

TABLE OF CONTENTS

INTRODUCTION	1
ENVIRONMENTAL IMPACT OF THE SYNTHETIC POLYMERS	1
STRATEGIES FOR PLASTIC WASTE MANAGEMENT	4
1- MECHANICAL RECYCLING	6
2- INCINERATION (WASTE TO ENERGY)	6
3- BIODEGRADATION (BIOLOGICAL RECYCLING)	7
BIODEGRADABLE POLYMERS	8
PERFECTION OF STARCH AS A FILLER	8
APPLICATIONS OF BIODEGRADABLE POLYMERS	9
1. MEDICAL APPLICATIONS	9
2. AGRICULTURAL APPLICATIONS	10
3. PACKAGING	10
REVIEW OF LITERATURE	13
1. NATURAL BIODEGRADABLE POLYMERS	13
1.1. POLYPEPTIDES OF NATURAL ORIGIN	13
1.2. BACTERIAL POLYESTERS	13
1.3. POLYSACCHARIDES	14
1.3.1. <i>Cellulose</i>	15
1.3.2. <i>Chitin and chitosan</i>	16
1.3.3. <i>Alginic acid</i>	16
1.3.4. <i>Starch</i>	16
2. POLYMERS WITH HYDROLYZABLE	20
BACKBONES	20
2.1. POLYESTERS	23
2.2. POLYCAPROLACTONE	23
2.3. POLYAMIDES	24
2.4. POLYURETHANES AND POLYUREAS	24
2.5. POLYANHYDRIDES	25
3. POLYMERS WITH CARBON BACKBONES	25
3.1. POLY(VINYL ALCOHOL) AND POLY(VINYL ACETATE)	25
3.2. POLYACRYLATES	26
4. FACTORS AFFECTING BIODEGRADATION OF	
SYNTHETIC POLYMERS	27
4.1. POLYMER STRUCTURE	27
4.2. POLYMER MORPHOLOGY	28

4.3. RADIATION AND CHEMICAL TREATMENTS	28
4.4. MOLECULAR WEIGHT.....	29
5. MODE OF BIODEGRADATION	31
5.1. MICROORGANISMS.....	32
5.1.1. <i>Bacteria</i>	32
5.1.2. <i>Fungi</i>	32
5.2. ENZYMES.....	33
6. BLENDS OF BIODEGRADABLE AND NON- BIODEGRADABLE POLYMERS	33
7.1. POLYETHYLENE AND STARCH BLENDS.....	37
7.2. MODIFIED POLYETHYLENE AND STARCH BLENDS	49
MATERIALS AND METHODS.....	53
2.1. MATERIALS.....	53
2.2. METHODS	53
2.2.1 FILM PREPARATION	53
2.2.1.1 PREPARATION OF STARCH MASTER BATCH	53
2.2.1.2 PREPARATION OF STARCH-LDPE FILMS.....	53
2.2.2 CHARACTERIZATION OF THE FILMS	54
2.2.2.1 <i>Tensile Strength and Elongation</i>	54
2.2.2.2 <i>Water Absorption Test</i>	54
2.2.2.3 <i>Prolonged Water Absorption</i>	55
2.3.1 CHEMICAL ANALYSIS OF SOLUBLE STARCH, WHEAT FLOUR AND COMMERCIAL STARCH.....	55
2.4. DEGRADATION TESTS.....	55
2.4.1 <i>Thermal Degradation Test</i>	55
2.4.2 <i>Starch Hydrolysis Using α-Amylase Enzyme</i>	56
2.4.3 <i>Soil Burial</i>	56
2.5. MASS CHANGES	56
2.6. MIGRATION TEST	57
2.6.1 <i>Overall migration experiments</i>	57
RESULTS AND DISCUSSION.....	58
CHEMICAL ANALYSIS OF SOLUBLE STARCH, WHEAT FLOUR AND COMMERCIAL STARCH CHARACTERIZATION OF ORIGINAL FILMS	58
3.1. APPEARANCE OF FILMS.....	59
3.2. MECHANICAL PROPERTIES OF ORIGINAL FILMS.....	59
3.2.1. <i>Tensile Strength</i>	59

3.2.2. <i>Percent Elongation</i>	64
3.3. MECHANICAL PROPERTIES OF FILMS AFTER THERMO- OXIDATIVE DEGRADATION.....	69
3.3.1. <i>Tensile Strength</i>	69
3.3.2. <i>Percent Elongation</i>	95
BIODEGRADATION	119
3.4. MECHANICAL PROPERTIES OF FILMS AFTER SOIL BURIAL .	119
3.4.1. <i>Tensile Strength</i>	119
3.4.2. <i>Percent Elongation</i>	129
3.5. MECHANICAL PROPERTIES OF FILMS AFTER THERMO- OXIDATIVE DEGRADATION AND BIODEGRADATION	136
3.5.1. <i>Tensile Strength</i>	136
3.5.2. <i>Percent Elongation</i>	163
3.6. MECHANICAL PROPERTIES OF FILMS AFTER IMMERSION IN WATER	190
3.6.1. <i>Tensile Strength</i>	190
3.6.2. <i>Percent Elongation</i>	194
3.7. MECHANICAL PROPERTIES OF FILMS AFTER HYDROLYSIS BY A -AMYLASE.....	199
3.7.1. <i>Tensile Strength</i>	199
3.7.2. <i>Percent Elongation</i>	204
3.8. WATER ABSORPTION TEST	211
3.8.1 <i>Water Absorption in Hot and Cold Water</i>	211
3.8.2 <i>Prolonged Water Absorption Test</i>	214
3.9. MASS CHANGES	220
3.9.1. WEIGHT CHANGE AFTER THERMO-OXIDATION.....	220
3.9.2. WEIGHT LOSS AFTER STARCH HYDROLYSIS BY A - AMYLASE	231
3.9.3. WEIGHT LOSS AFTER SOIL BURIAL.....	241
3.10. MIGRATION TESTING.....	248
3.10.1. OVERALL MIGRATION	248
3.11. MICRO-ORGANISMS DEGRADING THE LDPE/STARCH FILMS.....	255
4.1. DEGRADATION MECHANISMS	255
4.1.1. MECHANISM OF THERMO-OXIDATION	255
4.1.2. BIODEGRADATION OF STARCH.....	258
4.1.3. MECHANISM OF BIODEGRADABILITY	259

ABIOTIC AND BIOTIC AGING	263
SUMMARY.....	271
REFERENCE.....	277

BIODEGRADATION	277
1.1 MECHANICAL PROPERTIES OF FILMS AFTER SOIL BURIAL	277
1.1.1 Tensile Strength	277
1.1.2 Percent Elongation	279
1.2 MECHANICAL PROPERTIES OF FILMS AFTER THERMO- OXIDATIVE DEGRADATION AND BIODEGRADATION	280
1.2.1 Tensile Strength	280
1.2.2 Percent Elongation	283
1.3 MECHANICAL PROPERTIES OF FILMS AFTER DEGRADATION IN WATER	280
1.3.1 Tensile Strength	280
1.3.2 Percent Elongation	284
1.4 MECHANICAL PROPERTIES OF FILMS AFTER HYDROLYSIS BY A-AMYLASE	289
1.4.1 Tensile Strength	289
1.4.2 Percent Elongation	294
1.5 WATER ABSORPTION TEST	291
1.5.1 Water Absorption in Hot and Cold Water	291
1.5.2 Prolonged Water Absorption Test	294
1.6 Mass Changes	299
1.6.1 Weight Change After Thermo-Oxidation	299
1.6.2 Weight Loss After Starch Hydrolysis by A- AMYLASE	291
1.7 Weight Loss After Soil Burial	291
1.8 Migration Testing	298
1.8.1 Overall Migration	298
1.9 MICRO-ORGANISM DEGRADING THE LDP/STARCH FILMS	299
2.1 DEGRADATION MECHANISMS	299
2.1.1 MECHANISM OF THERMO-OXIDATION	299
2.1.2 BIODEGRADATION OF STARCH	299
2.1.3 MECHANISM OF BIODEGRADABILITY	299

SUMMARY

Blends of LDPE with soluble starch, wheat flour and commercial starch were prepared by mixing starch (or flour) with styrene then blending the mixture with LDPE. The starch percents vary between 5 and 50% of the total weight. Their physical and mechanical properties were recorded and compared with pure LDPE.

The biodegradable plastic films had natural color but the films produced with wheat flour had a slightly yellowish color. All films had a normal texture with no visible bubbles or granules and no odor.

The tensile strength of pure LDPE (control) was found to be 8.36. For the samples of blend I, with soluble starch and styrene, the tensile strength ranged between 7.60-4.30 for starch percents between 5-50. While for blend II, with soluble starch, styrene, and polystyrene, with polystyrene, the tensile strength was higher. The values ranged between 7.85 for 5% starch and 4.5 for 50% starch. As for blend III, with wheat flour and styrene, the values ranged between 7.73 and 4.45 and for blend IV, with commercial starch and styrene, the values ranged between 7.65 and 4.37. It was observed that the increase in starch or wheat flour contents of the mixture was reversibly proportional to the tensile strength and the tensile strength for blends with polyethylene and soluble starch only (blend I) was the lowest of the four blends, and the blends with polyethylene, polystyrene and starch (blend II) was highest, while those with wheat flour (blend III) and commercial starch (blend IV) were in the middle.

There was a drastic reduction in the percent elongation with the increase in the starch content. The

value for pure PE (control) was 630.8 and for the samples of blend I, with soluble starch, the elongation ranged between 540-140 for starch percents between 5-50. While for blend II, with polystyrene, the decrease in elongation was less, the values ranged between 580 for 5% starch and 145 for 50% starch; as for blend III, with wheat flour, the values ranged between 530 and 133.1 and for blend IV, with commercial starch, the values ranged between 560.3 and 135.7.

Samples were tested for water absorption and all of the samples were insoluble in cold and boiling water. The samples turned somewhat softer after being immersed in water, but did not lose their mechanical integrity. Moisture uptake increased with immersion time and increasing starch content. A rapid moisture uptake was observed for all samples within the first few days of immersion, but this decreased slowly with time.

The thermo-oxidative test simulates the effect of heat in the environment. The changes in the tensile strength of LDPE/starch (or wheat flour) after the course of thermal oxidation was measured. These results show negligible changes in the tensile strength of the control sample as compared to that of the samples containing the additives. It was observed that an initial increase of strength was recorded, at day 2, followed by a fast decrease of the film integrity starting at day 5 of incubation. It was also observed that at higher temperatures, the tensile strength is lower.

After the investigation of thermo-oxidation it was observed that the oxidation processes take advantage of the high temperatures (40–50°C) and the time. The results of the investigation show that the materials degrade quickly with the increase of temperature.

It was also observed that after 10 weeks of soil burial, the mechanical properties of the films decrease, mainly, due to starch removal from the films. Also, for the weight loss a drastic decrease was observed after 10 weeks of soil burial thereafter it proceeded slowly.

The LDPE/ starch strips showed weight loss after treating with α -amylase in boiling water (approximately 95°C). This weight loss is due to hydrolysis and leaching of the starch. A similar experiment, in which the sample strips were boiled without the enzyme α -amylase, was carried out to apply the leaching correction. The rate of starch hydrolysis increases with the increase in starch content of the sample. This is because higher starch content offers more sites for the hydrolysis reactions. Samples treated with α -amylase for different periods, and from the results obtained, it can be seen that tensile strength and elongation at break decreased with time of immersion and starch content.

The influence of addition of starch on the overall migration of these films, with different food simulants, was studied, at different temperatures (-4°, 25° and 40°C). All values were significantly lower than the upper limit for overall migration set by the EU (10 mg/dm²) for food grade plastics packaging materials.

CONCLUSIONS

In most cases, plastic materials should manage a predetermined service life before physical degradation commences. There should be no significant changes in the physical and mechanical properties of the material during its service life. However, after the material has served its primary purpose, rapid biodegradation and disintegration should occur. Thus, all biodegradable polymers are in a delicate balance between the achievement of useful technological performance and a rapid and effective biodegradability.

In general, the higher the starch content the worse the performance of the composite materials (lower tensile strength and percent elongation) but the higher their biodegradability. The degradability of LDPE/starch blends was confirmed by weight loss measurements and changes in mechanical properties.

Starch-LDPE composites absorb moisture in proportion to the amount of starch added. The ability of the composites to absorb moisture not only reduces their mechanical properties but also make them susceptible to fungal attack.

Degradation studies show that the composites exhibit varying degrees of degradation. In α -amylase solution, although hydrolysis of the starch granules was restricted to only those on the surface, a significant drop in the mechanical properties occurred. Soil burial also resulted in weight loss, a reduction in mechanical properties

It is apparent that very little abiotic peroxidation is necessary to initiate biological attack by the microorganisms used.

These results are of considerable significance for commercial composting processes, in which degradable plastics are required to disintegrate to small fragments within the composting cycle time and to be subsequently absorbed into the soil environment as nutrients for growing plants.

It is shown that temperature is the most important factor influencing the rate of thermo-oxidative degradation of the materials.

Modified (styrene-grafted) starch can be used as a low cost biodegradable filler for thermoplastics such as LDPE. The starch hydrolysis study shows that the starch granules present on the surface of the polymer can be consumed by various fungi and bacteria which are commonly found in the compost environment. The thermal oxidation of the starch filled LDPE in an oven at 50°C was confirmed by the decrease in the mechanical properties. A pro-oxidant system plays a significant role in the rate controlling step of the degradation mechanism, enhancing the rate of thermal oxidation of the LDPE.

A number of environmental factors such as sunlight, oxygen, humidity, heat, microorganisms, etc., have a synergistic effect on the degradation rate. Starch filled LDPE is an environmentally compatible plastic which can be used for manufacturing agricultural mulches, transplantation bags and disposable packaging material.