298)}$ is the permeability of a standard gas (i.e. N_2) in a chosen standard polymer (i.e. rubber) and S is the scaling factor. By substituting $\log P^{*}_{(298)} = -12$ and $S = 0.122$ (Salame, 1986), the following equation is obtained, the applicability of which is restricted to amorphous polymers:

$$\log P_{(298)} = -12 - 0.053\pi \quad (9)$$

Table 4
Water vapour transmission rate (WVTR) of LDPE/rice or potato starch blends

	WVTR (g m^{-1} s^{-1} Pa^{-1}) × 10^{-13}
LDPE/rice starch weight ratio	
100/0	0.1 ± 0.02
95/5	0.8 ± 0.1
90/10	2.9 ± 0.3
80/20	30.3 ± 2.5
70/30	70.5 ± 6.3
60/40	160.0 ± 14.0
LDPE/potato starch weight ratio	
95/5	1.1 ± 0.1
90/10	2.7 ± 0.2
80/20	35.5 ± 3.2
70/30	78.8 ± 6.9
60/40	167.6 ± 12.8

For semicrystalline (sc) polymers a further modification (Salame, 1986) is necessary, leading to

$$\pi_{sc} = \pi_a - 41.5\log\alpha = \pi_a - 41.5\log(1 - x_c) \quad (10)$$

where α is the amorphous volume fraction and x_c is the crystallinity.

Hence the contributions to the molar permachor for semicrystalline LDPE, using the group contributions from data published by Salame (1986), are as follows:

$$\pi = N \times (\text{group contribution})_{-CH_2-} = 2 \times 15 = 30$$

thus

$$\pi = \Pi/N = 30/2 = 15$$

Therefore by applying first Eq. (10), where $x_c = 36.2\%$ (Table 5), and then Eq. (9) for N_2 in LDPE we get:

$$\pi_{sc} = \pi_a - 41.5\log(1 - x_c) = 15 - 41.5\log(1 - 0.362)$$

$$= 23.1 \log P_{(298)} = -12 - 0.053\pi_{sc}$$

$$= -12 - 0.053(23.1) = -13.2243$$

$$\Rightarrow \log P_{(298)} = 6.0 \times 10^{-14}\ \mathrm{cm}^2\ \mathrm{s}^{-1}\ \mathrm{Pa}^{-1}$$

which is in reasonable agreement with the experimentally found value 2.2 × 10^{-13} cm^2 s^{-1} Pa^{-1} (Table 5).

Fig. 7 shows the WAXDP traces of some representative LDPE/potato starch blends and of the homopolymers (LDPE and potato starch) as well. It is obvious that these blends are of semicrystalline nature (Tables 5 and 6) and as such there are some amorphous and some crystalline domains where the GP is favoured or not. In the case of

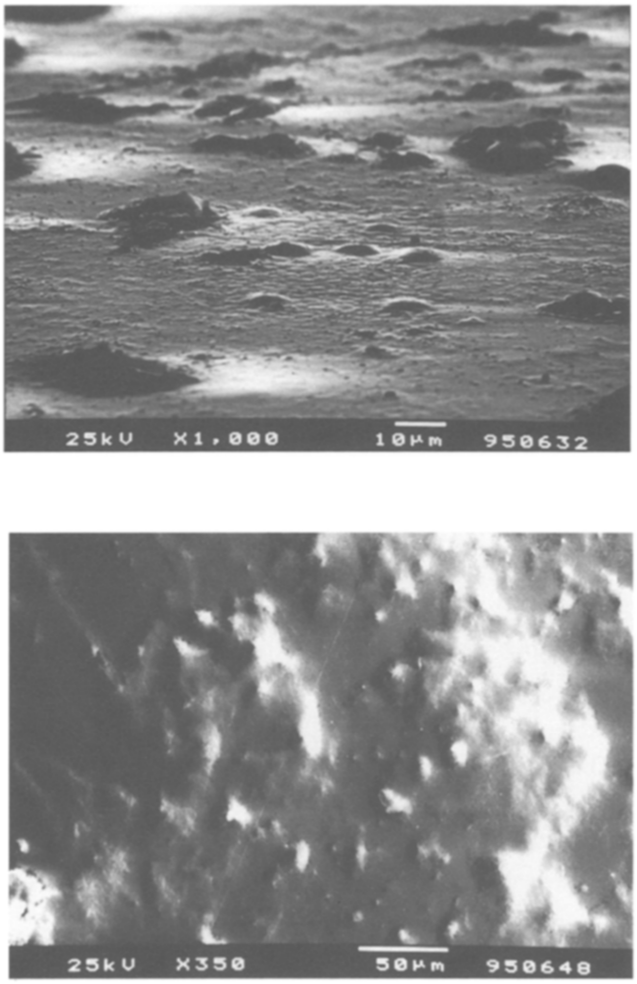


Fig. 5. SEM micrographs of a LDPE film containing potato starch showing protruded starch particles

laminated films it was suggested (Robertson, 1993) that the following formula (Eq. (11)) should be used for the permeability calculations:

$$1/P_{\text{lamin}} = (x_1/x_1 + x_2)1/P_1 + (x_2/x_1 + x_2)1/P_2 \qquad (11)$$

where P_1, x_1 and P_2, x_2 stand for the permeability and thickness of components 1 and 2, respectively.

If we apply Eq. (11) for the LDPE/rice starch (70/30) blend, using the weight ratios of LPDE and starch for x_1 and x_2, respectively, and the corresponding permeability values (to N_2) of the pure components [$P_{\text{LDPE}} = 2.2 \times 10^{-13}\,\text{cm}^2\,\text{s}^{-1}\,\text{Pa}^{-1}$ (Table 5) and $P_{\text{rice starch}} = 7.3 \times 10^{-14}\,\text{cm}^2\,\text{s}^{-1}\,\text{Pa}^{-1}$ (Arvanitoyannis et al., 1994)], the calculated permeability for the blend is $1.37 \times 10^{-13}\,\text{cm}^2\,\text{s}^{-1}\,\text{Pa}^{-1}$. This value is somewhat lower than the experimentally found $5.9 \times 10^{-12}\,\text{cm}^2\,\text{s}^{-1}\,\text{Pa}^{-1}$ (Table 5). Such deviations between the experimental values and those calculated using the above semiempirical modelling approaches could be attributed to several factors, including accessibility of polar groups, relative strength of water–water *versus* the water–polymer interactions, level of crystallinity (i.e. presence and size of microcrystallites) and void geometry and blend morphology (van Krevelen, 1990; Mueller-Plathe, 1991a, b, 1992).

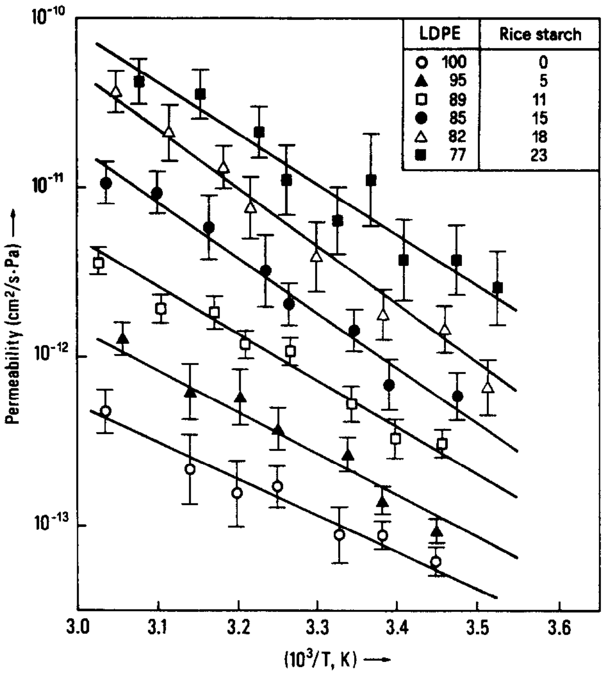


Fig. 6. Oxygen permeability of LDPE/rice starch blends *versus* the inverse temperature ($10^3/T$)

Both the diffusivity and permeability dependence on temperature are expressed by the Arrhenius relationships (Eq. (12) and Eq. (13)). The apparent activation energies of diffusion and permeation can be calculated from the

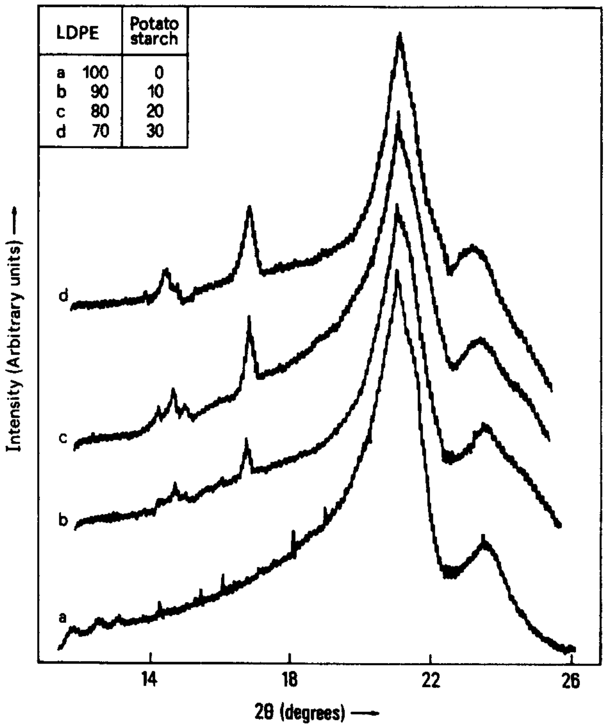


Fig. 7. WAXDP traces of some representative LDPE/potato starch blends

Table 5
Gas permeability (N_2, CO_2) and percentage crystallinity (%Xc determined from WAXDP) of LDPE/rice starch blends with various moisture contents at room temperature (22 ± 1°C)

LDPE/rice starch	Moisture content[a]	%Xc WAXDP	Gas permeability ($cm^2\ s^{-1}\ Pa^{-1}$)	
			N_2	CO_2
100/0	0	36.2	$2.2 \pm (0.1) \times 10^{-13}$	$4.2 \pm (0.3) \times 10^{-12}$
95/5	0	34.5	$3.5 \pm (0.2) \times 10^{-13}$	$6.8 \pm (0.6) \times 10^{-12}$
	3	33.9	$4.7 \pm (0.4) \times 10^{-13}$	$9.5 \pm (0.1) \times 10^{-12}$
	6	33.6	$6.5 \pm (0.6) \times 10^{-13}$	$0.8 \pm (0.2) \times 10^{-11}$
90/10	0	31.3	$7.1 \pm (0.3) \times 10^{-13}$	$1.3 \pm (0.1) \times 10^{-11}$
	4	30.0	$8.4 \pm (0.2) \times 10^{-13}$	$3.8 \pm (0.3) \times 10^{-11}$
	9	28.8	$8.7 \pm (0.3) \times 10^{-13}$	$6.0 \pm (0.1) \times 10^{-11}$
80/20	0	27.4	$9.4 \pm (0.7) \times 10^{-13}$	$2.1 \pm (0.2) \times 10^{-11}$
	8	25.6	$2.7 \pm (0.6) \times 10^{-12}$	$6.6 \pm (0.1) \times 10^{-11}$
	15	24.2	$3.8 \pm (0.2) \times 10^{-12}$	$7.9 \pm (0.6) \times 10^{-11}$
70/30	0	21.9	$5.9 \pm (0.1) \times 10^{-12}$	$1.1 \pm (0.2) \times 10^{-10}$
	9	20.5	$8.5 \pm (0.4) \times 10^{-12}$	$1.8 \pm (0.1) \times 10^{-10}$
	12	18.4	$9.9 \pm (0.1) \times 10^{-12}$	$2.8 \pm (0.3) \times 10^{-10}$
	17	17.2	$2.3 \pm (0.5) \times 10^{-11}$	$4.7 \pm (0.1) \times 10^{-10}$
60/40	0	17.5	$4.7 \pm (0.7) \times 10^{-11}$	$8.0 \pm (0.1) \times 10^{-10}$
	5	17.0	$6.6 \pm (0.2) \times 10^{-11}$	$1.9 \pm (0.6) \times 10^{-9}$
	12	16.8	$7.5 \pm (0.6) \times 10^{-11}$	$2.1 \pm (0.1) \times 10^{-9}$
	20	17.1	$9.6 \pm (0.1) \times 10^{-11}$	$3.0 \pm (0.2) \times 10^{-9}$

[a] Moisture as percent of initial feed blend composition (on a wet basis)

logarithmic expressions of Eq. (12) and Eq. (13).

$$D = D_0 \exp(-E_D/RT) \tag{12}$$

where D_0 is the diffusion coefficient, E_D is the activation energy of diffusion and R is the universal gas constant.

Similarly to Eq. (13), the temperature dependence of permeability can be expressed as

$$P = P_0 \exp(-E_P/RT) \tag{13}$$

where E_P is the apparent activation energy of permeation.

The corresponding logarithmic expressions of the Arrhenius equations (Eq. (12) and Eq. (13)), describing diffusivity and permeability, are as follows:

$$\ln D = \ln D_0 - E_D/RT \tag{14}$$

$$\ln P = \ln P_0 - E_P/RT \tag{15}$$

The permeability data for LDPE/potato starch followed reasonably well Eq. (15), as shown in Fig. 6. The activation energies of diffusion and permeation were calculated

Table 6
Gas permeability (O_2, N_2 and CO_2) and percentage crystallinity (%Xc determined from WAXDP) of LDPE/potato starch blends with various moisture contents at room temperature (22 ± 1°C)

LDPE/potato starch	Moisture content[a]	Gas permeability ($cm^2\ s^{-1}\ Pa^{-1}$)			%Xc WAXDP
		O_2	N_2	CO_2	
100/0	0	$8.0 \pm (0.7) \times 10^{-13}$	$2.2 \pm (0.1) \times 10^{-13}$	$4.2 \pm (0.3) \times 10^{-12}$	36.2
95/5	0	$1.1 \pm (0.1) \times 10^{-12}$	$3.3 \pm (0.3) \times 10^{-13}$	$8.5 \pm (0.7) \times 10^{-12}$	35.0
	3	$2.4 \pm (0.2) \times 10^{-12}$	$6.4 \pm (0.5) \times 10^{-13}$	$1.2 \pm (0.1) \times 10^{-11}$	34.1
	5	$3.0 \pm (0.3) \times 10^{-12}$	$8.0 \pm (0.7) \times 10^{-13}$	$1.5 \pm (0.2) \times 10^{-11}$	33.2
90/10	0	$2.0 \pm (0.2) \times 10^{-12}$	$5.5 \pm (0.4) \times 10^{-13}$	$1.4 \pm (0.1) \times 10^{-11}$	32.4
	3	$3.5 \pm (0.1) \times 10^{-12}$	$8.8 \pm (0.3) \times 10^{-13}$	$1.8 \pm (0.4) \times 10^{-11}$	29.7
	7	$4.2 \pm (0.1) \times 10^{-12}$	$1.1 \pm (0.2) \times 10^{-12}$	$2.5 \pm (0.2) \times 10^{-11}$	27.6
80/20	0	$3.3 \pm (0.3) \times 10^{-12}$	$8.0 \pm (0.1) \times 10^{-13}$	$3.2 \pm (0.1) \times 10^{-11}$	28.5
	8	$4.2 \pm (0.2) \times 10^{-12}$	$9.2 \pm (0.8) \times 10^{-13}$	$4.2 \pm (0.2) \times 10^{-11}$	26.8
	18	$8.0 \pm (0.2) \times 10^{-12}$	$2.0 \pm (0.4) \times 10^{-12}$	$5.8 \pm (0.6) \times 10^{-11}$	25.0
70/30	0	$1.3 \pm (0.4) \times 10^{-11}$	$6.4 \pm (0.1) \times 10^{-12}$	$1.1 \pm (0.2) \times 10^{-10}$	22.2
	6	$4.4 \pm (0.2) \times 10^{-11}$	$7.9 \pm (0.3) \times 10^{-12}$	$1.6 \pm (0.1) \times 10^{-10}$	20.8
	15	$5.3 \pm (0.1) \times 10^{-11}$	$9.2 \pm (0.3) \times 10^{-12}$	$2.1 \pm (0.1) \times 10^{-10}$	19.3
60/40	0	$3.8 \pm (0.2) \times 10^{-11}$	$8.7 \pm (0.5) \times 10^{-12}$	$2.3 \pm (0.2) \times 10^{-10}$	18.9
	5	$4.5 \pm (0.9) \times 10^{-11}$	$9.8 \pm (0.4) \times 10^{-12}$	$3.4 \pm (0.5) \times 10^{-10}$	17.4
	10	$1.3 \pm (0.2) \times 10^{-10}$	$3.1 \pm (0.6) \times 10^{-11}$	$6.2 \pm (0.1) \times 10^{-10}$	16.5
	18	$3.1 \pm (0.5) \times 10^{-10}$	$5.7 \pm (0.1) \times 10^{-11}$	$1.4 \pm (0.2) \times 10^{-9}$	16.4

[a] Moisture as percent of initial feed blend composition (on a wet basis)

Table 7
Activation energies for diffusion (E_D, kJ mol^{-1}) and permeation (E_P, kJ mol^{-1}) for LPDE/potato starch blends with different moisture contents

LPDE/potato starch	Moisture content[a]	N_2		O_2		CO_2	
		E_D^b	E_P^c	E_D^b	E_P^c	E_D^b	E_P^c
100/0	0	37.2 ± 2.8	42.3 ± 4.5	40.5 ± 3.1	46.7 ± 3.8	42.8 ± 4.0	48.4 ± 5.0
95/5	0	34.1 ± 2.8	38.9 ± 3.3	37.0 ± 3.3	41.8 ± 4.3	39.2 ± 3.3	43.4 ± 3.8
	3	32.0 ± 2.5	36.3 ± 3.3	34.1 ± 3.2	38.4 ± 3.6	35.7 ± 2.8	38.4 ± 3.5
	5	29.8 ± 2.2	33.1 ± 2.9	32.2 ± 2.8	36.0 ± 2.9	34.0 ± 3.2	36.5 ± 3.5
90/10	0	32.1 ± 1.9	34.5 ± 2.6	33.9 ± 2.5	37.0 ± 3.4	35.6 ± 3.0	38.5 ± 3.2
	3	30.3 ± 1.8	32.7 ± 2.4	32.3 ± 2.8	35.0 ± 3.3	33.4 ± 2.0	35.7 ± 3.1
	7	27.1 ± 2.4	29.4 ± 2.2	29.8 ± 1.7	31.3 ± 3.0	30.9 ± 2.6	33.4 ± 3.2
80/20	0	28.5 ± 2.5	30.7 ± 2.9	30.5 ± 2.9	33.3 ± 2.6	33.0 ± 3.3	34.9 ± 3.2
	8	25.7 ± 2.5	28.0 ± 2.2	27.6 ± 2.4	29.8 ± 3.0	29.3 ± 2.8	31.2 ± 3.0
	18	21.8 ± 2.0	24.1 ± 2.2	23.7 ± 2.5	26.0 ± 2.1	25.2 ± 2.2	27.6 ± 2.6
70/30	0	26.0 ± 2.3	28.5 ± 2.7	28.1 ± 2.5	30.3 ± 2.7	29.8 ± 2.4	31.7 ± 2.7
	6	23.9 ± 2.1	26.0 ± 2.0	26.4 ± 1.9	28.5 ± 2.5	28.0 ± 1.9	29.1 ± 2.6
	15	21.0 ± 1.8	23.3 ± 1.9	23.8 ± 2.2	25.6 ± 1.6	23.5 ± 2.2	26.3 ± 1.9
60/40	0	23.0 ± 2.1	25.3 ± 1.9	24.9 ± 1.9	27.0 ± 2.4	26.5 ± 2.4	29.0 ± 2.5
	5	20.6 ± 1.8	23.2 ± 2.8	22.0 ± 2.0	24.9 ± 2.5	24.7 ± 2.1	26.2 ± 1.9
	10	18.0 ± 1.6	20.4 ± 1.9	20.3 ± 1.8	24.0 ± 2.1	23.0 ± 2.0	24.9 ± 2.4
	18	15.6 ± 1.5	18.6 ± 1.7	18.1 ± 2.0	22.1 ± 1.9	20.1 ± 1.7	23.5 ± 1.8

[a] Moisture as percent of initial feed blend composition (on a wet basis)
[b] Calculated according to Eq. (14)
[c] Calculated according to Eq. (15)

according to Eq. (14) and Eq. (15) for LDPE/rice starch blends (Table 7). The activation energy of diffusion is of great importance because it involves the work of separation of chains and, in the absence of any specific interactions between the groups of the food (polymer) matrix and the diffusing gas particle, an increase in E_D with penetrant molecular size (Table 7) is anticipated. Gas transmission occurs when the conditions are favourable mainly with regard to the availability of the thermal energy required for chain separation or loosening of the structure. Therefore, the introduction of starch molecules within the LDPE network decreases, at least locally, the required energy per unit chain separation (Table 7). It should be noted that, as previously reported (Barrer and Skirrow, 1948; Albertsson et al., 1994), the number of chain segments to be loosened for the completion of unit diffusion process for a nitrogen molecule is smaller than for oxygen. Moving to higher temperatures, the chain mobility in the polymer network increases, encouraging the formation of further cavities and interconnecting channels, and finally resulting in higher diffusivity and permeability values and thereby lower activation energies. It is also apparent from the permeability $-1/T$ plots Fig. 6) that there is no discontinuity as found with fully amorphous starch-based biopolymer blends in the glass transition region (Arvanitoyannis et al., 1996; Psomiadou et al., 1996; Arvanitoyannis et al., 1997), presumably due to the high crystallinity levels of LDPE in the blends.

3.4. Biodegradability studies

Simulating conditions in an anaerobic bioreactor to those in a typical landfill is very important because the disposal of most plastics takes place in landfills. Although extrapolation of bioreactor behavior to 'real world conditions' such as landfills is complicated by many factors, the anaerobic reactor employed for the current investigation is by far more biologically effective than a typical landfill (Krupp and Jewell, 1992). Therefore, even short-term exposure might approximate several times longer landfill burial time (see Figs. 8 and 9 for % elongation lowering *versus* various exposure times). The bioreactors were extremely efficient biodegrading environments since they showed a remarkable consistency and reproducibility in biodegrading almost 96% of the used sorghum/cellulose substrate. The pH was kept at

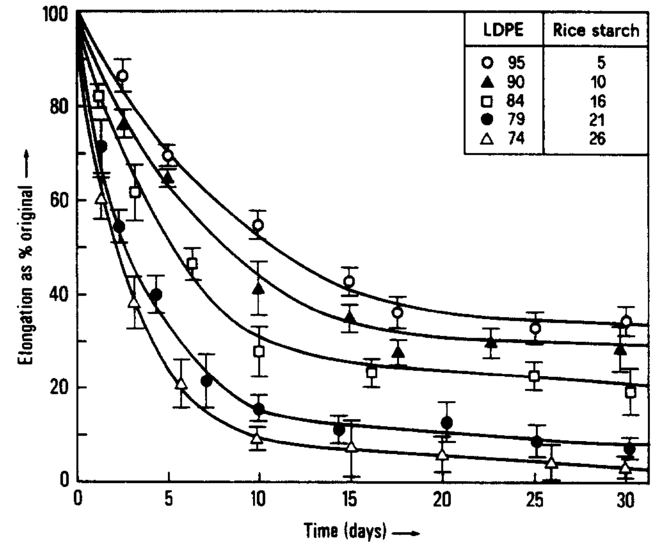


Fig. 8. Elongation as percentage of the original *versus* time (days) after exposure of LDPE/rice starch blends to anaerobic bioreactors

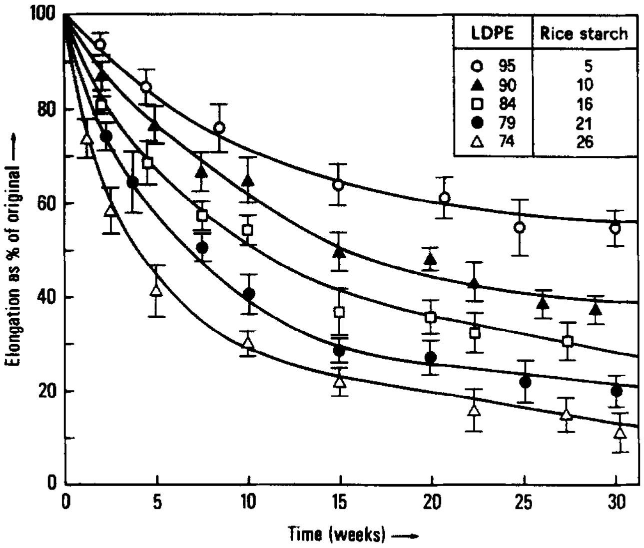


Fig. 9. Elongation as percentage of the original *versus* time (weeks) after burial of LDPE/rice starch blends in soil

6.7–7.0 and the dissolved O_2 was 2–6 mg l^{-1}. BOD curves for several LDPE/rice starch blends and rice starch are given in Fig. 10. As can be seen from Fig. 11 the magnitude of film mass loss after bioreactor exposure corresponds to the magnitude of BOD excretion by the film. Although in our experiments there was a good agreement between mass loss and BOD values, previous attempts to extrapolate experimentally obtained BOD valued were not successful (Krupp and Jewell, 1992). The previously observed incomplete biodegradation of starch in LDPE/rice starch blends (Krupp and Jewell, 1992) has been attributed to the physical protection offered by the synthetic polymer to the starch particles. In the present work, an almost 50–60% starch removal was observed and there was even some indication of early LDPE degradation as well (Table 8).

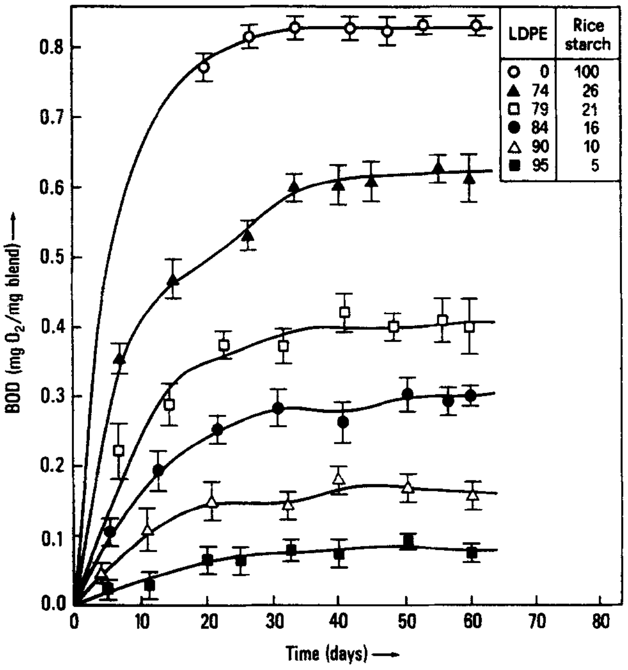


Fig. 10. Biochemical oxygen demand (BOD, mg O_2/mg of LDPE/rice starch blends) of LDPE/rice starch blends measured *versus* time (days)

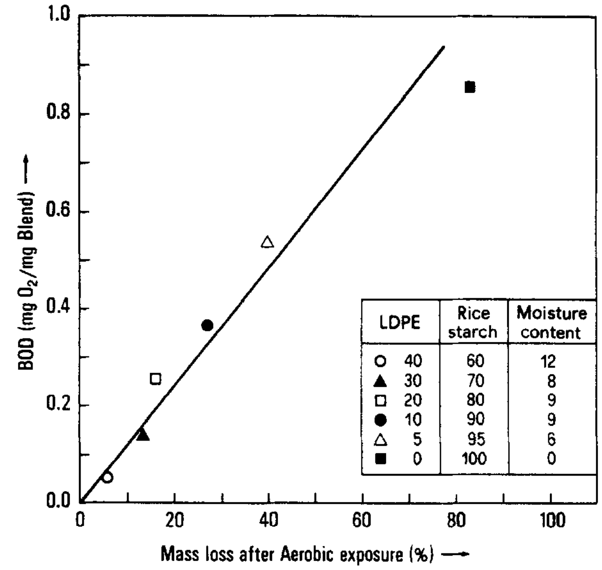
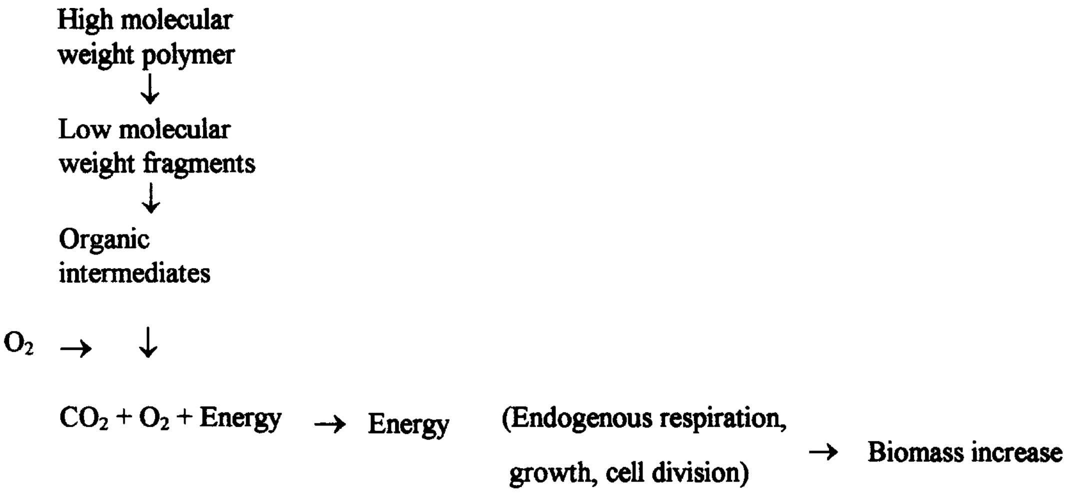


Fig. 11. Biochemical oxygen demand (BOD, mg O_2/mg of LDPE/rice starch blends) of LDPE/rice starch blends against percentage mass loss after aerobic exposure for 30 days (C.V. for at least quatruplicate measurements of BOD and mass loss after biodegradation did not exceed 4.9 or 3.7%, respectively

Previous studies were focused both on proving and establishing the degradability of HDPE or LDPE (Albertsson, 1978; Albertsson et al., 1978; Albertsson and Ranby, 1979; Albertsson et al., 1994) and on starch grafted with synthetic polymers (Tahan and Zilkha, 1969; Dennenberg et al., 1978; Fanta et al., 1979). Incorporation of starch in LDPE was previously reported to impart biodegradability to LDPE/starch blends (Griffin, 1994; Lourdin et al., 1995) and resulted in the commercial utilization of a LDPE/Starch blend (90/10), which was reported as being biodegradable (Griffin, 1994). In general, the main stages describing the biodegradation of a high molecular weight polymer are as follows (Andrady, 1994):

Although in the case of HDPE there is still no concluding evidence with regard to its biodegradability, several mechanisms (Fig. 12) (Lenz, 1993; Albertsson and Karlsson, 1994) have been occasionally suggested, based on studies with LDPE, involving either enzymatic oxidation, dehydrogenation and carbon–carbon breaking processes that lead to degradation of hydrocarbons; the products are two- to four-carbon organic compounds that can act as substrates and can be metabolized by microbial cells (Lenz, 1993). Therefore, the observed decrease of percentage elongation and weight losses (Tables 8 and 9, Figs. 8 and 9), both for experiments involving soil burial and bioreactor exposure should be attributed, in the first place, to starch removal (below described as a three-phase process) and degradation (Fig. 12) previously described (Wool and Cole, 1988), and in the second place,



to gradual and rather slow degradation of LDPE as shown in Fig. 13.

In the light of our findings (Tables 8 and 9, Figs. 8–11) and those previously published (Gould et al., 1990; Narayan, 1991), the biodegradability of blends whose starch content is below 10% seems to proceed at a slow rate. Application of the percolation theory and computer simulation of biodegradation to LDPE/starch blends (Stauffer, 1985; Peanasky et al., 1991) supports the notion that higher starch contents are required for enhanced biodegradability. Degradation of LDPE/rice starch blends is closely related to the accessibility of rice starch to microorganisms (Stauffer, 1985; Peanasky et al., 1991). Although various factors are to be taken into account with regard to starch accessibility such as number, mobility and reproduction rate of microbes (Wool, 1995), it is thought that the kinetics of LDPE/rice starch blends degradation can be visualized as following a three-phase process:

3.5. First phase

Amorphous starch chains, easily accessible, by the microbes are normally those located near the surface. Further progress of the microbes to the interior of the LDPE/starch blend should be rather interpreted with the help of the percolation theory (Albertsson, 1978).

3.6. Second phase

This phase consists of a further, even deeper, invasion of microbes which, however, cannot be considered yet a

Table 8
Percentage weight losses of LDPE/rice starch blends after their burial in soil for various times

LDPE/rice starch	Moisture content[a]	% weight losses				
	Burial time (days):	20	40	60	180	360
100/0	0	[—]	[—]	[—]	0.8 ± 0.2	1.5 ± 0.1
95/5	0	0.5 ± 0.1	0.8 ± 0.2	1.4 ± 0.2	1.8 ± 0.2	2.9 ± 0.3
	3	0.7 ± 0.1	1.1 ± 0.2	1.7 ± 0.1	2.7 ± 0.2	3.9 ± 0.3
	6	1.2 ± 0.2	1.7 ± 0.2	2.4 ± 0.3	3.5 ± 0.4	4.9 ± 0.4
90/10	0	0.7 ± 0.1	1.2 ± 0.2	1.9 ± 0.1	3.4 ± 0.3	4.9 ± 0.5
	4	1.0 ± 0.2	1.5 ± 0.1	2.2 ± 0.2	4.1 ± 0.3	5.5 ± 0.6
	9	1.4 ± 0.1	2.3 ± 0.2	3.5 ± 0.4	5.2 ± 0.4	7.8 ± 0.7
80/20	0	1.5 ± 0.1	2.6 ± 0.2	3.6 ± 0.3	5.3 ± 0.4	7.5 ± 0.7
	9	2.0 ± 0.3	3.0 ± 0.3	4.6 ± 0.4	6.7 ± 0.6	9.8 ± 0.9
	15	2.9 ± 0.4	4.7 ± 0.4	6.3 ± 0.5	8.9 ± 0.8	11.7 ± 1.1
70/30	0	2.3 ± 0.2	3.0 ± 0.2	5.5 ± 0.3	8.8 ± 0.7	10.5 ± 0.9
	8	3.3 ± 0.2	3.9 ± 0.4	7.2 ± 0.6	10.3 ± 1.0	12.8 ± 1.1
	12	4.1 ± 0.5	5.0 ± 0.3	9.4 ± 0.8	13.3 ± 1.2	15.6 ± 1.4
	17	4.9 ± 0.4	5.8 ± 0.6	10.9 ± 1.0	16.2 ± 1.1	19.3 ± 1.3
60/40	0	2.8 ± 0.2	3.7 ± 0.4	6.2 ± 0.6	9.7 ± 1.0	11.3 ± 1.4
	5	3.5 ± 0.3	5.1 ± 0.5	8.5 ± 0.7	12.5 ± 0.9	14.2 ± 1.5
	12	4.7 ± 0.4	6.0 ± 0.6	11.0 ± 0.9	15.0 ± 1.4	17.3 ± 1.8
	20	5.9 ± 0.6	7.5 ± 0.8	13.9 ± 1.2	18.3 ± 1.8	20.8 ± 2.1

[a] Moisture as percent of initial feed blend composition (on a wet basis)

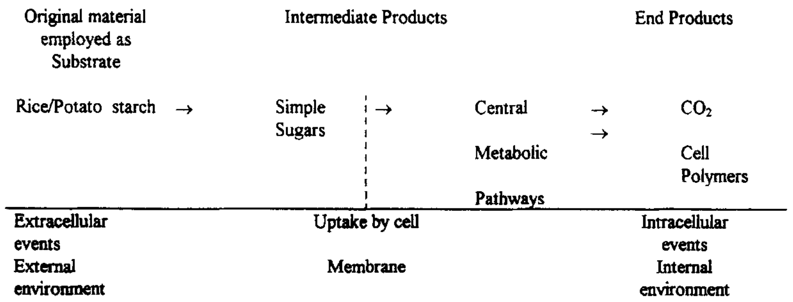


Fig. 12. Descriptive model for starch biodegradation

thorough one because of the persisting physically unaccessed 'starch islets'. The resulting 'holes or voids', mainly due to vacation of starch sites, are occupied by either microbes or water thus leading to extensive degradation of the blend.

3.7. Third phase

The more the degradation approaches its final stage, the available microbes decrease in number because of lack of nutrients. The very high surface area generated by removal of starch from the polymer blends enhances considerably the chemical degradation processes which, in turn, promote further biodegradation. The latter is a very promising aspect of the degradation pathway and is anticipated to be of considerable advantage in several novel biodegradable plastic formulations (Wool, 1995).

4. Summary

LDPE/rice or potato starch blends were prepared and their mechanical, WVTR and GP properties were measured and correlated to their composition and structure. High starch contents promoted brittleness and resulted in lower tensile strength and modulus and higher GP and WVTR. Blends containing increased amounts of water exhibited improved percentage elongation because of water plasticization of the composite matrix. Degradability of samples tested by immersion in bioreactors and burial in soil showed a substantial decrease in mechanical strength, tensile and flexural modulus and percentage elongation.

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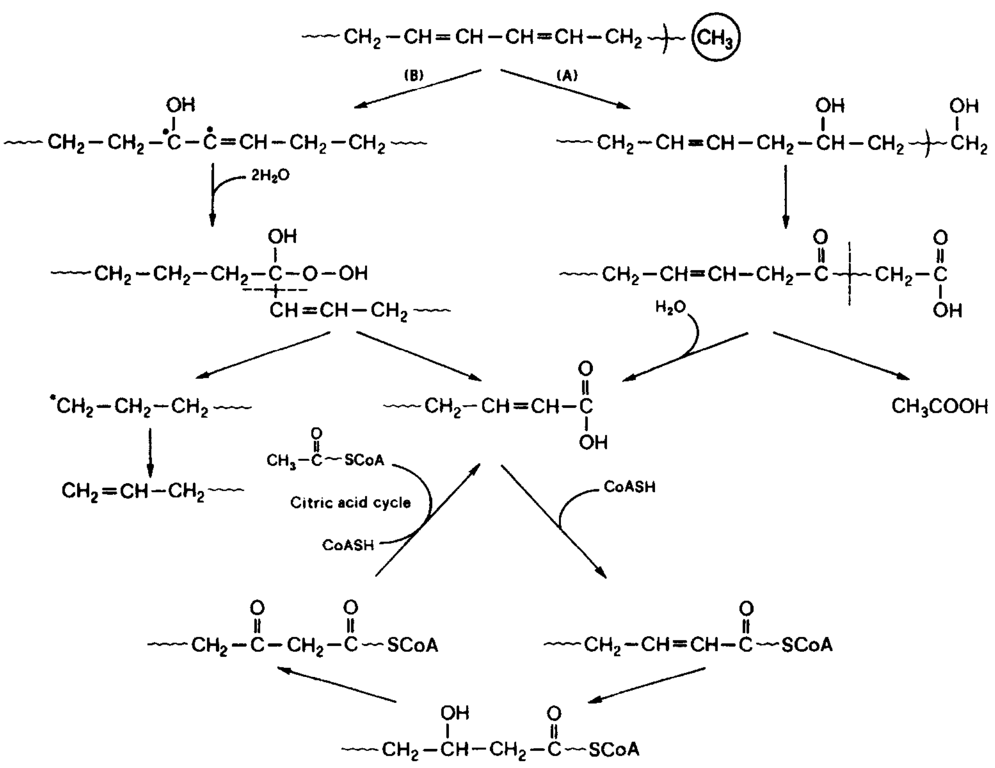

Fig. 13. Tentative model for the biodegradation mechanism of LDPE: (*A*) via oxidation of both main chains and end groups and (*B*) via oxidation of exclusively main chain ends (Lenz, 1993; Albertsson and Karlsson, 1994, 1995)

Table 9
Percentage weight losses of LDPE/rice starch blends after their exposure to aerobic and anaerobic bioreactors for various times

LDPE/rice starch	Moisture content[a]	% weight losses			
		Anaerobic		Aerobic	
Exposure time to bioreactor (days):		90	180	90	180
100/0	0	0.2 ± 0.1	0.9 ± 0.2	0.1 ± 0.1	0.6 ± 0.1
95/5	0	0.4 ± 0.1	2.3 ± 0.2	0.3 ± 0.1	1.9 ± 0.2
	3	1.0 ± 0.2	2.8 ± 0.1	1.0 ± 0.1	2.4 ± 0.3
	6	1.4 ± 0.1	3.6 ± 0.3	1.1 ± 0.2	2.9 ± 0.3
90/10	0	1.7 ± 0.1	3.8 ± 0.3	1.5 ± 0.1	3.5 ± 0.2
	4	2.0 ± 0.2	4.4 ± 0.2	0.8 ± 0.2	4.0 ± 0.3
	9	1.8 ± 0.1	6.3 ± 0.4	1.2 ± 0.1	5.6 ± 0.3
80/20	0	2.1 ± 0.2	6.6 ± 0.3	1.8 ± 0.1	5.9 ± 0.2
	9	3.0 ± 0.3	7.8 ± 0.4	2.6 ± 0.2	6.9 ± 0.3
	15	4.6 ± 0.3	9.5 ± 0.6	4.1 ± 0.2	8.4 ± 0.5
70/30	0	2.7 ± 0.3	9.8 ± 0.4	2.3 ± 0.2	8.0 ± 0.7
	8	4.8 ± 0.4	11.2 ± 0.6	4.1 ± 0.4	10.0 ± 1.2
	12	5.5 ± 0.4	13.3 ± 0.7	5.0 ± 0.6	12.2 ± 1.5
	17	6.8 ± 0.5	15.9 ± 0.8	6.1 ± 0.6	13.7 ± 1.4
60/40	0	3.4 ± 0.4	12.5 ± 0.9	3.0 ± 0.3	11.1 ± 1.0
	5	5.8 ± 0.3	14.9 ± 1.4	5.3 ± 0.4	12.6 ± 1.1
	12	8.3 ± 0.7	16.7 ± 1.8	8.1 ± 0.9	14.5 ± 1.3
	20	10.5 ± 1.2	21.4 ± 1.6	9.9 ± 0.8	18.8 ± 1.8

[a] Moisture as percent of initial feed blend composition (on a wet basis)

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