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Improving the Biodegradability and Mechanical Strength of Corn Starch-LDPE Blends through Formulation Modification

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ABSTRACT

Six corn starch-LDPE film blends containing starch in the range 5-40 % by weight, oleic acid as a Lewis catalyst with concentration of either 5 % or 10 %, maleic anhydride as a coupling agent with concentration of either 2 % or 10 % and benzoyl peroxide as free radical initiator with concentration of either 0.1 % or 0.25 % were prepared. Fungal growth tests (ASTM G21) using *Penicillium funiculosum* were carried out on the samples made according to the above formulations. Tensile tests (ASTM D638) and SEM imaging were also carried out on the samples before and after incubation with *Penicillium funiculosum* for three weeks. The results of ASTM G21 test and SEM imaging showed that the increase in starch content from 5 % to 40 % in the formulations containing all three additive increases the biodegradability of the samples whereas increase in the concentration of oleic acid from 5 % to 10 % has an opposite effect. Formulations containing only 5 % starch with a fairly high concentrations of additives or 40 % starch with no additives supported none or very little growth after three weeks, which indicates the importance of the concentration of starch and the presence of additives on the biodegradability of starch-LDPE film blends. Tensile test results showed that increase in starch content in the range of 20-30 % leads to a decrease in the values of the tensile strength and increase in the values of the elongation-at-break whereas further increase up to 40 % has the opposite effect. Tests with blends containing 40 % starch and no additive or 5 % starch with a fairly high concentration of additives resulted in low yield stresses and high elongation-at-break values. Increase the concentration of oleic acid from 5 % to 10 % in the blends resulted in a decrease in both the yield stress and elongation-at-break values.

Key Words:
polyethylene;
starch;
biodegradable;
Penicillium funiculosum.

INTRODUCTION

Around fifty percent of synthetic polymers are used for packaging applications which 90 percent of them find their way to municipal garbage. Due to their stability, long life and non-biodegradability, disposal of synthetic polymers is fraught with problems. These plastics just pile up in landfill sites, and their incineration results in heat generation and causes air pollution. The worst offender is polyethylene which has the highest usage volume in packaging applications.

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The biodegradability of synthetic polymers like polyethylene can be enhanced by the addition of biodegradable additives to the formulation of plastics [1-3]. One of the most common degradable fillers used in plastic formulations is starch [4,5]. Raw starch is considered to be a cost effective additive and meets the requirement of high thermal stability, minimum interference with flow properties, and minimum disturbance of product [6,7]. Polyhedral starches, such as rice or corn starch have been proposed as suitable dry filler in plastic films [8]. In plastics containing blends of polyethylene with starch, microbes initially attack starch resulting in an increase in the porosity and surface to volume ratio of the polymer blend and a consequent enhancement of its biodegradability. In order to attack the starch, the microbes, should first adhere to the surface of the polymer, so polymers that have a rougher surface finish are more prone to microbial attack. Scanning electron microscopy analysis have shown that starch based polymers have a textured surface whereas PE has a smooth surface [9]. It has been shown that increase in the starch content and decrease in the starch granule size enhance the biodegradability of the plastic blends [10-12].

The biodegradability of the polyethylene-starch blends can be further enhanced by the addition of other additives such as autooxidants (for example unsaturated fatty acids and their derivatives), photo degraders (for example aromatic or aliphatic ketone), chemical degraders (for example an aliphatic polyhydroxy carboxylic acid) and various compatibilizers [8,13,14]. In the former case peroxides are formed, after the contact of the plastic with metal salts in the soil. It results in the breakup of the polymer into low molecular weight carboxylic acids that are easily metabolized by the microbes in the soil.

Lee et al. [15] reported degradation of polyethylene molecules by lignin degrading bacteria in those films containing starch and pro-oxidants. Sharma et al. [16] found that the incorporation of pro-oxidant which consisted of metal salts and unsaturated elastomer enhanced the thermo-oxidative degradation rate of sago starch filled LLDPE composites. The use of glycerol plasticized starch has also been found to affect the degradability of the plastic blends [12].

On the other hand, the addition of starch to polyolefin blends results in a reduction in their mechanical strength which necessitates an increase in the thickness of bags made from this blends [9] unless other measures are used to combat this problem. These measures include the chemical modification of starch [8,17-21], the use of compatibilizers, such as oxidized polyethylene [22], fatty acids [8], and ethylene-*co*-acrylic acid [23]. The amount of starch in the blend also affects its mechanical properties. Increaseing the starch content is shown to worsen the mechanical and rheological properties and the processability of the system [24-26]. The size and type of starch in the starch based PE films also affects its physical properties. For example Lee [15] found a strong negative correlation between tensile and yield strength values of the films and average starch granule diameter. Mani and Bhattacharya [27] found that amylose to amylopectin ratio of starch affect the physical properties of starch/PE blends.

In this study the incorporation of additives in the indigenous raw corn starch based LDPE blends has been considered as a means of improving the mechanical properties and biodegradability of plastic films made form these blends. In this respect, the effect of the concentration of raw corn starch and the addition of various concentrations of benzoyl peroxide as free radical producer, maleic anhydride as a coupling agent and oleic acid as the Lewis acid catalyst on the mechanical properties and biodegradability of starch-LDPE blends has been investigated. Maleic anhydride, by enhancing the interfacial interaction between the PE and starch phases, makes them more compatible with each other. This results in an increase in the stability of the morphology in the mixing process. It also enhances the mechanical properties of the resulting mixture through an increase in the physical on chemical interfacial bonds.

Materials Methods

Low density polyethylene (LDPE from Bandar Emam Petrochemical Co.), commercial grade corn starch (Glucosan Co.) and technical grades of benzyl peroxide, maleic acid, and oleic acid (all three from Merck) were used in the preparation of the starch-LDPE film blends. Mixing was accomplished using Haake mixer at 140°C and 60 rpm. Materials were added to the mixer in the order of LDPE, benzoyl peroxide, maleic anhydride, and starch at 1-2 minute time intervals. Starch was dried to moisture content below 1% for 12 h in an oven at 70°C and then added to the mixer. This

Table 1. Formulation of the six starch based LDPE film blends.

Blend number	Starch (% wt)	Maleic anhydride (% wt)	Oleic acid (% wt)	Benzoyl peroxide (% wt)
1	5	10	10	0.25
2	20	2	5	0.1
3	30	2	5	0.1
4	40	2	5	0.1
5	40	2	10	0.1
6	40	-	-	-

was done to avoid the formation of the porous film. In order to carry out biodegradability and mechanical tests a press was used to turn the samples into the sheets. Six starch based LDPE film blends (Table 1) were made and tested. In these formulations corn starch, maleic anhydride, benzoylperoxide, and oleic acid are used as the biodegradable component, the coupling agent, the free radical initiator, and the Lewis acid catalyst, respectively [28].

The biodegradability of the samples was carried out according to the ASTM G21-70 [29]. In this method the samples were placed in carbon limited agar medium. After inoculation with *Penicillium funiculosum*, the samples were incubated at 29±1°C for three weeks. The extent of microbial growth was assessed according to the following rating:

0: no colony growth

1: less than 10% of the surface of the samples covered with colonies

2: between 10-30% of the surface of the samples covered with colonies

3: between 30-60% of the surface of the samples covered with colonies

4: between 60-100% of the surface of the samples covered with colonies

Tensile test was carried out according to ASTM D638 [30] using Instron 6025 plastic testing system. This test together with SEM imaging were performed on the six blends prior and after ASTM G21 test. In the case of the SEM imaging and tensile tests that carried out after the ASTM G21 test, the samples were initially soaked for 5 minutes in mercury chloride solution, washed with distilled water, and dried in air.

RESULTS AND DISCUSSION

The Effect of the Concentration of Corn Starch and Various Additives on the Mechanical Properties of the Corn Starch LDPE Blends

Two undesirable effects of the incorporation of starch into plastic films are the reduction in the yield stress and elongation-at-break values of the films. The values of these two parameters for the corn starch based plastic blends prepared in this study are shown in Table 2.

It can be seen that the blend without any additive (blend 6) has a very low yield stress (5.137 Mpa) but a fairly high elongation-at-break (53.41%). Incorporation of the three additives in blends 4 and 5 results in a significant increase in the yield stress and a considerable decrease in the elongation-at-break values of these samples. The latter case is the result of the incorporation of starch granules in the polymer matrix, which has a negative influence on the stretching properties of the plastic. The blend that contains the lowest amount of starch (blend 1) exhibits a fairly low tensile strength value (3.547 Mpa) but a moderate elongation-at-break value (34.96%). It should be noted that this blend also contains the highest concentration of the three additives (namely 10% maleic anhydride, 0.25% benzoyl peroxide and 10% oleic acid). The results of blends 2-4 in Table 2 show the effect of the increment of the starch amount in the blends (in the range of 20-40%) on their mechanical properties. Since the concentrations of the three additives are the same in three of them. These results show that increase in the concentration of starch from 20% to 30% has actually resulted in the increase in the yield stress and elongation-at-break values. Whereas, further increase in the starch content to 40%

Table 2. The yield stress and elongation-at-break values of the six starch based LDPE blends.

Blend number	1	2	3	4	5	6
Yield stress (Mpa)	5.137	7.669	9.580	9.059	6.345	3.547
Elongation-at-break (%)	34.96	20.83	25.85	18.915	11.597	53.41

has worsen the mechanical properties of the blends (a slight decrease in the yield stress and a significant reduction in the elongation-at-break values).

Arvanitoyannis et al. [31] using rice and potato starch and Psomiadou et al. [32] employing wheat starch have also reported that an increase in the starch content above 30% has an adverse effect on the mechanical properties of LDPE-starch blends. However, Nawang et al. [33] found a decrease in elongation-at-break value but an increase in the tensile strength value by increasing in the amount of starch in the range 5-25% in LLDPE-sago starch composites.

On the other hand, Chandra and Rustgi [34] have found increase in tensile strength and decrease in elongation-at-break values by increasing in starch contents in the range 10-60% blends of maleated linear LDPE with corn starch.

The discrepancy between the findings of this study and the reports in the literature and amongst themselves seems to suggest that there is an interaction between the effect of starch's type and concentration and additive's type and concentration on the mechanical properties of starch-LDPE blends. The interaction between starch's type and concentration has been previously reported by Lim et al. [35] who found that, for starch contents up to 15%, the effect of its concentration increase on the yield strength and elongation-at-break values of the starch-LLDPE blends depended on the starch source.

Results presented in Table 2 also give some indication of the effect of some of the additive concentration on the mechanical properties of starch-LDPE blends. Blends 4 and 5 have the same starch (40%), maleic anhydride (2%) and benzoyl peroxide (0.1%) contents but the former contains 5% whilst, the latter consists of 10% oleic acid. Comparison of the mechanical properties of the blends 4 and 5 in Table 2 shows that increasing the concentration of oleic acid in the corn starch-LDPE blends has resulted in a significant decrease in their both the yield stress and elongation-at-break values.

Table 3 shows the values of yield stress and elongation-at-break for samples of the six corn starch-LDPE blends when subjected to three weeks of incubation with *Penicillium funiculosum*. The corresponding results of the ASTM G21 tests with *Penicillium funiculosum* is presented in Table 4. It can be seen that blends 3 and 4 which show high fungal growth, also show a large reduction in the values of the tensile stress and elongation-at-break. This is the result of incubation with the fungal culture. Whereas, the reduction in these parameters for blends 1 and 6 which have yielded none or little fungal growth after three weeks is correspondingly low.

The only anomaly in the results is those for blends 2 and 5. Blend 5 has only exhibited moderate fungal growth after three weeks. It shows a significant worsening of the mechanical properties similar to the results obtained for blend 4 which is supported by high fungal growth. This is also the blend that contains the highest concentration of oleic acid. This observation suggests that oleic acid contributes to the worsening of mechanical properties under conditions employed in the ASTM G21 test.

Although, the results for blends 2 and 6 in Table 3 are not very dissimilar, results in Table 4 indicate significant fungal growth after three weeks for the former and no growth for the latter. This seems to indicate the enhancing effect of the formulation employed for

Table 3. Percentage change in the values of the tensile strength and elongation-at- break of the six blends as a result of 3 weeks incubation of samples with *Penicillium funiculosum*.

Blend number	Decrease in the tensile strength (%)	Decrease in elongation-at-break (%)
1	0	2
2	10	23
3	21	40
4	26	50
5	27	48
6	12	18

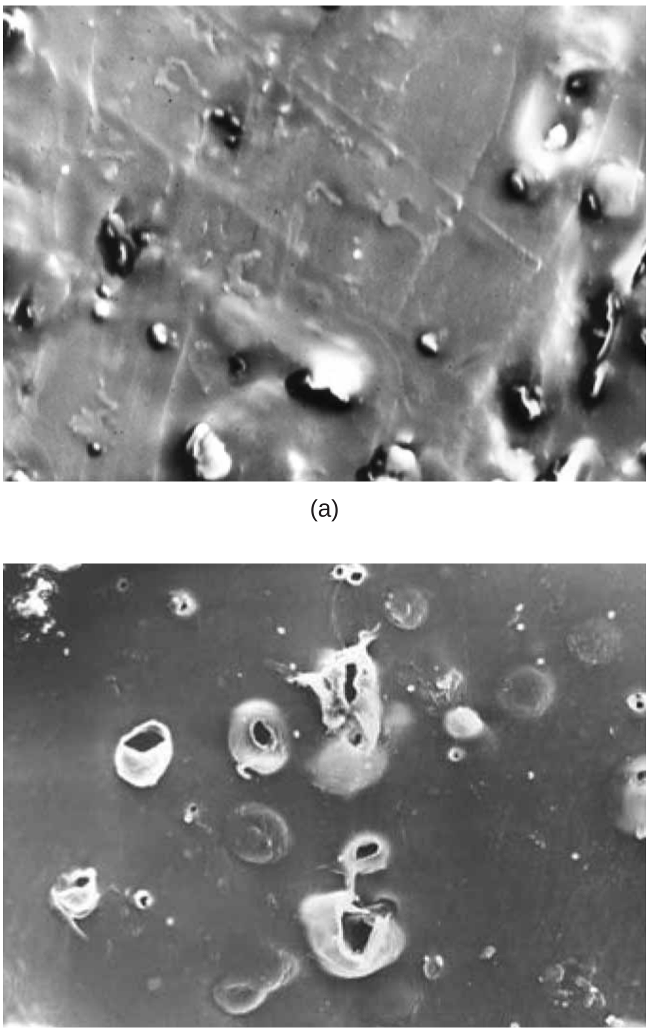
Table 4. Results of the ASTM G21 test with *Penicillium funiculosum* on the six blends.

Blend number	Rating
1	0
2	3
3	4
4	4
5	2
6	1

blend 2 on the mechanical properties of the starch-LDPE blend even after three weeks incubation with the fungal culture. However, the results are not sufficient to make any conclusive statements in this regard.

The Effect of the Concentration of Starch and Various Additives on the Biodegradability of Corn Starch LDPE Blends

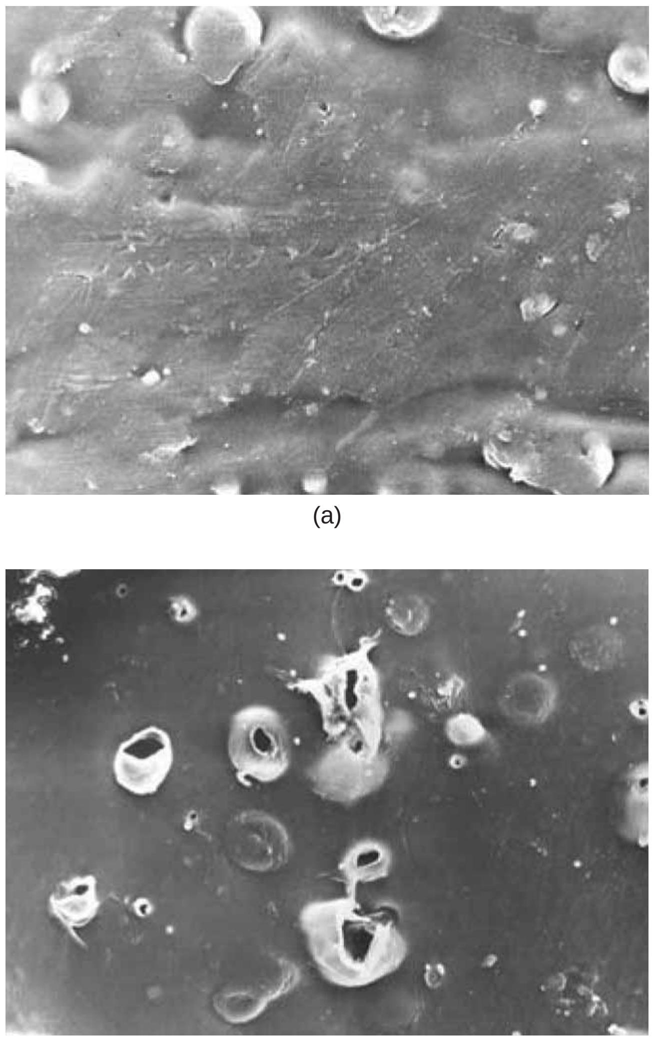
The results of the ASTM G21 test (Table 4) show little fungal growth after three weeks for blend 1 which contains additives and 5% starch and no growth for blend 6, which has largest starch content, but no additives. This indicates the importance of both the starch concentration and the presence of the appropriate additives in the coposition of starch based biodegradable LDPE films. Arvanitoyannis et al. [31] have previously reported that the biodegradability of rice or potato starch based LDPE films was enhanced when the starch content exceeded 10%. However, Chandra and Rustgi [34] found heavy fungus growth in maleated starch-LLDPE blends only when the starch content was above 30%. In this study heavy fungus growth after three weeks has been observed with blends containing 30% or 40% starch and all the three additives. Blend 5 that contains the highest concentration of oleic acid (10%) has supported only moderate fungal growth after three weeks, which indicates the inhibitory influence of oleic acid on fungal growth. Blend 2 shows less fungal



(a)

(b)

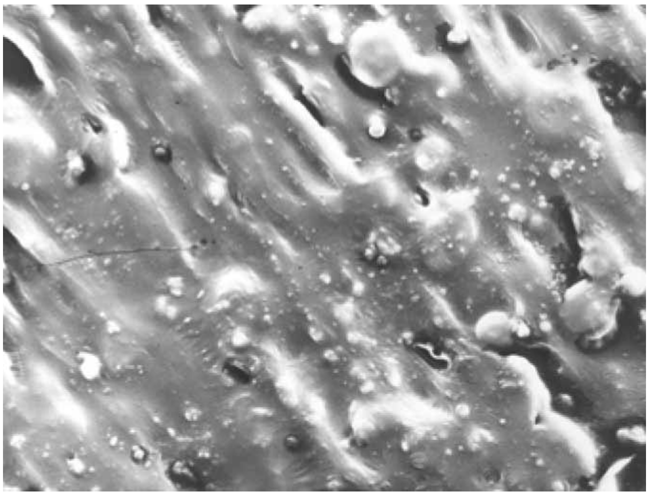
Figure 1. SEM Images (magnification × 400) of (a) blend 2 before, and (b) after 3 weeks Incubation with *Penicillium funiculosum*.



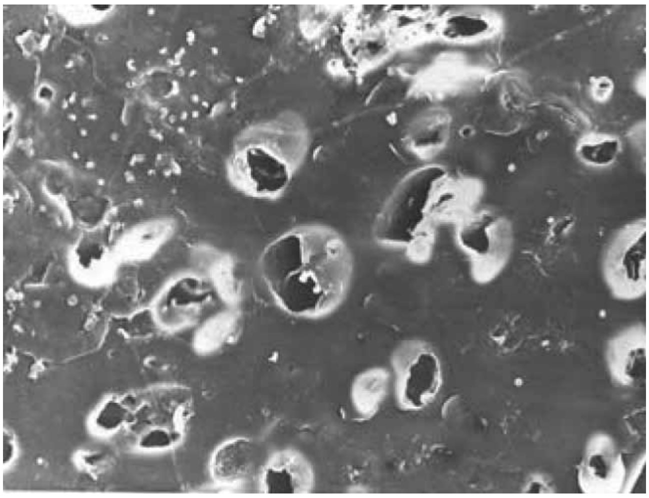
(a)

(b)

Figure 2. SEM Images (magnification × 400) of (a) blend 3 before, and (b) after 3 weeks Incubation with *Penicillium funiculosum*.



(a)



(b)

Figure 3 SEM Images (magnification × 400) of (a) blend 4 before, and (b) after 3 weeks Incubation with *Penicillium funiculosum*.

growth compared to blends 3 and 4, which suggests the influence of starch concentration on the extent of fungal growth (and hence biodegradability) of corn starch-LDPE blends.

SEM images of blends 2, 3, and 4 before and after 3 weeks incubation are shown together in Figures 1-3, respectively. These illustrate the increase in porosity of these starch-LDPE blends as a result of fungal growth. These pictures show again the higher fungal growth is associated with blends 3 and 4 compared to blend 2.

CONCLUSION

In this work the approach of varying the starch and additives content of starch-LDPE blends have been investigated in order to achive to the plastic formulations with desirable mechanical properties but no environmental problems when were disposed. The results showed that both the starch and additive concentrations in the formulation of the starch based LDPE blends affect the mechanical properties (tensile stress and elongation-at-break values) and biodegradation rates (as measured by the ASTM G21 test). Increase of starch content to 20% and above lead to an enhancement to the rate of biodegradation as long as suitable additives were employed.

The highest rate of biodegradation was obtained with blends composed of starch in the range 30-40% and additives of oleic acid (5%), maleic anhydride (2%) and benzoyl peroxide (0.1%). SEM Images of the corn starch based plastic blends illustrated the significant increase in the porosity of the plastic blends. This is the result of the penetration and metabolization of starch by the fungi in blends containing starch concentrations of 30% and the appropriate concentration of additives.

The incorporation of starch in the LDPE blend without the incorporation of any additive lead to blends with very low tensile strength values. Without additives (especially coupling agent) starch-LDPE blends have fairly high elongation-at-break values due to the resulting inhomogeneous blend. Incorporation of additives such as a coupling agent leads to a more homogeneous polymer and consequently decrease in the elongation-at-break values. Results of the present study showe that the increment in starch content in the range 5-40% lead to an initial increase and then decrease in the value of the tensile stress. In the range 20-40% of starch, the highest tensile strength and elongation-at-break values were obtained with blend containing 30% starch and additives of the same concentration. It is lead to the highest biodegradation rates. The concentration of starch and additives was also found to have some effect on the mechanical properties of the blend after 3 weeks incubation with *Penicillium funiculosum*.

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