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Biodegradable films made from low density polyethylene (LDPE), wheat starch and soluble starch for food packaging applications. Part 2

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Blends of LDPE and wheat or soluble starch were extruded, hot pressed and studied, after conditioning at various relative humidities, with regard to their mechanical properties and gas/water permeabilities before and after storage. Several theoretical and semiempirical calculations for mechanical properties and gas permeability are applied and possible interpretations are provided for occasionally observed deviations between the experimental and the theoretical values. Some of the semiempirical models predicted reasonably well the mechanical behaviour of the films. The presence of starch, at contents >30%, had an adverse effect on the mechanical properties of LDPE/starch blends. The degradability of several LDPE/starch blends and the accompanying changes in their mechanical properties are also assessed. Gas permeability and water vapour transmission rate increased proportionally with the starch content in the blend. Copyright © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Plastics have gained a unique position in food packaging technology for a number of quite different reasons including: (a) higher strength, elongation and barrier properties against waterborne organisms responsible for food spoilage, (b) lower cost and higher energy effectiveness, and (c) lightness and water resistance (Guilbert, 1986).

The continuous growth of polymer materials for food packaging applications in conjunction with their recalcitrance toward degradation and their visibility in the environment when discarded have stimulated further research in the field of food packaging. It has been estimated that 2% of all plastics eventually reach the environment, thus contributing considerably to a currently acute ecological problem. For this reason there has been a recent trend toward preparation of degradable natural or synthetic polymers or natural/synthetic blends. Starch is a promising raw material because of its annual availability from many plants, its rather excessive production with regard to current needs, its low cost and its being environmentally friendly (Lourdin *et al.*, 1995). Starch-based plastics initially attracted some research interest but their development was not as expected, mainly because of their deficiencies with regard to mechanical properties and water transmission (Griffin, 1994; Lenz, 1993; Otey *et al.*, 1974). In an attempt to overcome this problem, synthetic polymer/starch blends have been investigated (Griffin, 1994; Otey *et al.*, 1974; Shogren, 1993; Lawton and Fanta, 1994). The main advantages of these blends could be summarized as follows (Scott and Gilead, 1995):

1. properties tailoring by proper selection of components and their ratios;
2. lower cost by using blending (i.e. co-extrusion, casting) instead of synthetic routes for novel materials;
3. ecological factors (environmentally friendly and usage of plastic wastes).

The aim of this paper was to prepare LDPE/wheat or soluble starch blends, varied in starch or moisture

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content, and to study their properties and their biodegradation rate. Several methods were used for assessing the latter, such as mass losses, changes in mechanical properties, and biochemical oxygen demand by exposure to bioreactor.

EXPERIMENTAL

Materials

Wheat and soluble starch were purchased by Wako (Japan) and LDPE was a gift from Asahi Chemicals (Japan).

Extrusion

LDPE and wheat and soluble 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: temperature zones 120, 120, 120 and 110°C (slot die); L/D: 500/30; Feed Motor and Mix Motor 2.0 and 50 rpm, respectively. The extrudates were subsequently hot pressed (110°C, 15 min, 560 N/m^2) to prepare specimens for measurement of mechanical properties.

Preparation of blends for gas permeability measurements

Wheat starch (starch/water 30% w/w) was rendered amorphous by gelatinizing and roller drying (one process) at 140°C, roller drier speed 10 rpm, pressure 221 kPa, gap 1 mm, diameter 165 mm, and width 150 mm. Mixtures of LDPE and gelatinized wheat and soluble starch were passed through the roller drier to obtain blends of appropriate composition. Preparation of films of LDPE with wheat or soluble starch for permeability measurements was carried out by pressing the samples at 110–120°C for 15 min (Arvanitoyannis and Blanshard, 1993; Arvanitoyannis *et al.*, 1994). The conditioning of samples at different relative humidities was as previously described (Arvanitoyannis *et al.*, 1994).

Wide angle X-ray measurements

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

Measurements of permeability

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

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

$$J_i = -D_{i(c_i)} \frac{\mathrm{d}c_i}{\mathrm{d}x} \tag{1}$$

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

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

$$D = \frac{d^2}{6\theta} \tag{2}$$

where d is the thickness of the film and θ is the time lag for the permeation. The lag is related to the time required by the gas for passing through the film and establishing an equilibrium with an originally gas-free chamber. 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:

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

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).

Water vapour transmission rate (WVTR) measurements

The WVTR measurements were carried out as previously reported (Martin-Polo *et al.*, 1992).

Mechanical properties

Tensile strength and percentage elongation

Tensile strength and percentage elongation were measured on dumbbells, after their equilibration at various relative humidities, using an Instron Universal Testing Instrument (model 1122) operated according to ASTM (1989). Measurement conditions and calculations of tensile strength and percentage elongation were made as previously described (Arvanitoyannis and Psomiadou, 1994; Arvanitoyannis *et al.*, 1995).

Three point bending test

All samples were cut with a scalpel, scissors or saw into bars, approximately 150×10×2.40 mm, and stored for at least 3 weeks over saturated salt solutions at room temperature to obtain water contents which were measured on three replicates by drying at 105°C to constant weight. Three point bend tests were carried out at room temperature using an Instron Texturometer at a crosshead speed of 1 mm/min on samples previously equilibrated at various Rh's at room temperature. 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.

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.

Biodegradability experiments

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 mixture of α-cellulose and dried milled sorghum twice a week at a loading rate 1.42 g of solids per 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 86% as previously reported (Krupp and Jewell, 1992). Both aerobic and anaerobic reactors were in function for 180 days at 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 ensure 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 and 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).

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 weighing.

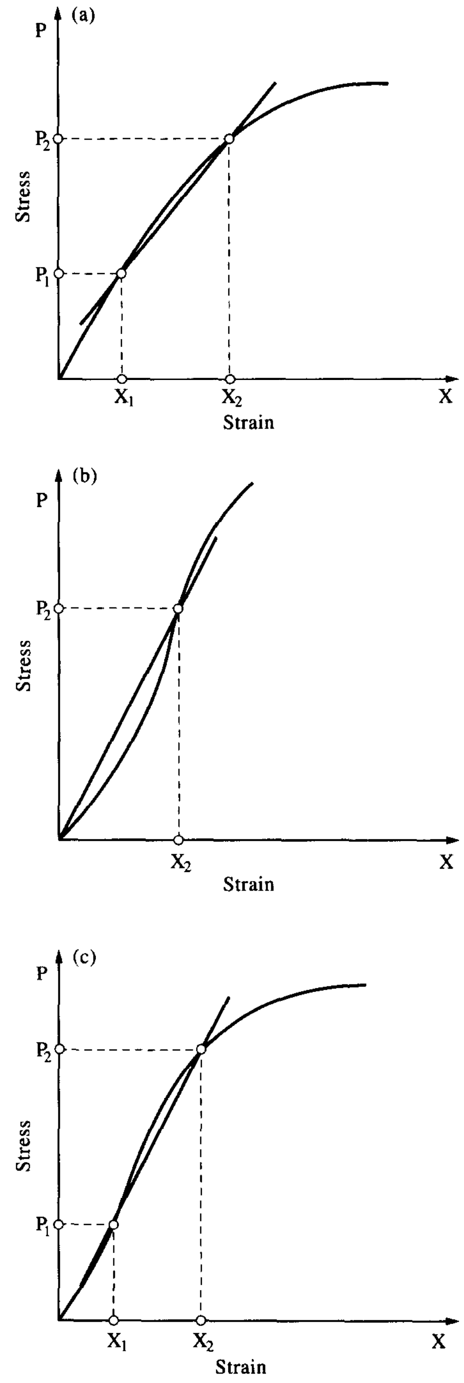

Fig. 1. Calculation modes of flexural modulus from the three point bend test: (a) chord; (b) secant; (c) least squares.

Determination of biochemical oxygen demand (BOD)

The oxygen demand of waste water was measured in most cases by using the standard 5 day BOD method. Although the method on its own does not constitute a direct method 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. The 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 number of mg of oxygen consumed per mg of plastic film added to the BOD bottle (mg O_2 per mg PE) expresses 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 the bottle had been stoppered, the sample was incubated at 60°C for the solubilization required time. The solid film sample was removed and the BOD test was carried out. Apart from the sample addition, the blanks were prepared in a similar way to the above described procedure.

Theoretical BOD calculation

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

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

Therefore, from eqn (4) 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. By dividing this number by the compound molecular weight, the oxygen consumption in BOD units (mg O_2 per mg PE) can be determined. The theoretical BODs for starch and LDPE are 1.07 and 3.08, respectively (Krupp and Jewell, 1992). 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 were kept in the reactor for up to 180 days. Unexposed films were also tested for BOD for comparison purposes.

RESULTS AND DISCUSSION

Mechanical properties

Tensile strength and modulus and percentage elongation

Nielsen (1974) derived a model relating elongation ε to filler volume fraction V:

$$\varepsilon_c = \varepsilon_0(1 - V^{1/3}) \quad (5)$$

where ε_c and ε_0 are the elongation to break of the composite and the pure polymer matrix, respectively, and V is the filler volume fraction. According to this model, whichever part of the polymer matrix (LDPE) happens to be between two or more filler particles it should be subjected to a considerably larger strain because of the lack of elongation of the rigid filler particles. Although eqn (5) was found to describe rather satisfactorily glass bead-filled polymers (Willett, 1994), in the case of our blends (Fig. 2(a)) quite

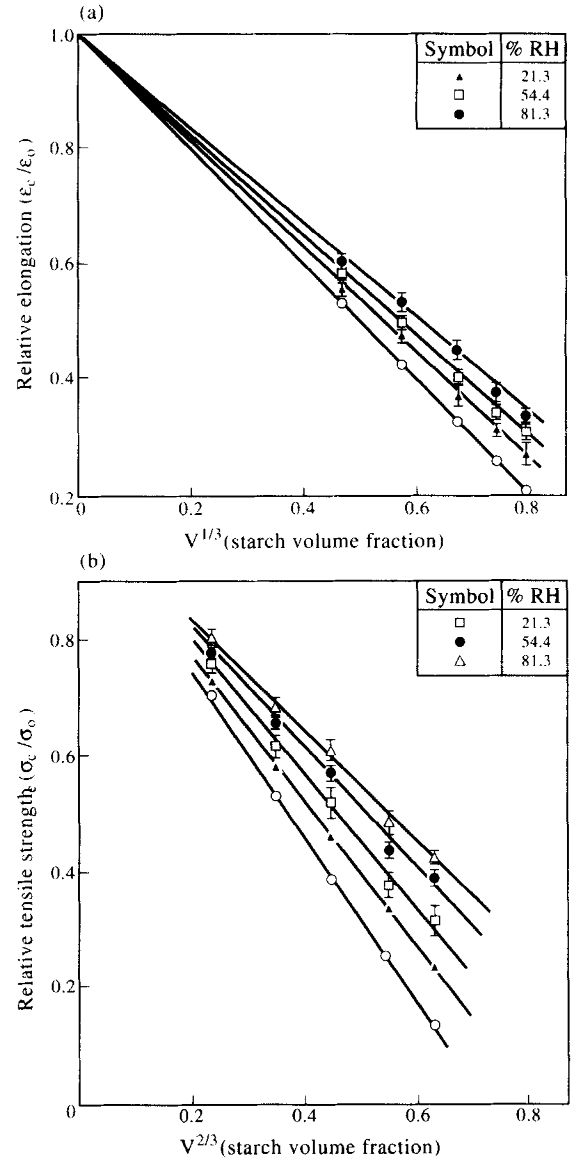

Fig. 2. (a) Relative elongation of LDPE/wheat starch blends, conditioned at different relative humidities, versus starch volume fraction. Line with symbol (o) represents theoretical calculation of $\varepsilon_c/\varepsilon_0$ using eqn (5) for the corresponding filler volume fraction V. (b) Relative tensile strength of LDPE/wheat starch blends, conditioned at different relative humidities, versus starch volume fraction. Lines with symbols (▲) and (o) represent theoretical calculation of σ_c/σ_0 using eqns (8) and (9), respectively, for the corresponding filler volume fraction V.

significant discrepancies were found. The conversion of weight fractions to volume fractions was obtained using the following equation (Willett, 1994):

$$V_i = \frac{w_i/d_i}{\sum w_i/d_i} \tag{6}$$

where w_i and d_i are the weight and density of a component in the composite. The average densities used for starch and LDPE were 1.4 and 0.92 g/ml, respectively (Willett, 1994).

An improved form of eqn (5) was, later on, put forward again by Nielsen and Landel (1994), mainly in an effort to take into account the particle size distribution effects since, in practice, spheres are almost never uniform:

$$\sigma_c = \sigma_0[1 - (V/V_m)^{2/3}] \tag{7}$$

where σ_c and σ_0 are the tensile strength of the composite and the pure polymer, respectively, and V and V_m are the filler volume fraction and the maximum volume fraction the filler can obtain due to packing considerations. By assuming that the filler particles are uniformly distributed, of spherical shape and of equal radius and that hexagonal close packing or cubic packing of uniform spheres occurs, a simplified model of the so called 'geometric nature' is derived:

$$\sigma_c = \sigma_0(1 - 1.21V^{2/3}). \tag{8}$$

Another slightly modified equation based on an average value of V_m = 0.625 (range between 0.5 and 0.75) is the following:

$$\sigma_c = \sigma_0(1 - 1.36V^{2/3}). \tag{9}$$

Similarly to eqn (7), the subscripts c and 0 stand for the composite and the LDPE matrix, respectively. When eqns (8) and (9) were applied to LDPE/starch blends, the results were in reasonable agreement with the experimental values (Fig. 2(b)) probably because no adhesion whatsoever, between LDPE/starch, is assumed. Furthermore, no transfer of applied stress from LDPE to starch particles is assumed to occur and thus increasing the load bearing surface area.

More complicated models, taking into account degrees of adhesion and stress concentration effects, have been proposed as well (quoted by Nielsen, 1974). However, these models were not applied in this case in view of their complexity.

Although there are two crystalline and two amorphous microphases in the LDPE/starch blend, in an attempt to simplify modelling of the mechanical properties, the most commonly adopted approach is to apply the following eqns (10) and (11), initially proposed for composite structures (Ashby and Jones, 1985):

$$E_{\text{blend}} = V_{\text{starch}}E_{\text{starch}} + (1 - V_{\text{starch}})E_{\text{LDPE}} \tag{10}$$

$$E_{\text{blend}} = \frac{1}{\frac{V_{\text{starch}}}{E_{\text{starch}}} + \frac{(1-V_{\text{starch}})}{E_{\text{LDPE}}}}. \tag{11}$$

If we apply eqns (10) and (11) to the LDPE / wheat 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 (E_{LDPE} = 195 MPa (Table 1) and $E_{\text{wheat starch}}$ = 23.1 MPa (Kirby *et al.*, 1991), the calculated tensile moduli for the blend are 143.43 MPa and 40.3 MPa, respectively. These values are somewhat higher or lower than the experimental one (103 MPa, Table 1); the latter is almost the average of the two calculated values.

The data analysis of mechanical properties using eqns (10) and (11) showed that the starch particles greatly affected the tensile modulus because the experimental values are considerably lower than those

Table 1. Tensile strength, tensile modulus and percentage elongation of LDPE/soluble starch blends

LDPE/soluble starch	Moisture content	Tensile strength (MPa)	Tensile modulus (MPa)	Percentage elongation
100/0	0	8.34±0.72	195±17	627±40
95/5	0	7.75±0.47	172±19	510±35
	3	6.11±0.52	125±10	545±40
	7	4.87±0.31	99±8	570±45
90/10	0	7.33±0.59	151±12	360±40
	4	5.87±0.40	112±9	485±35
	10	4.55±0.35	78±6	520±40
80/20	0	6.60±0.28	123±10	195±20
	8	4.39±0.35	72±7	340±30
	16	5.05±0.30	57±4	425±40
70/30	0	5.53±0.28	92±8	138±20
	7	4.10±0.30	61±5	250±18
	15	3.48±0.17	39±4	365±30
	20	3.15±0.20	27±3	450±42
60/40	0	4.70±0.32	78±5	73±6
	5	3.95±0.25	52±3	140±10
	15	3.27±0.16	28±2	260±20
	30	2.10±0.11	17±2	410±35

predicted by the linear mixture law (eqn (10)). One of the most commonly applied equations for describing the elastic modulus of particle-filled composites is the Kerner equation, which, provided that the filler is more rigid than the matrix, can be used in its simplified version:

$$E = E_0[1 + (V/1 - V)15(1 - v)/(8 - 10v)] \tag{12}$$

where E and E_0 stand for the moduli of the composite and the matrix, respectively, V is the filler volume fraction and v is the Poisson's ratio of the matrix.

The modulus data of composites derived by the application of the Kerner equation fit reasonably well the experimentally obtained values (Fig. 3). Any deviations between theoretical and experimental values could be attributed to insufficient adhesion and/or enhanced slippage at the LDPE/starch granule interface. The presence of a compatibilizing agent such as EAA (a copolymer of ethylene and acrylic acid) has previously been shown to improve considerably the Kerner's equation fitting to the experimental data (Willett, 1994).

The Harpin–Tsai equation constitutes another popular and extensively used formula for describing the effect of spherical filler particles on modulus (Harpin and Kardos (1976) quoted by Willett, 1994):

$$E = E_0 \frac{1 + \frac{(7-5v)}{(8-10v)} \frac{(R-1)V}{R\left[\frac{(7-5v)}{(8-10v}\right]}}{1 - \frac{(R-1)V}{R+\left[\frac{(7-5v)}{(8-10v}\right]}}. \tag{13}$$

where R and v stand for the ratio of the filler modulus to the matrix modulus and the Poisson's ratio of the matrix, respectively. Application of this formula did not provide a satisfactory fit for the experimental data.

Therefore, an alternative equation was employed, first applied by Willett (1994) for composites of LDPE/granular starch:

$$E = E_0 \frac{1 + 1.9\frac{(R-1)V}{R+1.9}}{1 - \frac{(R-1)V}{R+1.9}}. \tag{14}$$

Although the curve from this data fitting gives a better approximation than the previous one, thus emphasizing the importance of each particular filler type, a coincidence of the two data sets might be feasible only if the exact value of the ratio [(7−5v)/(8−10v)] was used instead of 1.9. By employing this equation, the calculated modulus is greatly influenced by the Poisson ratio v of LDPE. The latter lies within the range 0.43–0.50 (Willett, 1994, van Krevelen, 1990) and when v moves to the upper limit (0.50) and R either remains constant or increases, E increases.

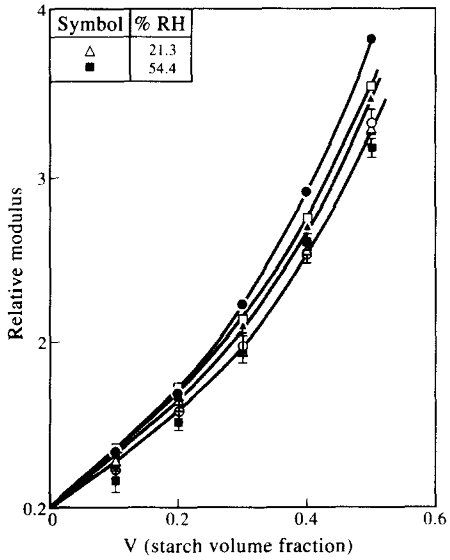

Fig. 3. Relative modulus of LDPE/wheat starch blends, conditioned at different relative humidities, versus starch volume fraction. Lines with symbols (○) and (▲), (□) and (●) represent theoretical calculation of E_c/E_0 using eqns (12) [where v equals 0.43 and 0.49 for the first and second symbol, respectively] and (14) [where R equals 42.2 and 234.4 for the third and fourth symbol, respectively] for the corresponding filler volume fraction V. Lines with symbols (△) and (■) represent experimental data.

As long as the starch content in the blends does not exceed 20%, the mechanical properties of the LDPE/starch blends still lie within the operational limits. Figure 4 shows typical SEM micrographs after fracture where the blend morphology and the distribution of each component can be clearly seen. The wheat starch particles are deformed and interspersed within the LDPE matrix. Although in several previous publications the failure modes of PE (Chudnovsky *et al.*, 1995; Stojmirovic *et al.*, 1992; Wang *et al.*, 1989; Kadota *et al.*, 1993; Huang and Brown, 1990; Brown and Wang, 1988; Lu and Brown, 1991; Balta-Calleja *et al.*, 1978) were investigated and analysed, a tentative failure mechanism of PE/starch blends was only recently put forward (Arvanitoyannis *et al.*, 1997). Brittle and ductile constitute the two main failure modes. Whichever of these two prevails depends not only on the deformation features and whether there is fast or slow crack growth (Chudnovsky *et al.*, 1995; Stojmirovic *et al.*, 1992) but also on the conditioning of the sample over certain relative humidities. Therefore, the ensuing plasticization of our LDPE/starch blends could be due to penetration of water and the filling of voids.

To provide a proper insight of the failure occurring in our composite materials the two main mechanisms describing the plastic deformation of semicrystalline polymers should be briefly described:

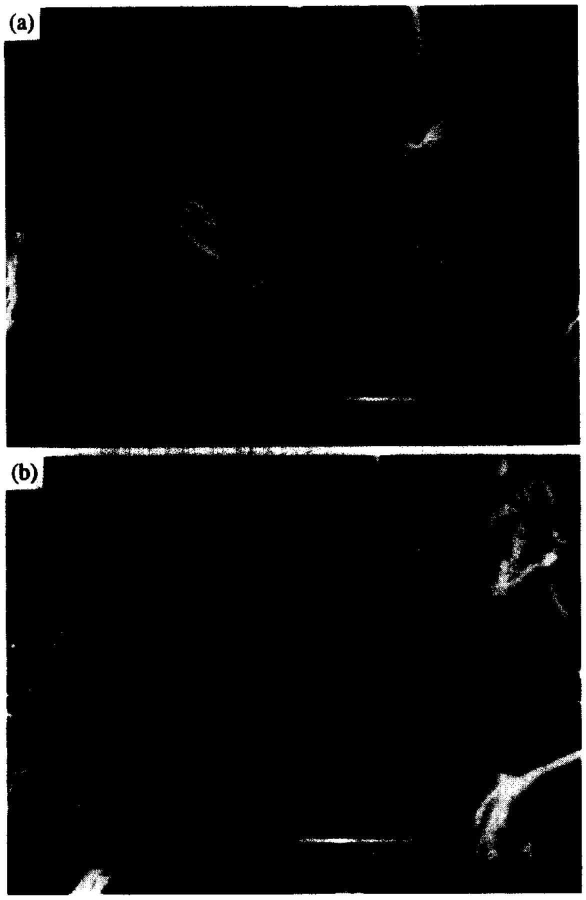

Fig. 4. SEM micrographs of various LDPE/soluble starch blends after their fracture: (a) 80/20; (b) 60/40.

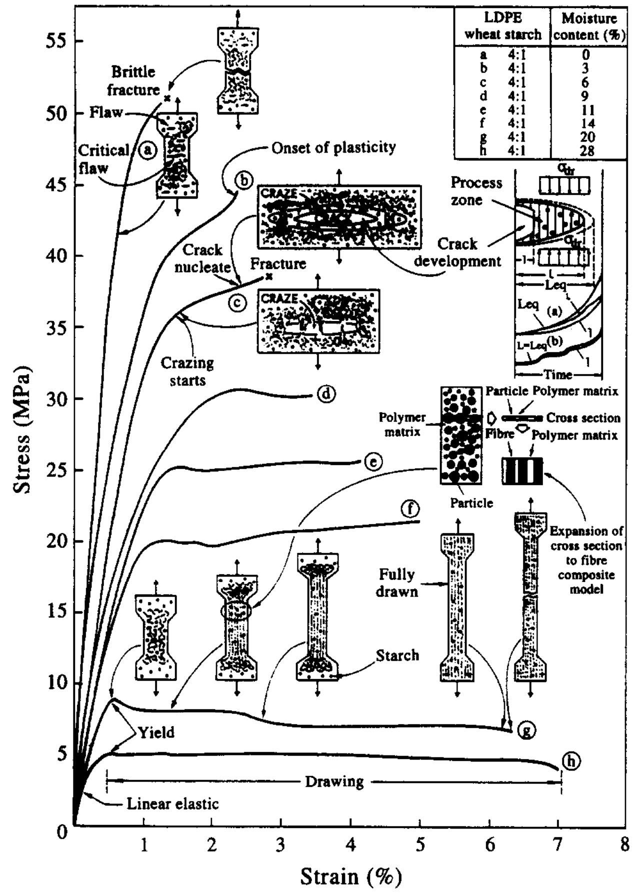

Fig. 5. Stress–strain curves of 70/30 LDPE/wheat starch blend with various water contents. Schematic representaation of crack layer growth mechanism in LDPE/wheat starch blend. Inset shows the time dependent crack development processes: l and L are the crack length and the crack layer length, respectively; L_{eq} is the length at which the process zone is in stable state; σ and σ_{dr} stand for the remote stress and drawing stress, respectively; (a) and (b) modes stand for smooth and stepwise crack layer growth, respectively.

(1) micronecking consists of a complete unfolding of lamellae, usually visualized as remelting and recrystallization of microcrystals, leading to the unravelling and transformation of lamellae into densely packed microfibrils. Cavitation, though in theory a phenomenon occurring almost simultaneously with micronecking, is of limited range because of the high energy barrier that has to be overcome.

(2) crystallographic transformation—which occurs without any apparent destruction of crystalline order apart from some minor slipping due to simple shear transformation of crystals.

The most commonly occurring deformation is that of the amorphous state, and in particular of the rubbery state, because of the very little stress required. Therefore, the amorphous phase is first deformed, followed by the activation of crystallographic mechanisms. Figure 5 shows that orientation of the amorphous phase initially occurs, whereas the crystalline phase is oriented either slightly or in the opposite direction, probably because of interlamellar sliding. Gradually and proportionally to the exerted stretching, both phases tend to become highly oriented. Synoptically presented, lamellae stretch out, become thinner, undergo lattice rotation to align the molecules and the lamellae (parallel to flow direction), finally resulting in severe fragmentation of the lamellae.

As can be seen from Table 1, for LDPE/starch blends with less than 20% starch content (dispersed component) it is the matrix LDPE which mainly dominates the plastic deformation (Arvanitoyannis *et al.*, 1997; Schroeter *et al.*, 1992). In the close vicinity of inclusions (starch particles as fillers) stresses are prone to appear because of misfit of the LDPE matrix and the starch particles (filler). Therefore, some variability of standard deviation (Tables 1–3) could probably be attributed to the non-homogeneous orientation of the produced LDPE/starch blend but also to several other reasons, including (Wu, 1992, Ward and Hadley, 1993, Chang and Chu, 1992, Gent *et al.*, 1994; Haward, 1987):

(1) slippage in the interfacial area (particle/matrix);
(2) detachment of the particle/matrix connection or 'pulling out' of the starch particle;
(3) fracture of the brittle and/or ductile phase.

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

LDPE/wheat starch	Moisture content	Flexural strength (MPa)	Modulus 1 (MPa)	Modulus 2 (MPa)	Modulus 3 (MPa)
95/5	0	12.8±1.5	188.7±13.5	—	—
	3	9.0±0.8	182.5±16.0	—	—
	7	5.8±0.4	158.7±12.0	—	—
90/10	0	13.7±1.0	194.0±14.5	211.4±18.5	173.4±12.4
	4	8.4±0.7	180.3±16.3	192.5±16.0	161.8±13.0
	10	6.0±0.5	151.4±13.4	140.0±12.3	123.5±11.2
80/20	0	15.0±1.4	210.0±18.0	230.5±19.4	190.4±14.5
	7	6.2±0.5	159.5±13.2	176.4±13.5	142.5±12.2
	16	4.7±0.3	125.6±11.0	141.5±12.4	111.4±10.0
70/30	0	15.9±1.2	237.9±20.5	260.1±21.5	220.5±18.6
	7	9.2±0.8	201.3±17.3	231.5±20.0	175.8±14.3
	14	4.5±0.5	144.0±11.7	163.0±12.6	119.0±9.2
	20	4.0±0.2	103.8±8.2	118.7±10.3	88.4±6.5
60/40	0	18.1±1.6	259.9±18.5	300.0±21.3	217.4±19.6
	8	12.0±1.0	218.0±19.0	261.2±18.5	202.0±16.8
	15	8.1±0.6	165.3±13.4	178.9±12.4	141.4±11.7
	30	3.4±0.2	104.5±8.5	121.6±10.2	87.8±6.2

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

LDPE/soluble starch	Moisture content	Flexural strength (MPa)	Modulus 1 (MPa)	Modulus 2 (MPa)	Modulus 3 (MPa)
95/5	0	11.9±1.3	170.5±14.2	—	148.3±12.5
	3	9.8±0.7	161.2±12.5	—	136.5±11.8
	8	5.2±0.4	149.4±13.0	—	124.0±10.9
90/10	0	12.6±1.2	180.7±15.6	191.5±12.5	157.3±13.2
	4	7.8±0.6	154.8±12.4	170.0±13.6	130.0±10.6
	10	5.1±0.4	133.4±11.6	159.3±11.2	111.2±8.8
80/20	0	13.8±1.5	187.6±14.8	207.8±20.8	160.5±13.4
	8	5.4±0.3	130.4±11.0	151.6±16.2	108.8±8.9
	16	4.1±0.4	111.3±10.5	120.0±11.0	87.6±7.6
70/30	0	15.0±1.3	208.0±18.6	237.3±15.3	182.4±15.3
	7	8.5±0.6	180.5±16.5	208.4±17.8	155.4±13.8
	15	3.9±0.2	123.7±10.4	139.7±11.7	91.6±8.0
	20	3.6±0.3	85.2±7.3	97.4±8.3	60.2±5.4
60/40	0	16.9±1.5	221.5±17.5	268.3±20.5	192.5±14.3
	5	10.9±1.0	194.8±14.8	238.4±19.6	170.6±13.4
	15	7.2±0.6	145.6±12.0	151.0±12.3	118.4±10.2
	30	3.1±0.2	83.4±6.5	98.9±8.6	60.1±4.8

Although the point has been made that the LDPE matrix behaviour influences to a great extent the mechanical properties of the blend at high LDPE/starch ratios, the growth of crystallites of LDPE and their possible disturbance should also be taken into account. Polymers, based on their fracture mode, can be generally classified as brittle (crazing under stress because of chain breaking) or pseudoductile (prone to yielding) (Wu, 1992). According to Wu (1992) the ratio T_a/T_β (where $T_a = T_g$ and T_β is a secondary relaxation related to localized skeletal motions) can provide valuable information for the brittleness and ductility of the homopolymer or blend. The relaxation occurring at T_a, known as T_g, is at 275 K for LDPE and the β- relaxation (T_β) equals 165 K for the same polymer. Therefore, yielding of LDPE arises from the onset of skeletal bonds motions under stress and occurs at considerably lower temperature than that at which the tensile strength is usually tested (room temperature). Furthermore, whenever tensile experiments of LDPE were carried out at higher than T_g temperatures, segmental motions of the C_{10}–C_{100} range, chain alignments, mutual chain sliding, and motions either in the crystalline domains or at domain interfaces were shown to occur (Kozlowski, 1995). However, in the case of wheat starch, the moisture content resulting from relative humidity conditioning is of great importance in view of the induced plasticization and the change in fracture mode occurring upon deformation. It has been shown that the fracture mechanism of starch extrudates changes from brittle to plastic when moisture content increases beyond 15% (Attenburrow and Davies, 1993).

In starch (wheat or soluble) the brittle/ductile transition occurs only very near T_g, which drops substantially at high moisture contents, thus resulting in brittle behaviour (crazing) at room temperature (Willett, 1994).

Although a part of the total fracture energy is due to crack development, debonding of the LDPE/starch interface and yielding of LDPE bridges is usually manifested in the development of microfilaments formed during plastic deformation of the ductile LDPE (Fig. 4, SEM micrographs). Lower starch contents in the LDPE/starch blends (Table 1) resulted in higher elongation values because of the smaller number of starch particles, which leads to fewer 'crazes'.

Three point bend test

An increase in flexural modulus proportional to the starch content in the blend is shown in Tables 2 and 3. The presence of distinct starch domains was not found to have any plasticizing effect on the LDPE matrix. On the contrary, a higher strength composite structure is produced within which the crack can propagate at quite a high rate in view of the lack of homogeneous orientation and detachment or pulling out of the starch particle/LDPE connection. When LDPE/starch blends were conditioned over various relative humidities, they absorbed considerable amounts of moisture which had a beneficial effect upon the flexibility of the three point bend specimens (Table 2). Any observed large variability of standard deviation (Tables 2 and 3) might be due to non-uniform water distribution, because of the particularities encountered in the morphology of these blends. It is noteworthy that high water contents enhanced the flexibility of samples and managed to restrict their brittleness substantially .

Water vapour transmission rate (WVTR)

LDPE does not absorb large quantities of water because no clustering centres are available, since polyethylene is hydrophobic and no nucleation means exist (Yasuda and Stannett, 1962) if no previous oxidation has taken place. An increase in starch content is followed by a substantial increase in water uptake (Table 4), justifiable in terms of starch's hydrophilic properties (French, 1984, Blanshard, 1987) and extensive disruption of the LDPE matrix. The blends of LDPE with soluble starch show an even more pronounced WVTR, compared to LDPE/wheat starch blends, attributable to their lower molecular weight and to their dextrinized character.

Gas permeability (GP) and percentage crystallinity (%Xc) from WAXDP

Both LDPE and HDPE have been thoroughly investigated with regard to their GP (Yasuda and Stannett, 1962; van Krevelen, 1990) because of their extensive use in food packaging applications. LDPE is a semicrystalline polymer having both amorphous (intralamellar, interlamellar and interspherulitic) and crystalline (ribonlike lamellae) areas (Michaels and Bixler, 1961). The presence of starch particulates as fillers within the LDPE matrix, apart from disturbing the continuity of the LDPE network and contributing to the inhomogeneity of the system, enhances substantially the GP of the LDPE/starch composite structure because of their strong hydrophilic character. The water is either strongly bound (0–12%) or present as capillary moisture (12–30%). The standard methodology for GP modelling consists of applying Salame's equation (Salame, 1986) as follows:

$$N \times \pi = \Pi = \Sigma(N_i \times \pi_i) \quad (15)$$

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

$$P_{(298)} = P^*_{(298)}\exp(-S\pi) \quad (16)$$

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 a 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:

$$\log P_{(298)} = -12 - 0.053\pi. \quad (17)$$

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

$$\pi_{sc} = \pi_a - 41.5\log\alpha = \pi_a - 41.5\log(1 - x_c) \quad (18)$$

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

Table 4. Water vapour transmission (WVTR) of LDPE/wheat or soluble starch blends

	WVTR ($g\,m^{-1}\,s^{-1}\,Pa^{-1} \times 10^{-13}$)
LDPE/wheat starch	
100/0	0.1±0.02
95/5	1.0±0.09
90/10	3.0±0.13
80/20	27.3±3.4
70/30	73.5±8.7
60/40	165.2±14.5
LDPE/soluble starch	
95/5	1.7±0.13
90/10	4.8±0.35
80/20	39.5±5.8
70/30	85.3±6.9
60/40	198.7±15.8

Table 5. Gas permeability (N_2, O_2 and CO_2) and percentage crystallinity (%Xc determined from WAXDP) of LDPE/wheat starch blends at room temperature (22±1°C)

LDPE/wheat starch	Moisture content	%Xc WAXDP	Gas permeability ($cm^2 s^{-1} Pa^{-1}$)		
			N_2	O_2	CO_2
100/0	0	36.2	$2.2(\pm0.1)\times10^{-13}$	$8.0(\pm0.7)\times10^{-13}$	$4.2(\pm0.0)\times10^{-12}$
95/5	0	35.1	$3.6(\pm0.2)\times10^{-13}$	$1.3(\pm0.1)\times10^{-12}$	$7.6(\pm0.5)\times10^{-12}$
	3	34.3	$5.5(\pm0.4)\times10^{-13}$	$2.7(\pm0.4)\times10^{-12}$	$0.4(\pm0.02)\times10^{-11}$
	7	34.0	$7.3(\pm0.6)\times10^{-13}$	$3.8(\pm0.4)\times10^{-12}$	$1.2(\pm0.1)\times10^{-11}$
90/10	0	32.2	$6.4(\pm0.5)\times10^{-13}$	$2.5(\pm0.6)\times10^{-12}$	$1.5(\pm0.2)\times10^{-11}$
	4	31.5	$9.1(\pm0.7)\times10^{-13}$	$4.4(\pm0.5)\times10^{-12}$	$3.0(\pm0.2)\times10^{-11}$
	10	29.8	$9.8(\pm0.9)\times10^{-13}$	$5.6(\pm0.7)\times10^{-12}$	$4.7(\pm0.5)\times10^{-11}$
80/20	0	29.0	$9.0(\pm1.0)\times10^{-13}$	$5.1(\pm0.4)\times10^{-12}$	$3.3(\pm0.4)\times10^{-11}$
	8	26.9	$4.1(\pm0.5)\times10^{-12}$	$6.4(\pm0.7)\times10^{-12}$	$6.1(\pm0.5)\times10^{-11}$
	16	25.7	$6.2(\pm0.6)\times10^{-12}$	$9.3(\pm0.8)\times10^{-12}$	$8.9(\pm1.2)\times10^{-11}$
70/30	0	20.3	$7.9(\pm0.7)\times10^{-12}$	$2.1(\pm0.2)\times10^{-11}$	$1.6(\pm0.1)\times10^{-10}$
	7	19.6	$9.2(\pm0.8)\times10^{-12}$	$6.0(\pm0.5)\times10^{-11}$	$1.9(\pm0.2)\times10^{-10}$
	15	17.5	$1.4(\pm0.2)\times10^{-11}$	$8.3(\pm0.7)\times10^{-11}$	$2.1(\pm0.3)\times10^{-10}$
	20	17.6	$3.3(\pm0.4)\times10^{-11}$	$1.8(\pm0.3)\times10^{-10}$	$7.2(\pm0.6)\times10^{-10}$
60/40	0	18.3	$9.7(\pm0.8)\times10^{-12}$	$6.2(\pm0.6)\times10^{-11}$	$5.4(\pm0.6)\times10^{-10}$
	5	17.0	$4.2(\pm0.6)\times10^{-11}$	$8.7(\pm0.6)\times10^{-11}$	$8.0(\pm0.7)\times10^{-10}$
	15	16.1	$6.1(\pm0.5)\times10^{-11}$	$2.5(\pm0.3)\times10^{-10}$	$2.9(\pm0.4)\times10^{-9}$
	30	15.3	$9.5(\pm0.8)\times10^{-11}$	$6.8(\pm0.5)\times10^{-10}$	$4.4(\pm0.5)\times10^{-9}$

from data published by Salame (Salame, 1986), are as follows:

$$\Pi = N \times (\text{Group contribution})_{-\mathrm{CH2}-} = 2 \times 15 = 30.$$

Thus

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

Therefore by applying first eqn (18), where $x_c = 36.2\%$ (Table 5), and then eqn (17) for N_2 in LDPE we get

$$\pi_{sc} = \pi_\alpha - 41.5\log(1 - x_c)$$
$$= 15 - 41.5\log(1 - 0.362) = 23.1$$

$\log P_{(298)} = -12 - 0.053\pi_{sc} = -12 - 0.053\ (23.1)$
$= -13.2243 \Rightarrow \log P_{(298)} = 6.0\times10^{-14}\,cm^2\,s^{-1}\,Pa^{-1}$,
which is in reasonable agreement with the experimental value of $2.2\times10^{-13}\,cm^2\,s^{-1}\,Pa^{-1}$ (Table 5).

Some typical WAXDP traces of LDPE/wheat starch blends are shown in Fig. 6. From Tables 5 and 6 it becomes clear that GP values mainly depend on the crystalline/amorphous domains ratio. An increase in this ratio results in lower GP values whereas the presence of more amorphous domains enhances GP by facilitating gas passage through the films. Another possible approximation for the semiempirical calculation of GP is eqn (19). Although this equation is primarily appropriate for laminated films, it could be tentatively used with the assumption that thickness can be substituted by the weight fraction contribution of each component (Robertson, 1993).

$$1/P_{\mathrm{lamin}} = (x_1/x_1 + x_2)(1/P_1) + (x_2/x_1 + x_2)(1/P_2) \tag{19}$$

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

By substituting the following values, $P_{\mathrm{LDPE}} = 2.2\times10^{-13}\,cm^2\,s^{-1}\,Pa^{-1}$ and $P_{\mathrm{wheat\ \ starch}} = 7.1\times10^{-15}\,cm^2\,s^{-1}\,Pa^{-1}$ (Arvanitoyannis, unpublished results) for LDPE/wheat starch (70/30 w/w), we obtain $2.2\times10^{-14}\,cm^2\,s^{-1}\,Pa^{-1}$. Although there are many factors to which the observed deviations between experimental and calculated values could be attributed, the most important ones are related to blend morphology, nonhomogeneous distribution of the two components and geometry and the size of microcrystallites or voids.

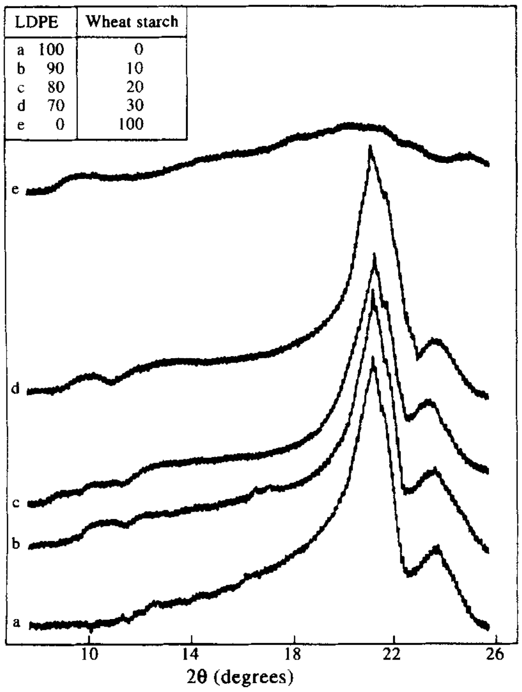

Fig. 6. WAXDP of some representative LDPE/wheat starch blends.

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

LDPE/soluble starch	Moisture content	%Xc WAXDP	Gas permeability ($cm^2\,s^{-1}\,Pa^{-1}$) N_2	O_2	CO_2
95/5	0	34.7	$4.7(\pm0.5)\times10^{-13}$	$3.6(\pm0.8)\times10^{-12}$	$9.5(\pm0.9)\times10^{-12}$
	3	33.9	$5.8(\pm0.4)\times10^{-13}$	$4.8(\pm0.5)\times10^{-12}$	$3.2(\pm0.4)\times10^{-11}$
	8	33.0	$9.7(\pm0.6)\times10^{-13}$	$6.3(\pm0.7)\times10^{-12}$	$5.0(\pm0.6)\times10^{-11}$
90/10	0	31.3	$9.0(\pm0.8)\times10^{-13}$	$4.5(\pm0.5)\times10^{-12}$	$6.4(\pm0.7)\times10^{-11}$
	4	30.2	$1.3(\pm0.1)\times10^{-12}$	$7.7(\pm0.6)\times10^{-12}$	$8.5(\pm0.7)\times10^{-11}$
	10	28.9	$2.0(\pm0.2)\times10^{-12}$	$9.8(\pm0.8)\times10^{-12}$	$9.9(\pm1.0)\times10^{-11}$
80/20	0	27.8	$1.2(\pm0.1)\times10^{-12}$	$7.0(\pm0.8)\times10^{-12}$	$5.7(\pm0.6)\times10^{-11}$
	8	25.6	$3.0(\pm0.4)\times10^{-12}$	$9.3(\pm0.8)\times10^{-12}$	$8.8(\pm0.9)\times10^{-11}$
	16	24.0	$4.9(\pm0.5)\times10^{-12}$	$2.4(\pm0.3)\times10^{-11}$	$2.2(\pm0.3)\times10^{-10}$
70/30	0	19.1	$9.1(\pm0.8)\times10^{-12}$	$3.7(\pm0.4)\times10^{-11}$	$2.8(\pm0.3)\times10^{-10}$
	7	18.0	$1.5(\pm0.2)\times10^{-11}$	$8.4(\pm0.6)\times10^{-11}$	$3.5(\pm0.4)\times10^{-10}$
	15	16.3	$2.1(\pm0.1)\times10^{-11}$	$0.9(\pm0.1)\times10^{-10}$	$4.6(\pm0.5)\times10^{-10}$
	20	16.6	$4.5(\pm0.3)\times10^{-11}$	$3.5(\pm0.4)\times10^{-10}$	$9.7(\pm0.8)\times10^{-10}$
60/40	0	17.0	$2.0(\pm0.3)\times10^{-12}$	$9.0(\pm0.8)\times10^{-11}$	$7.1(\pm0.6)\times10^{-10}$
	5	15.9	$6.4(\pm0.5)\times10^{-11}$	$1.8(\pm0.2)\times10^{-10}$	$9.5(\pm0.8)\times10^{-10}$
	15	14.2	$8.7(\pm0.7)\times10^{-11}$	$4.9(\pm0.6)\times10^{-10}$	$4.3(\pm0.3)\times10^{-9}$
	30	12.5	$2.6(\pm0.3)\times10^{-10}$	$9.2(\pm0.8)\times10^{-10}$	$6.7(\pm0.8)\times10^{-9}$

The temperature dependence of gas permeability (GP) and diffusion (GD) of our blends is described by the well known Arrhenius equations. The activation energies of diffusion and permeation were calculated from the corresponding logarithmic forms (20) and (21), as previously described (Arvanitoyannis *et al.*, 1994, Arvanitoyannis and Blanshard, 1993), and are given in Table 7.

$$\ln D = \ln D_0 - E_D/RT \tag{20}$$

$$\ln P = \ln P_0 - E_P/RT. \tag{21}$$

At this point, it is worth emphasising the importance of the activation energy of diffusion because of its relevance to the energy barrier for chain separation, necessary for the eventual 'loosening' of the structure.

Table 7. Activation energies for diffusion (E_D, $kJ\,mol^{-1}$) and permeation (E_P, $kJ\,mol^{-1}$) for LDPE/soluble starch blends different moisture contents

LDPE/ soluble starch	Moisture content	N_2		O_2		CO_2	
		E_D [a]	E_P [b]	E_D [a]	E_P [b]	E_D [a]	E_P [a]
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	33.0±1.7	36.7±2.9	35.7±3.6	41.8±3.8	44.1±3.6	50.5±2.9
	3	30.9±2.4	34.0±3.2	32.8±2.1	38.5±2.9	35.4±2.8	41.2±3.8
	7	28.3±1.9	31.5±3.4	30.0±1.9	34.7±3.2	33.7±4.0	38.0±4.3
90/10	0	31.3±2.8	33.0±2.6	31.2±3.4	36.3±3.8	33.4±3.5	38.5±4.3
	4	28.4±3.0	31.1±3.3	29.0±2.8	33.4±2.8	31.5±4.2	36.0±4.0
	10	25.0±2.6	27.9±2.9	26.8±1.9	30.1±2.3	28.9±3.0	32.5±3.5
80/20	0	26.3±1.9	29.4±3.2	27.9±2.4	31.4±2.7	31.2±3.7	34.0±4.3
	8	24.5±2.5	26.2±2.6	25.2±2.6	29.1±2.6	27.5±3.0	30.3±1.9
	16	22.7±2.7	24.4±2.4	21.3±2.0	26.9±2.8	24.3±2.3	28.5±3.4
70/30	0	23.8±3.4	26.7±2.6	25.8±1.8	28.7±4.2	27.7±3.2	30.8±3.8
	7	21.2±2.2	23.9±1.9	23.0±2.2	26.2±2.5	25.8±3.3	28.7±2.6
	15	19.0±1.6	21.4±2.4	20.2±1.9	24.3±2.8	23.3±2.8	26.0±3.2
	20	15.3±1.4	17.9±1.0	17.1±1.8	18.9±2.2	20.2±1.9	23.4±2.5
60/40	0	21.4±2.0	23.9±1.9	21.5±2.2	24.8±3.0	24.3±2.7	26.8±2.8
	5	17.2±1.8	20.5±2.2	18.4±1.9	22.1±2.6	21.5±3.3	23.7±2.5
	15	13.4±1.5	17.3±1.8	15.6±1.8	19.4±2.0	19.7±2.2	21.0±1.8
	30	8.5±0.9	11.7±1.3	11.8±1.5	13.9±1.2	16.3±2.0	18.8±1.3

[a] Calculated from eqn (20).
[b] Calculated from eqn (21).

Certainly, the incorporation of starch particles disrupts the LDPE network by imparting some flexibility and mobility and thereby reduces the required energy per unit chain separation (Table 7). An increase in temperature enhances even more the cavity and channel formation, thereby facilitating the diffusivity and permeability. The diffusion and permeation activation energies were found to fall in the following order with regard to the permeating gas:

$$E_D(N_2) < E_D(O_2) < E_D(CO_2).$$

This order is in agreement with that reported elsewhere (Arvanitoyannis *et al.*, 1994, Arvanitoyannis and Blanshard, 1993), assuming there is no interaction between the permeant gas and the matrix (LDPE/starch).

Biodegradability studies

The current practice of disposing most plastics consists of landfills, composting and incineration. A great deal of attention should be drawn to making conditions in an anaerobic bioreactor to simulate those of a representative landfill. Because there are too many uncontrollable factors in outdoor landfills, the bioreactor is considered to be more effective in terms of inducing the degradation procedure (Krupp and Jewell, 1992). In fact, bioreactors showed a noteworthy consistency and reproducibility, managing to biodegrade approximately 85% of the sorghum/cellulose substrate. Some representative curves of percentage elongation and BOD versus various exposure times for LDPE/starch blends are shown in Figs 7–9. Long landfill burial times are usually considered equivalent to considerably shorter exposure times in bioreactors. A reasonable agreement was found between mass loss and BOD values (Fig. 10) as in Arvanitoyannis *et al.* (1997). In the case of wheat starch the maximum starch removal was only 55% (Table 8) of the total starch content probably because of physical protection offered by the LDPE matrix to the occluded starch particles. In addition to the physical protection, starch accessibility is greatly affected by the number, mobility and reproduction rate of microbes. However, soluble starch exhibited much less recalcitrant behaviour by attaining up to 80% removal of the total starch content (Figs 9 and 10).

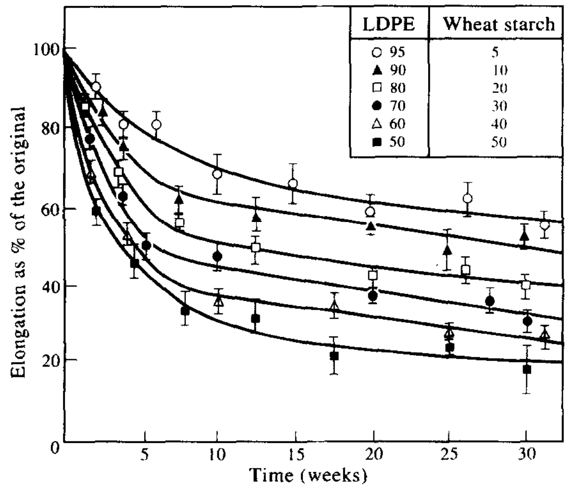

Fig. 7. Percent elongation of LDPE/soluble starch blends following burial in soil.

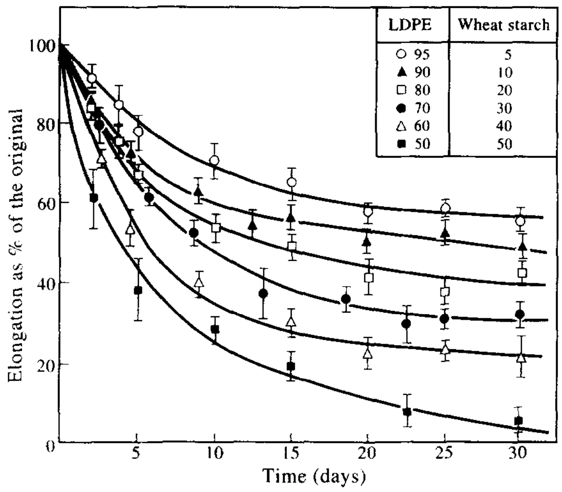

Fig. 8. Percent elongation of LDPE/soluble starch blends following exposure to anaerobic biorectors.

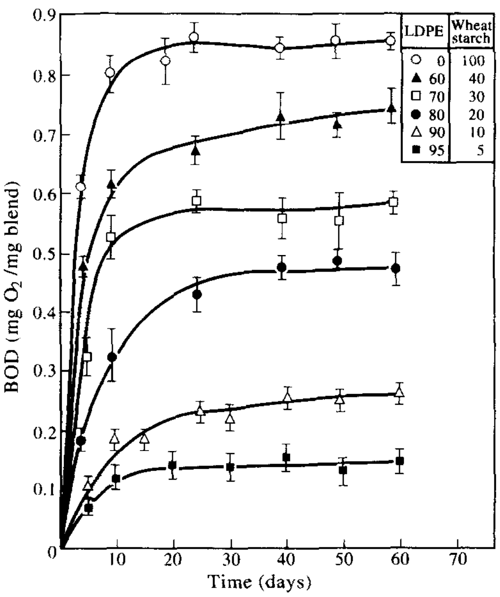

Fig. 9. Biochemical oxygen demand (BOD, mg O_2 per mg of LDPE/soluble starch blends) versus time (days).

The functional improvement and degradability of starch (Dennenberg *et al.*, 1978; Fanta *et al.*, 1979; Tahan and Zilkha, 1969) and LDPE or HDPE

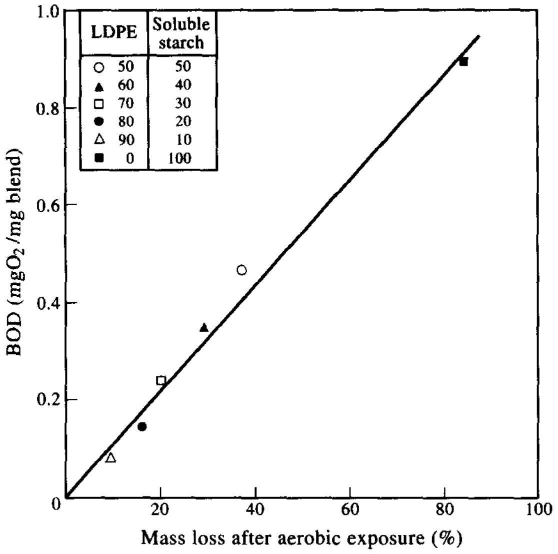

Fig. 10. Biochemical oxygen demand (BOD, mg O_2 per mg of LDPE/soluble starch blends) against percentage mass loss after aerobic exposure for 30 days (CV, for at least quadruplicate measurements of BOD and mass loss after biodegradation, did not exceed 5.3 and 3.4%, respectively).

(Albertsson, 1978, Albertsson *et al.*, 1994; Albertsson and Ranby, 1979, Albertsson *et al.*, 1978, Albertsson and Karlsson, 1994) have been the subject of many investigations. LDPE/starch blends have been commercially used for the past 15–20 years (Griffin, 1994). The generally accepted degradation scheme of high molecular weight (MWt) carbohydrate material consists of the following stages:

High MWt → Low MWt → Organic Fragments → $Co_2 + O_2$ +
↑
O_2

Energy → Energy → Endogenous respiration,
Biomass Growth
Cell division

Both soil burial and bioreactor exposure experiments showed a decrease in percentage elongation and considerable weight losses (Table 8, Fig. 9), which could be described as a two stage process (Krupp and Jewell, 1992, Arvanitoyannis *et al.*, 1997). The first stage consists of partial starch removal and only at a later stage does slow rate degradation of LDPE occur (Figs 11 and 12). Most investigations focused on LDPE advocated enzymatic oxidation, dehydrogenation and carbon–carbon breaking processes as the predominant degradation mechanisms of LDPE (Albertsson and Karlsson, 1994, Albertsson *et al.*, 1994). However, the biodegradation rate of LDPE/starch blends can be effectively accelerated only if the starch content is higher than 10%. Similar conclusions were reached by other researchers (Narayan, 1991; Gould *et al.*, 1990; Goheen and Wool, 1991; Wool, 1989, 1995) who, in addition, applied the percolation theory (Stauffer, 1985) assisted by computer simulation (Peanasky *et al.*, 1991).

Table 8. Percentage weight losses (%Wt Losses) of LDPE/wheat starch blends after their exposure to aerobic and anaerobic bioreactors for various time periods

LDPE/wheat starch	Moisture content	% Weight losses			
		Exposure time to bioreactors (days)			
		Anaerobic		Aerobic	
		90	180	90	180
100/0	0	0.2±0.1	0.9±0.2	0.1±0.05	0.6±0.1
95/5	0	0.5±0.1	2.4±0.2	0.4±0.01	2.1±0.2
	3	1.2±0.2	3.0±0.4	1.1±0.1	2.8±0.3
	7	1.9±0.3	3.5±0.3	2.0±0.2	3.9±0.5
90/10	0	1.3±0.4	3.2±0.2	1.1±0.1	3.0±0.3
	4	2.1±0.3	4.8±0.5	1.9±0.2	5.1±0.6
	10	3.6±0.5	6.0±0.4	3.3±0.3	6.5±0.5
80/20	0	1.8±0.2	6.2±0.5	1.5±0.1	5.8±0.7
	7	3.4±0.3	8.5±0.3	3.2±0.2	7.7±0.9
	16	5.3±0.6	10.9±1.0	5.5±0.6	11.4±1.0
70/30	0	3.0±0.5	8.7±0.6	2.7±0.2	7.2±0.6
	7	4.6±0.4	11.0±0.9	4.4±0.3	10.4±0.9
	14	7.0±0.5	13.8±1.1	6.7±0.3	13.5±1.5
	20	8.4±0.7	19.2±1.5	8.8±0.7	18.8±1.6
60/40	0	4.2±0.5	12.8±0.8	3.9±0.3	9.5±0.7
	8	6.6±0.7	16.5±1.4	6.4±0.5	13.7±0.9
	15	11.3±0.9	19.7±1.8	10.8±1.2	18.9±1.9
	30	16.8±1.2	27.3±2.1	17.0±1.5	29.7±3.3

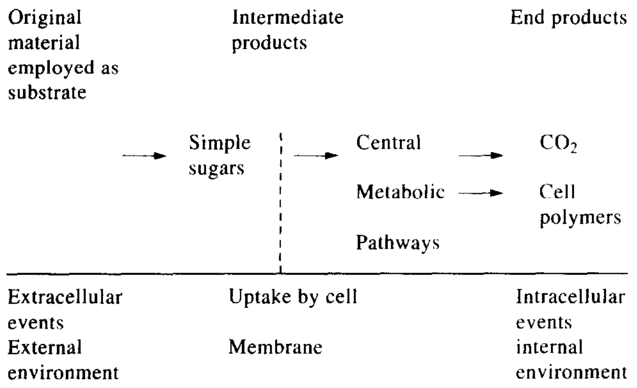

Fig. 11. Descriptive model for starch degradation.

CONCLUSIONS

Blends of LDPE with wheat or soluble starch were prepared and their mechanical properties were recorded and compared with several semiempirical models, originally derived for composite materials based on synthetic polymers. Some of these semiempirical models were found to predict surprisingly well the mechanical behaviour of LDPE/starch blends whereas others failed in this respect. Possible reasons or probable explanations were given in both cases. In general, the higher the starch content the worse the performance of the composite materials (lower tensile strength and modulus, higher GP and WVTR) but the higher their biodegradability. An increase in moisture content of these composite materials induced plasticization of the samples. The degradability of LDPE/starch blends was confirmed by weight loss measurements and changes in mechanical properties.

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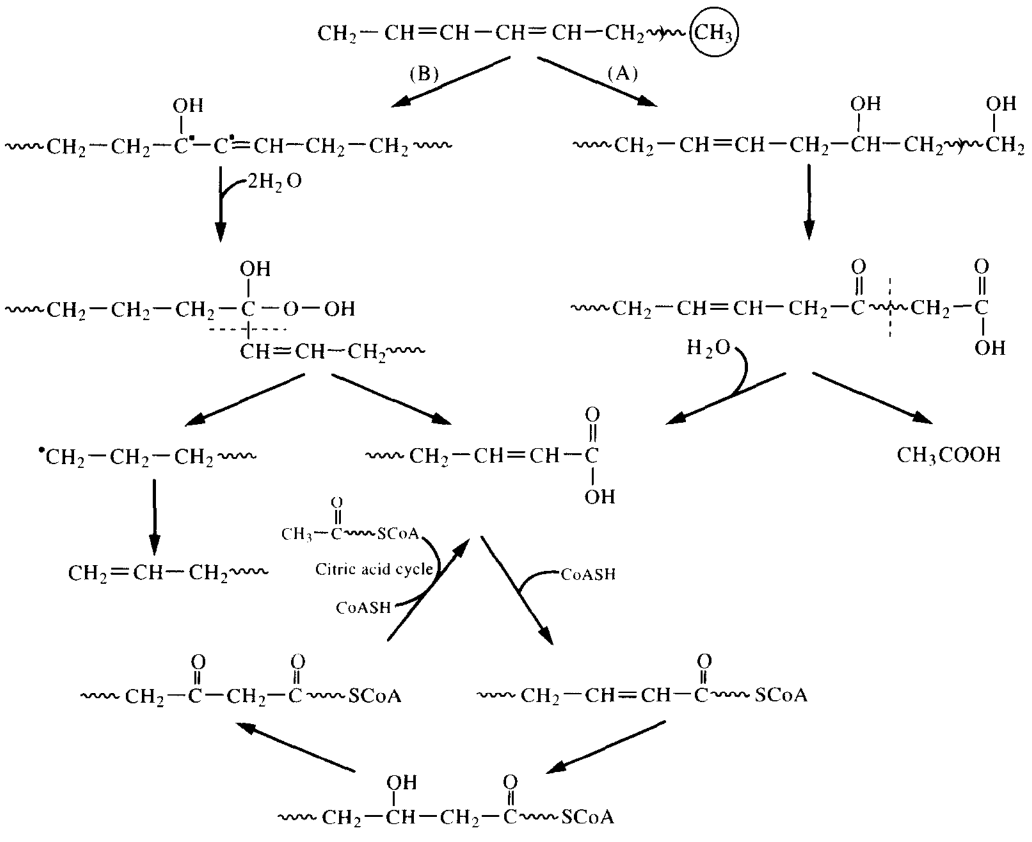

Fig. 12. Tentative model for the biodegradation mechanism of LDPE: (A) via oxidation of both main chains and end groups; (B) via oxidation of exclusively main chain ends (Albertsson and Karlsson, 1994; Lenz, 1993).

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