

Material Behavior

Testing of polyvinyl alcohol and starch mixtures as
biodegradable polymeric materials

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Abstract

The mechanical properties, thermal behaviour and biodegradation of some polymeric materials based on polyvinyl alcohol and starch, in the presence of urea (used as a micro-organism nitrogen source/plasticizer) and glycerine (used as a plasticizer) have been studied. The chemical composition optimization of the analysed blends was carried out using a second order factorial experimental design. The progress of biodegradation was evidenced by means of scanning electronic microscopy, differential scanning calorimetry and thermogravimetric measurements. The evaluation of the weight loss of the samples at the end of the biodegradation process was also carried out. The weight loss after 18 days of inoculation with microorganisms is between 38 and 73% by weight and is influenced by the composition of the blend as well as by the nature of the microorganism used. During biodegradation, plasticisers (glycerine and urea) and starch are consumed together with some amorphous structures from polyvinyl alcohol. The crystalline structures of polyvinyl alcohol which remained after biodegradation show high values of enthalpy, and contribute to an increase in the apparent thermal stability of the biodegraded samples. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Biodegradable polymers have been a subject of interest for many years because of their potential to protect the environment by reducing non-biodegradable synthetic plastic waste [1–5]. Biodegradation involves enzymatic and chemical degradation by living microorganisms [6–8].

In essence, the enzymatic degradation of polymers takes place by hydrolysis and oxidation.

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Most synthetic polymers cannot be degraded by microorganisms. To increase their biodegradability, non-biodegradable polymers are associated with fully biodegradable polymers, such as aliphatic polyesters [9,10], or natural polymers [11,12].

Products from agricultural sources, with reference to starch and protein especially, constitute a good alternative in developing degradable materials [13]. Starch, a mixture of amylose and amylopectin, is a renewable and fully biodegradable polymer, readily available in high purity and at low cost. Unfortunately, the starch has no physico-mechanical characteristics, as well as processing properties, good enough to allow the whole replacement of the composite materials based on petroleum hydrocarbons. The products from starch are mostly water soluble and brittle. Some properties of starch can be improved by blending with synthetic polymers.

There are few data published regarding the biodegradability of polyvinyl alcohol (PVA)/starch mixtures [14–16]. Particular attention was given to the biodegradation of the starch component as a function of the amylose/amylopectin ratio [17]. The mixtures of PVA/starch were studied regarding their processability [14] or mechanical properties [18] especially.

In this paper we report on the results of preliminary findings regarding the mechanical properties as well as the thermal behaviour of blends based on starch in mixture with PVA. The synthesis of the blends was carried out with the main objective of obtaining some experimental parameters, which can then be used to study the biodegradation process of the polymeric materials. The biodegradation of PVA/starch mixtures was carried out in the presence of some bacteria and fungi localized in sediments obtained from activated sludges of municipal sewage plant and from landfill.

2. Experimental

2.1. Materials

The raw materials used in our experiments are available as commercial products. Industrial corn starch, a white fine powder with 2% by weight moisture content, acidity 2.0 (cm³ 0.01 N NaOH solution) and around 1% by weight proteins and lipids was provided by Amidex-Tg, Secuiesc, Romania. The PVA polymer, with hydrolysis degree 88%, polymerization degree 1200, saponification index 140±30 mg KOH/g, K value 65±5 and 2% by weight ash, was obtained from Romacryl-Rasnov, Romania. Other materials used in this study were urea, glycerine, NaCl, Na₂HPO₄, analytical grade reagents being obtained from Reactivul-Bucharest, Romania, and agar supplied by Fluka, Switzerland.

2.2. Film preparation

The films tested in the biodegradation experiment were obtained by casting some mixtures of starch, PVA, glycerine and urea from watery solutions. Firstly, the watery solutions of PVA (25% by weight) and starch (20% by weight) were prepared. The mixtures utilized for casting of the films were achieved using a second order factorial experimental design [19,20], and were obtained in a flask of 0.5 l provided with a stirrer, thermometer and a water bath heated at temperatures in the range 60–80°C. The mixture was homogenized by vigorous stirring for 2 h at 70°C. Then,

urea (used as a microorganism nitrogen source and/or plasticizer) dissolved in glycerine (used as a plasticizer) as a preliminary step, was introduced into the flask and the obtained mixture was stirred for 1 h. The operation continued by filtration of the warm mixture by means of a G₁ filtrable crucible, after which the viscosity of the mixture was corrected with hot distilled water (around 40°C) to a value of 80–100 cP. A series of films was obtained by casting these blends from the solutions. The films obtained with dimensions 300×100 mm in size and 250±5 µm thick were dried in air at 30–40°C. Tests of the mechanical properties were made before biodegradation. Table 1 lists the composition of the films used.

2.3. Sample biodegradation

Specimens with dimensions of 100×10 mm and 250±5 µm thick were taken for the biodegradation test. A solid medium (devoid of carbon source), used as the biodegradation medium, was placed in a petri dish with a diameter of 120 mm. The composition of the solid medium was as follows: NaCl 3 g, NaHPO₄ 2 g, agar–agar 18 g, and distilled water 1000 ml. The medium was sterilized at 0.8 daN/cm² (120°C) for 30 min, and then it was inoculated with microorganisms taken from activated sludges of municipal sewage plant and from landfill. The fungi isolated from the mud were identified to be *Penicillium viridicatum* and *Fusarium* sp. The fungi isolated from landfill were *Penicillium* sp. and *Cephalosporium* sp. The bacteria isolated from landfill (noted B₁) were not identified up to the present. The film specimens (three specimens from each tested sample), weighed by means of an analytical balance with high precision (±0.0001), were placed on the surface of the hydrated mineral agar–agar medium in petri dishes. The specimens were maintained at 28°C for 18 days, after which they were analysed regarding the growth of microorganisms on their surfaces and their weight loss.

2.4. Chemical composition optimization

A second order factorial experimental design has been applied [19,20]. The experimental programme was carried out on the basis of the independent variables (g), as follows: starch amount (X₁), PVA amount (X₂), glycerine amount (X₃) and urea amount (X₄). The independent variables codification is listed in Table 2.

Table 1
Composition of the films exposed to biodegradation

Sample	Component amount (g)			
	Starch	PVA	Glycerine	Urea
1	60	40	14	6
2	50	30	12	4
3	40	40	18	6
4	40	60	14	6
5	30	50	16	8

Table 2
Codification of the independent variables

Blend components	Independent variables	Codification level				
		–2	–1	0	1	2
		Component content (g)				
Starch	X_1	20	30	40	50	60
PVA	X_2	60	50	40	30	20
Glycerine	X_3	10	12	14	16	18
Urea	X_4	10	8	6	4	2

3. Characterization techniques

3.1. Mechanical properties

The tensile strength as well as the elongation at break were evaluated using a mechanical dynamometer of TIRA TEST-2200 type (Germany). The samples (100×10×0.2 mm) were conditioned in a vacuum oven containing CaCl_2 , at 50°C, residual pressure 0.01 kgf/cm² for 2 h. Three determinations were carried out for each sample, and the results were taken as their average values.

3.2. Scanning electronic microscopy (SEM)

The morphology of the surface of the films, before and after biodegradation, was investigated using a scanning electronic microscope of BS 340 TESLA type (Czechia Republic). Because the studied films are dielectric polymers with few emissions of secondary electrons, the films were covered with pure metallic Ag. The laying down of Ag was carried out using evaporation of the metal under a high vacuum, to give a thickness of around 15–20 Å.

3.3. Differential scanning calorimetry (DSC)

DSC measurements of some of the samples, non-biodegraded and/or biodegraded in the presence of B_1 bacteria, were carried out by means of a Mettler-12E type differential scanning calorimeter (Switzerland), with a heating rate of 10°C/min in a nitrogen atmosphere. The first heating run was carried out with a 10–12 mg sample, deposited in an open aluminium pan in the temperature range between room temperature and 170°C. The second heating run was performed with samples which were suddenly cooled to 6°C. Pure indium was used as a standard for calorimetric calibration.

3.4. Thermogravimetric measurements

Thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out with a MOM-Budapest derivatograph (Hungary) in the following conditions: sample weight 50 mg, heating rate 12°C/min, maximum limit of heating 600°C, reference material a- Al_2O_3 .

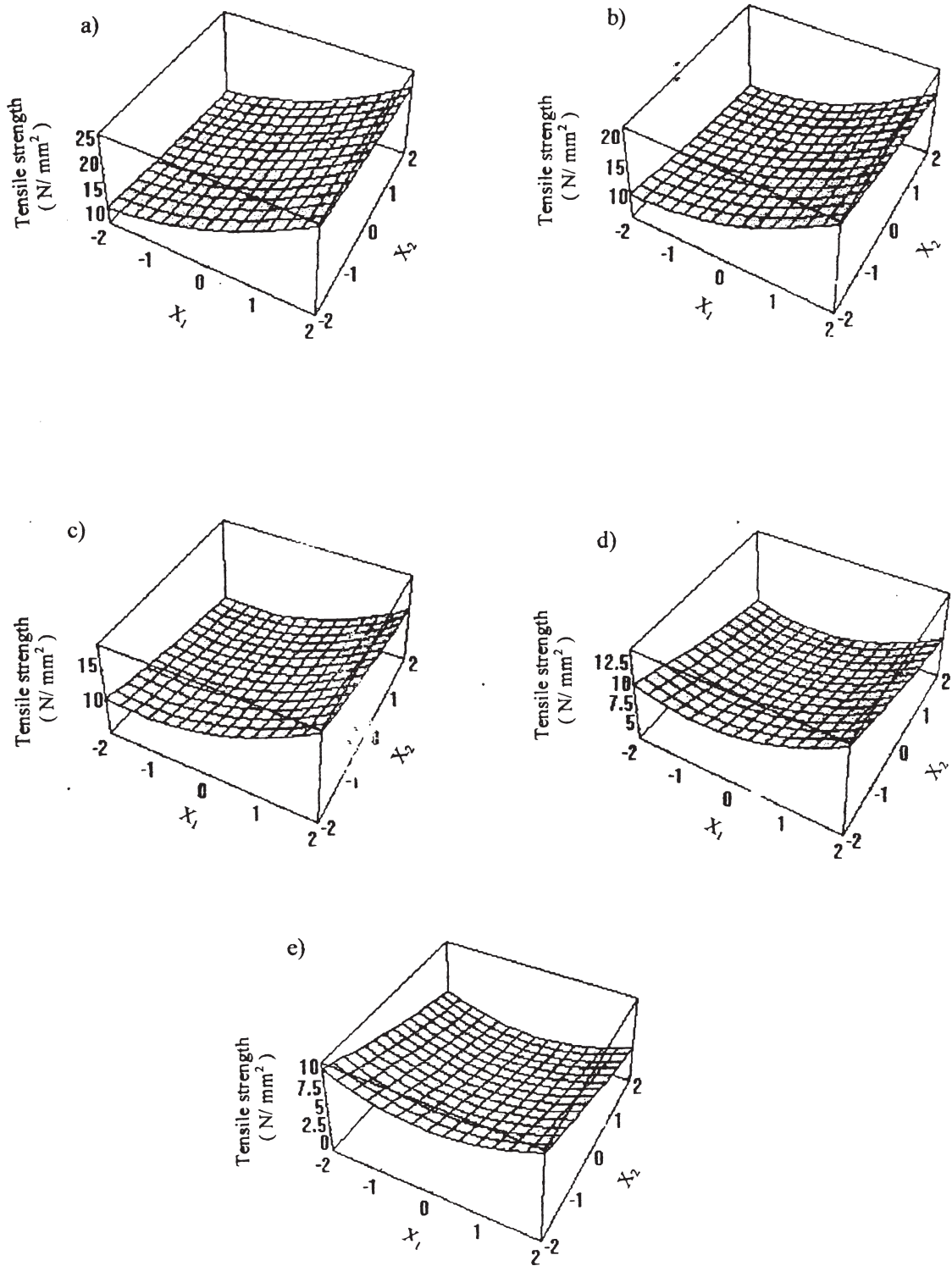


Fig. 1. Variation of the tensile strength versus concentration in starch (X_1) and in APV (X_2), in conditions when the X_3 and X_4 independent variables (see Table 2) are maintained constantly: (a) $X_3 = -2$ and $X_4 = 2$; (b) $X_3 = -1$ and $X_4 = 1$; (c) $X_3 = 0$ and $X_4 = 0$; (d) $X_3 = 1$ and $X_4 = -1$; (e) $X_3 = 2$ and $X_4 = -2$.

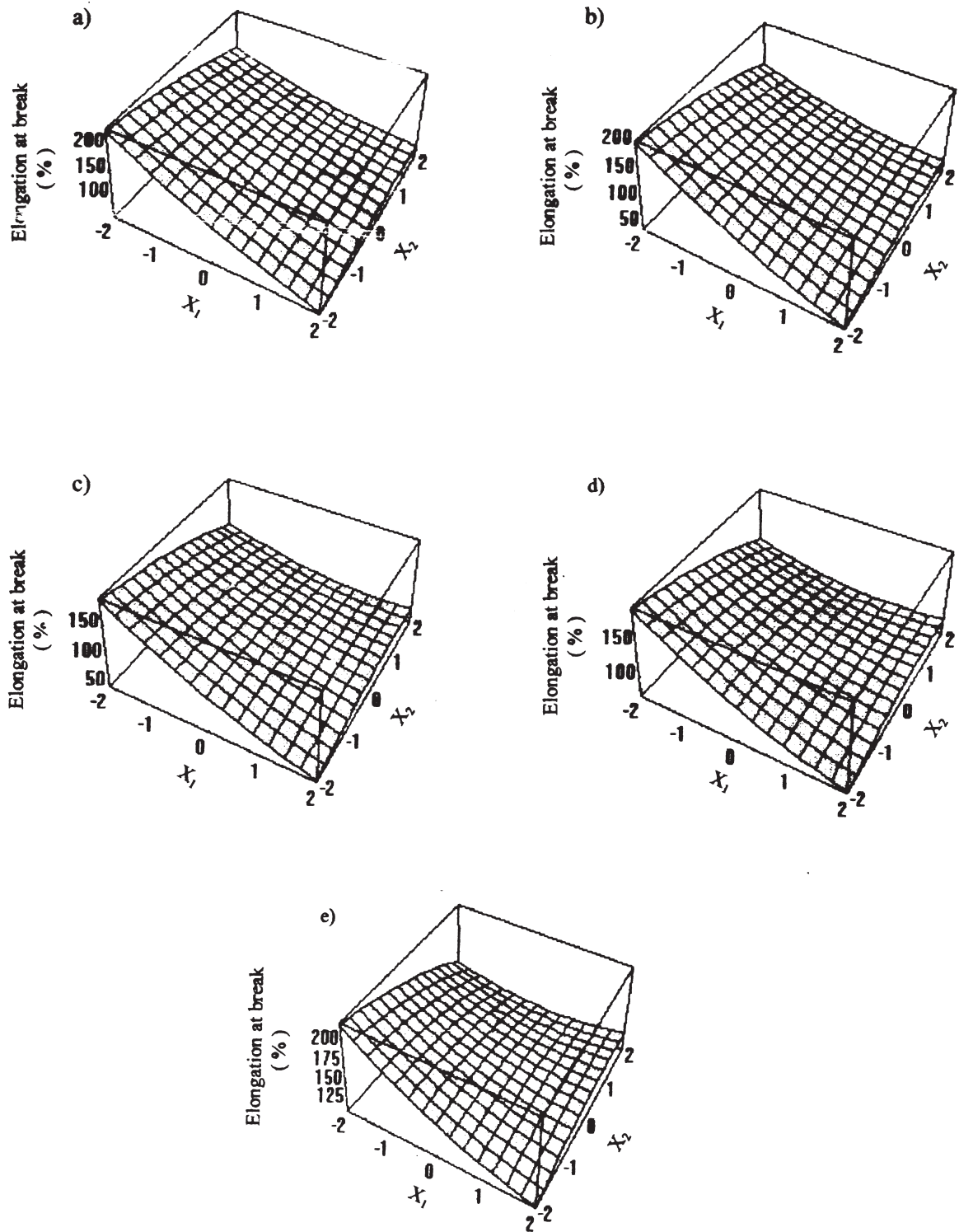


Fig. 2. Variation of the elongation at break versus concentration in starch (X_1) and in APV (X_2), in the same conditions as those mentioned in Fig. 1.

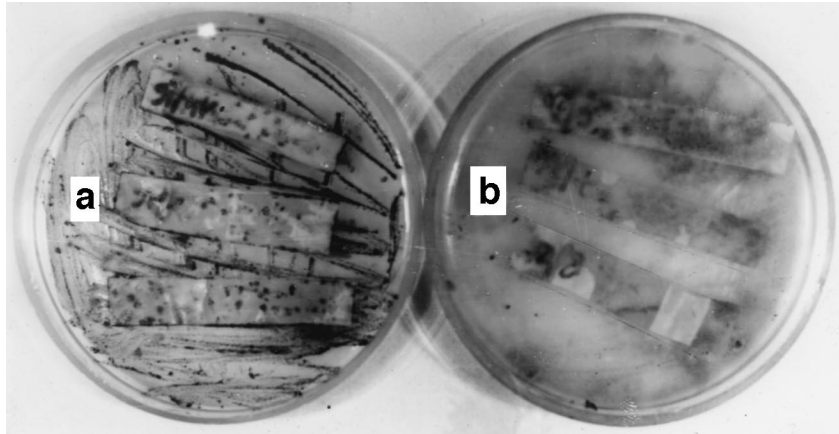


Fig. 3. *Penicillium* sp. (a) and *Cephalosporium* sp. (b) filaments developed at the surface of the films after 18 days of biodegradation in medium which was inoculated with fungi isolated from landfill.

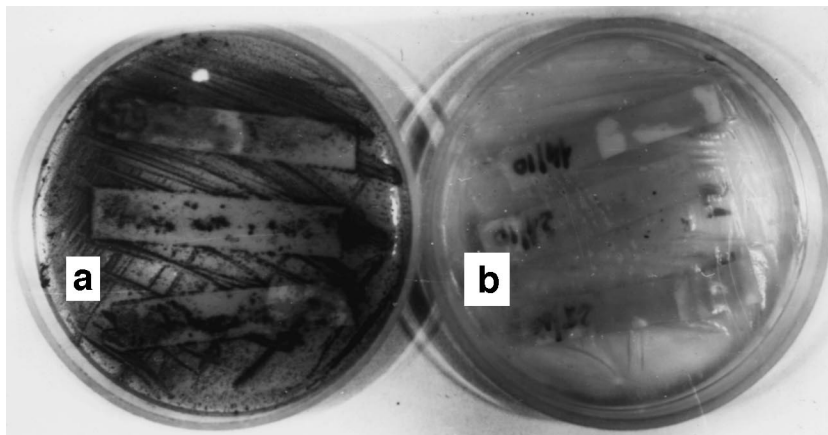


Fig. 4. *Penicillium viridicatum* (a) and *Fusarium* sp. (b) filaments developed at the surface of the films after 18 days of biodegradation in medium which was inoculated with fungi isolated from activated sludges of municipal sewage plant.

4. Results and discussion

Data processing on an IBM compatible PC computer led to the following regression equations:

(a) tensile strength (Y_1):

$$Y_1 = 9.0675 + 1.765X_1 + 0.6854X_1^2 - 0.0075X_1X_2 - 0.42X_1X_3 + 0.415X_1X_4 - 1.1342X_2 + 0.1079X_2^2 + 0.3587X_2X_3 + 0.5688X_2X_4 - 1.1992X_3 + 0.1104X_3^2 + 0.1238X_3X_4 + 1.3808X_4 + 0.1129X_4^2$$

(b) elongation at break (Y_2):

$$Y_2 = 101.105 - 22.6313X_1 + 3.5591X_1^2 + 6.0106X_1X_2 + 2.6769X_1X_3 - 1.3431X_1X_4 - 6.7296X_2$$

$$-2.5247X_2^2 - 2.0519X_2X_3 - 2.0319X_2X_4 + 4.1596X_3 + 6.4753X_3^2 - 2.6156X_3X_4 - 2.0896X_4 + 0.0791X_4^2$$

On the basis of the regression equations the level surfaces were plotted in conditions in which the independent variables took values in the range -2 , -1 , 0 , 1 and 2 , respectively. Fig. 1(a–e) shows the dependence between the tensile strength and the simultaneous variation of both X_1 and X_2 , in conditions in which X_3 and X_4 were maintained constantly.

It can be observed that the tensile strength continually increases with an increase of the PVA amount. The maximum value of the tensile strength (25 N/mm^2), [see Fig. 1(a)] is obtained for the lower limits of both X_3 and X_4 independent variables (10% and 2%, respectively). The influence of the PVA amount upon the tensile strength is in a straight line throughout, while the starch amount leads to a gentle decrease of the tensile strength in the first part of the interval (20–40% by weight) and to a pronounced increase of this parameter in the second part of the interval (40–60% by weight).

An increase of the amount of glycerine and urea in the systems towards the maximum value (18% and 10%, respectively) provokes a permanent decrease of the tensile strength from 25 N/mm^2 up to 10 N/mm^2 . This behaviour can be explained taking into consideration the fact that the increase of the plasticizer (glycerine) amount in the blend results in a greater mobility of both the starch and the PVA macromolecules. This makes the tensile strength of the blend decrease, with a faster rate at a lower concentration of PVA and starch especially. On the other hand, as discussed above, the increase of the amount of the starch and of the PVA in the blend ($X_1=2$ and

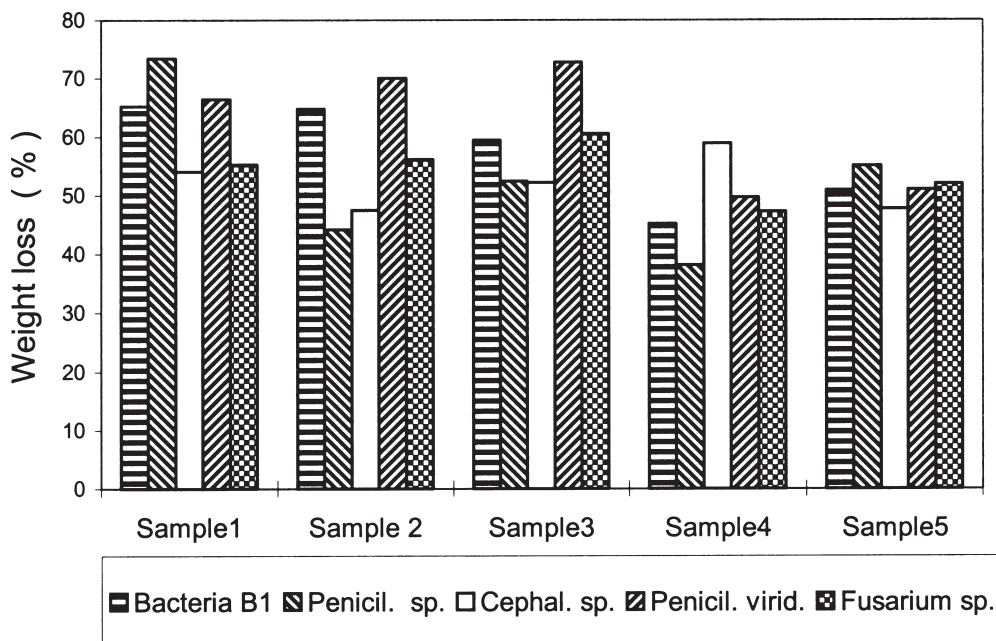


Fig. 5. Weight losses (%) as against the nature of the used microorganisms.

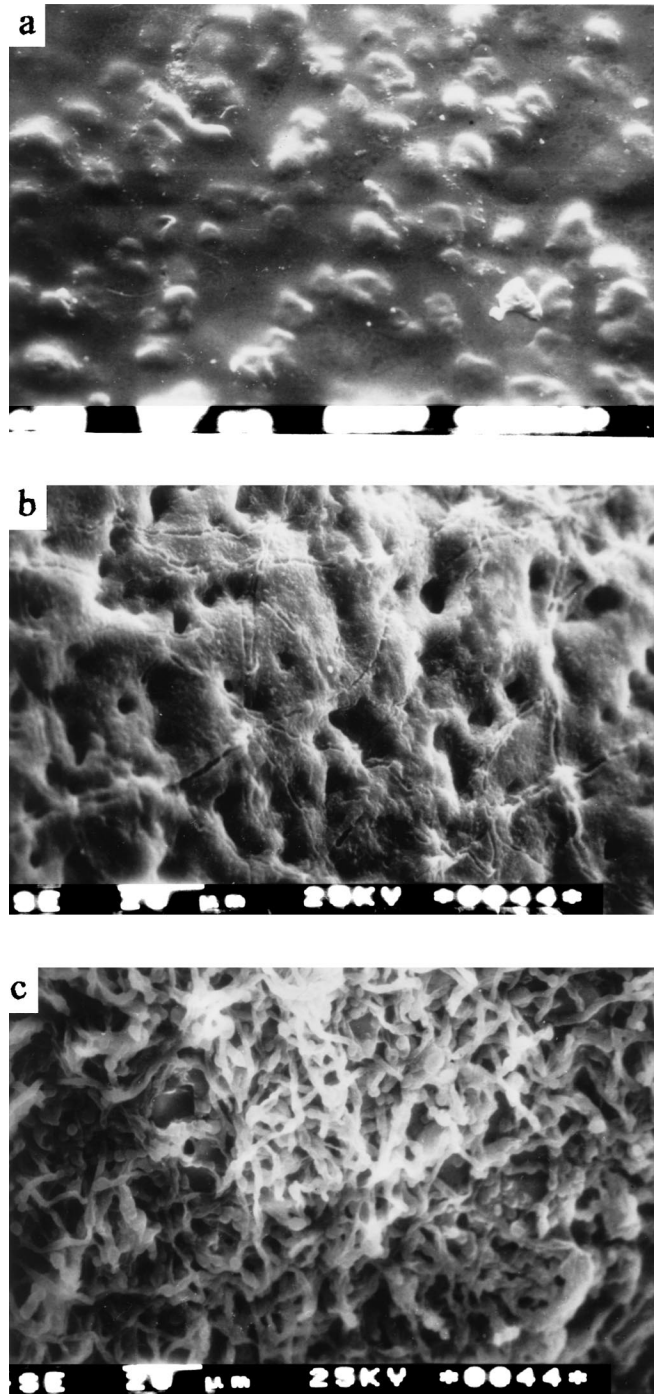


Fig. 6. SEM micrographs of sample 1 before and after biodegradation: (a) non-biodegraded initial sample; (b) sample biodegraded in the presence of bacteria B₁ isolated from landfill; (c) sample biodegraded in the presence of *Penicillium* sp. fungi isolated from landfill.

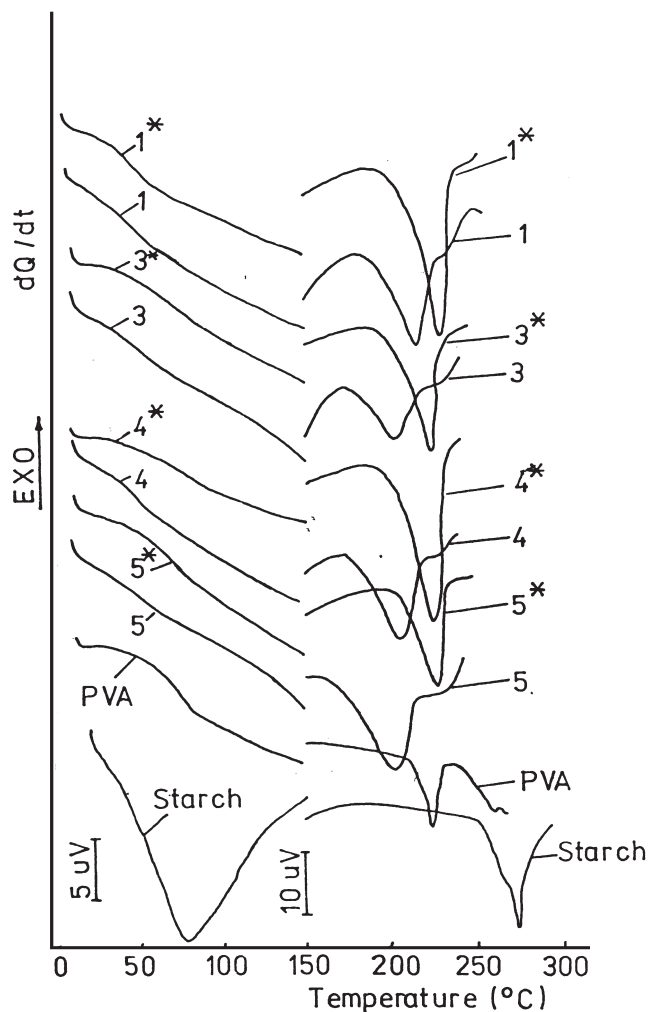


Fig. 7. DSC thermograms of PVA, starch samples 1, 3–5 before biodegradation, and samples 1*, 3*–5* after biodegradation.

$X_2 = -2$) leads to an increase of the tensile strength. This behaviour is, probably, due to the decrease of the macromolecular chain mobility as a result of the presence of the strong intermolecular hydrogen bonds, as well as the associations which are established between the macromolecules of the blend components. One of the first conclusions drawn from this study is that the tensile strength value varies between some limits in direct dependence with the manner in which the ratio of the independent variables is modified.

Figure 2(a–e), shows the dependence between the elongation at break versus starch (X_1) and APV (X_2) concentration, in conditions in which X_3 and X_4 were maintained constant.

This time it was observed that the elongation at break decreases with an increase of the starch amount, while the PVA concentration has little influence upon this parameter. Regarding the

influence of the plasticizer amount upon the elongation at break it can be remarked that this mechanical parameter varies between 50 and 200%, in conditions in which the plasticizer amount in the blend takes values in the range 10–18%. The values obtained for the elongation at break are high enough to allow the use of the films in various fields. The experimental data show that the films with sufficient values of both the tensile strength and the elongation at break are obtained using average values of X_1 and X_2 independent variables between -1 and $+1$ with respectively the lower values of the X_3 and X_4 independent variables (-2 and $+2$).

During exposure of the samples to biodegradation on the solid medium, which was inoculated with *Penicillium* sp. [Fig. 3(a)] and *Cephalosporium* sp. [Fig. 3(b)] fungi, filaments of the microorganisms developed on the surface of the polymer even within the first 5 days of incubation. The surface of the films covered by *Penicillium* sp., as well as by *Cephalosporium* sp., was around 5–10%. In the case of *Penicillium viridicatum* [Fig. 4(a)] and *Fusarium* sp. [Fig. 4(b)] the samples were covered to 15–20%. An abundant growth of fungi was noted for all the studied samples at the end of incubation (around 18 days), when they were covered over 80–90%.

The colonization of the film surface due to both bacteria and fungi led to a dramatic decrease of the physical–mechanical characteristics of the films, as well as significant weight losses.

The evaluation of the weight losses at the end of the testing duration was carried out on samples taken from the hydrated mineral agar–agar medium, cleaned carefully, dried at 50°C under vacuum and weighed on an analytical balance. The weight losses were determined as the difference between the net weight of the sample before and after biodegradation and were expressed as percentages. Fig. 5 shows the weight losses of the films exposed to biodegradation in the presence of various species of fungi and bacteria.

As can be observed, all the analysed samples show important weight losses between 38 and 73%. The weight losses are influenced by the composition of the mixture, as well as by nature of the microorganism species. The highest values of weight loss were recorded for the films with a high content of starch in the mixture. The fungi isolated from activated sludges of municipal sewage plant exhibit a higher biodegradation capacity compared with that exhibited by fungi and bacteria isolated from landfill.

Table 3

Values of T_g , T_m and ΔH evaluated by means of the DSC measurements

Sample	T_g (°C)	T_m (°C)	ΔH (J/g)
Starch		Decomposition	
PVA	70	210	22.61
1	50	196	26.18
1 ^a	72	213	57.04
3	49	187	20.06
3 ^a	67	209	58.20
4	54	187	35.83
4 ^a	78	210	67.11
5	45	178	33.53
5 ^a	70	213	59.05

^a Biodegraded sample.

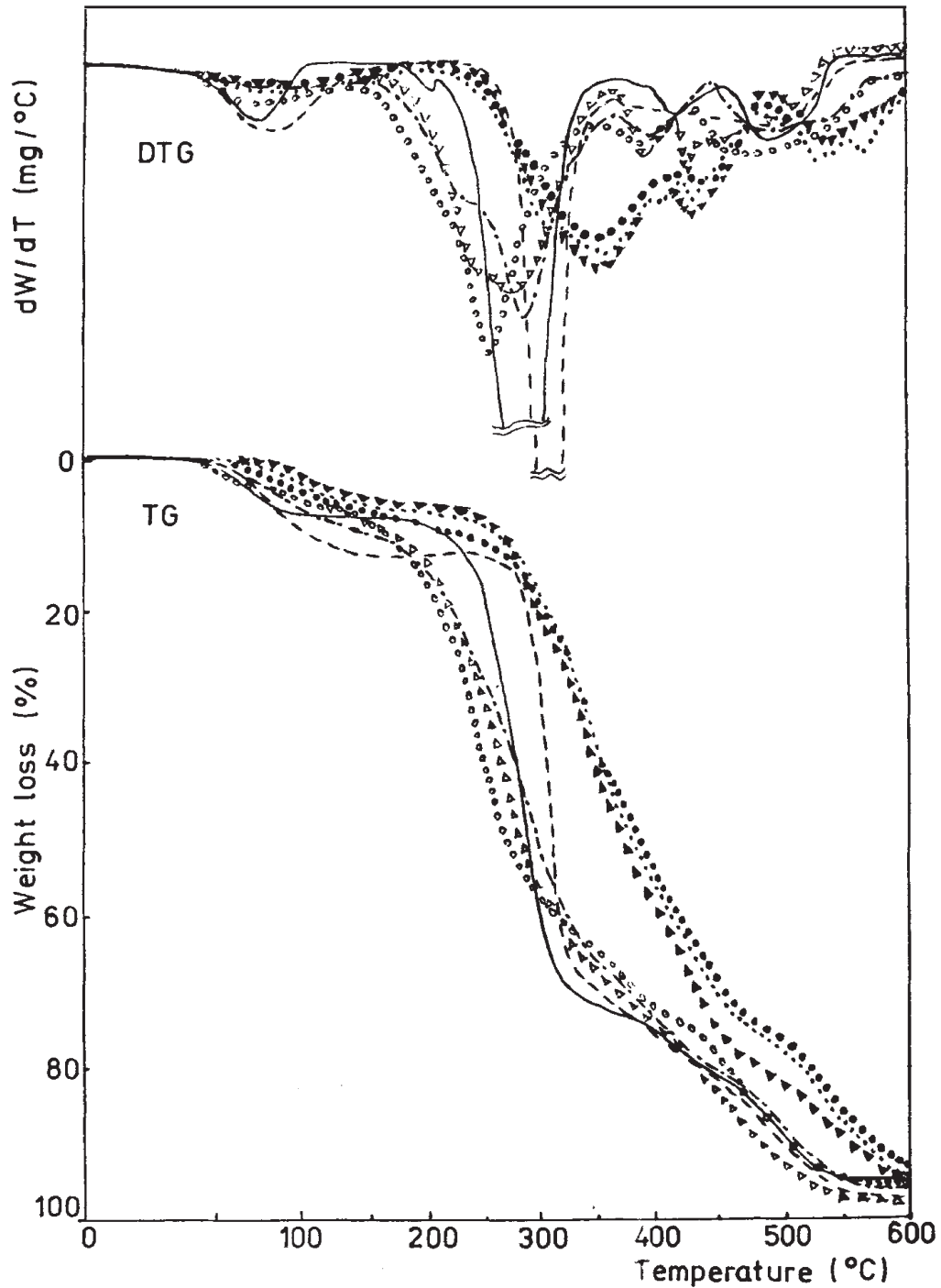


Fig. 8. TG and DTG curves of the films before and after biodegradation, the latter being carried out in the presence of bacteria B_1 from landfill: (—) PVA; (---) starch; (○ ○ ○) sample 1; (● ● ●) sample 1*; (- · - · -) sample 3; (· · ·) sample 3*; (△△△) sample 4; (▲▲▲) sample 4*.

In order to gain more information regarding the biodegradability, the change of morphology of the film surface was carried out. Fig. 6 shows some micrographs obtained by means of SEM.

The homogeneous dispersion of the two polymers used, in which the granular phase belongs to the starch, can be seen very clearly in Fig. 6(a). Fig. 6(b), as well as Fig. 6(c), show the micrographs obtained for the same sample as in Fig. 6(a), after biodegradation for 18 days in the presence of bacteria *B₁* and *Penicillium* sp. fungi. As can be seen, some important modifications of the film surface are observed, when spherical hole formations appeared due to colonization.

The progress of biodegradation reaction was evaluated by measuring glass transition temperature (T_g) and melting transition (T_m) using the DSC technique. The DSC thermograms recorded for the analysed samples shown in Fig. 7 allowed us to determine T_g , T_m , as well as the total enthalpy (ΔH). The values obtained for these parameters (Table 3) reflect the effect of the two plasticisers used in preparation of the samples.

Both T_g and T_m increased for biodegraded samples and are around the T_g and T_m values determined for PVA alone. Also, ΔH values evaluated for biodegraded samples are higher than those determined for non-biodegraded samples. These behaviours show cumulative effects of PVA upon hydrolysis and reorganization in the biodegradation process. During biodegradation the hydrolysis of starch takes place first, together with consumption of a part of the amorphous phase of PVA [21]. The crystalline regions remaining after biodegradation contribute to increase of ΔH enthalpy.

Weight loss as a function of temperature was studied by TG and DTG analysis. Fig. 8 and Table 4 show weight loss values evaluated for the analysed samples, before and after the biodegradation process.

Generally, the thermal degradation in dynamic conditions and in the presence of oxygen, shows four to six decomposition stages in the temperature range between 60 and 600°C. Curves in Fig.

Table 4
Weight losses (%) evaluated by thermal degradation

Sample	Starch/PVA ratio	Temperature (°C)				
		150	250	300	350	400
		Weight losses (%)				
Starch	100/0	13.0	13.5	35.6	71.2	77.0
PVA	0/100	8.2	19.0	64.5	73.6	78.2
1	60/40	6.6	20.2	46.2	60.2	66.6
1 ^a	60/40	7.4	12.0	22.4	44.1	59.6
2	50/30	10.0	20.4	45.0	63.4	70.0
2 ^a	50/30	7.2	10.5	21.8	43.1	59.0
3	40/40	10.2	25.6	47.0	64.6	72.4
3 ^a	40/40	7.1	10.3	22.4	42.4	60.2
4	40/60	9.2	27.1	50.0	65.3	71.2
4 ^a	40/60	6.6	8.4	19.4	40.2	59.3
5	30/50	9.1	31.2	51.8	66.6	73.0
5 ^a	30/50	7.2	10.0	23.5	45.6	58.8

^a Biodegraded sample.

8 and data in Table 4 show that the decomposition proper of the analysed samples occurs mainly in the range 150–400°C, at different rates, when the weight losses are between 66–73% recorded for the native samples, and around 60% for biodegraded samples.

It can be observed that the apparent thermal stability of the biodegraded samples is higher compared to that of the non-biodegraded samples. This behaviour can be due to modification of the starch/PVA ratio after biodegradation, the microorganisms consuming the two components in various proportions. Simultaneously, the plasticisers, glycerine and urea, are consumed totally during biodegradation. This results in a very brittle material which suffers degradation at higher temperatures. It is also interesting to note that during biodegradation amorphous regions are degraded faster than the crystalline regions [21]. The crystalline structures are thermally degraded at higher temperatures compared to amorphous structures and this could explain the higher thermal stability of the biodegraded samples.

5. Conclusions

Some preliminary results were obtained before biodegradation of blends based on starch, PVA, urea and glycerine. Generally, the tensile strength increases with increasing PVA amount, as well as starch amount and decreases with increasing glycerine and urea amount in the blends. An explanation of this behaviour can be due to the glycerine, which acts as a plasticizer, leading to a greater mobility of both the starch and PVA macromolecular chains and the presence of some strong intermolecular hydrogen bonds, as well as associations established between the macromolecules of the blend components. The elongation at break decreases with increasing starch amount in the blends, while the PVA concentration has little influence upon this parameter.

SEM, DSC and TG techniques can be used successfully for the study of biodegradation of polymeric materials. Biodegradation of polymeric materials based on PVA, starch, glycerine and urea in the presence of microorganisms takes place with an important decrease of the physical–mechanical characteristics of the samples, as well as significant weight losses. The weight loss is influenced by the composition of the blend, and by the nature of the microorganisms used. The highest values of weight loss were obtained for the samples with a high content of starch. During biodegradation, spherical holes appear due to colonization by the degrading microorganisms. The starch is first consumed by microorganisms, together with the amorphous part of PVA. The crystalline regions of PVA remaining after the biodegradation process contribute to an increase of ΔH enthalpy, as well as the apparent thermal stability of the biodegraded samples. The thermal degradation of the systems takes place after a complex mechanism, with many decomposition stages. Some of these stages are overlapped, especially the second and the third stages lying in the temperature range between 160 and 370°C. The starch and PVA polymers show an apparent thermal stability higher than that observed for the analysed blends.

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