International Journal of Technical Research and Applications e-ISSN: 2320-8163,
www.ijtra.com Volume 3, Issue 1 (Jan-Feb 2015), PP. 91-96

SOIL BURIAL DEGRADATION OF POLYPROPYLENE/ STARCH BLEND

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Abstract: This research deals with study of Degradation behavior of starch blended with different percentage of polypropylene (PP) .Twin screw extruder at 160- 190 °C and 50 rpm is used for manufacture of blend sheet. Degradation test achieved according to ASTM standard (D 638 IV and D570-98). Studies on their degradation properties were carried out by Soil burial test, Water absorption test and Hydrolysis test. The morphology test of the polypropylene / starch blend samples was obviously seen in the (Dino- Light- Digital Microscope), Results of soil burial test show that tensile strength and percentage of elongation of polypropylene / starch blend decrease with increasing the starch content and burial time. The hydrolysis test show the weight losses increasing with the increasing amount of starch. High percent of polypropylene found to decrease the amount of water absorption of the blend. The physical appearance and morphology studies of polypropylene / starch blend after burial test in soil and hydrolysis in water environment showed that all blend samples was obviously changed after 90-day study period, whereas the pure polypropylene samples remained unchanged.

Key Words- Polypropylene, Starch, Degradation properties, Dino-Light-Digital-Microscopy.

I. INTRODUCTION

Synthetic plastics such as polyvinyl chloride, polycarbonate, polystyrene, polypropylene, and polyethylene are used widely in daily life, food industry, biomedical fields, and agriculture. Use of these synthetic plastics has brought a heavy environmental pollution because they take hundreds of years to degrade. Thus, disposal of waste plastics has become a serious problem. In the past two decades, biodegradable materials have been drawing attention as an alternative to the petroleum-derived plastics [1-3].

PE and PP are some of the most dominant packaging materials and responsible by part of the problems in the disposal of one-trip packaging. They are high hydrophobic level, water repellence and high molecular weight and their lack of functional groups recognizable by microbial enzymatic systems. Being hydrophobic hydrocarbon polymers, poly olefins are resistant to hydrolysis and for this reason they cannot hydro biodegrade. Poly olefins, as commercial products, are also resistant to oxidation and biodegradation due to the presence of anti-oxidants and stabilizers [4].

Therefore, there has been an increasing interest in the development of biodegradable polymers by the synthesis of biodegradable polymers and by the incorporation of natural products as cellulose acetate and starch into polymers to enhance the potential biodegradability of poly olefins. The major degradation effect promoted by the microbial assimilation of the natural polymers in the blends is to increase of the surface area of the synthetic bulk material rendering it more susceptible to abiotic oxidation [4].

Natural biopolymers including starch, cellulose, and chitosan were tested, alone or combined with synthetic polymers, to explore the possibility of forming a fully or partially biodegradable film [1,5].

Among the natural polymers, starch is of interest. It is regenerated from carbon dioxide and water by photosynthesis in plants[6-8]. Owing to its complete biodegradability, low cost and renewability, starch is considered as a promising candidate for developing sustainable materials. In view of this, starch has been receiving growing attention since 1970s Many efforts have been exerted to develop starch-based polymers for conserving the petrochemical resources, reducing environmental impact and searching more applications [9].

Biodegradable starch-based plastics have recently been investigated for their great potential marketability in agricultural foils, garbage or composting bags, food packaging, fast food industry as well as biomedical fields [1].

Recently, starch was used as a main component in polymer blend, and it was not used in the native case, but it was used in plastic case, where the starch granules were plasticized by using plasticizers under heating, giving rise to a continuous phase in the form of a viscous melt which can be processed by using traditional plastic processing techniques, such as injection molding and extrusion. This kind of starch composite is called thermoplastic starch Several plasticizers have been used with starch to convert it into thermoplastic starch (TPS) to be used in polymer blends such as glycerol, ethylene bisformamide, and Urea, but the most used is glycerol [10-12].

Plasticized starch or thermoplastic starch (TPS) is prepared under specific extrusion conditions in the presence of plasticizers, such as glycerol and water. However, four challenges hinder TPS from becoming a commonly used plastic, including the following [11]:

1. Hydrophilic nature of TPS and its poor water resistance.
2. Deterioration of mechanical properties upon exposure to environmental conditions like humidity.
3. Brittleness in the absence of suitable plasticizers.
4. Soft and weak nature in the presence of some plasticizers.

Therefore, many attempts have been made to overcome these problems by blending starch with synthetic polymers such as PP[12].

Polypropylene (PP), a thermoplastic polymer, consists mainly of two elements, carbon and hydrogen. Hence, polypropylene is very similar in structure to its polyolefin counterpart polyethylene, with the exception of every other carbon atom in the backbone chain bonded to a methyl group [13].

Polypropylene has excellent chemical resistance and high purity. It has better mechanical properties than other polyolefin materials. In fact, polypropylene is the lightest of all commercial plastics with a good balance of properties. When employed in applications, polypropylene operates safely at temperatures up to 85˚C. Particularly in the automotive industry, polypropylene contributes to the fuel efficiency, reduced material cost, and passenger comfort [14].

The aim of this study is to: produce a "Blend polymer material" which is biodegradable under influence of environmental or biological factors using "starch" as a natural material and polypropylene as a synthetics material with different mixing ratios, Soil burial test, hydrolysis test and water absorption test are measured of the samples that prepared by twin extruder at 160-190°C with speed of screw 50 rpm.

II. EXPERIMENTAL PROCEDURES

A. Materials

Polypropylene pellets has a trade name of "575 S" with Melt Index 6.9 (g/10 min), Density 0.9 (g/cm^3), and Softening Point 230 (ºC) was supplied from Sabic Company, Saudi Arabia. Corn starch which is a white powder, provided by the food industry Riyadh, Saudi Arabia. Glycerol (glycerin, C3H8O3) was supplied from Fisher Chemicals, and has (molecular weight = 92gmol-1) was used as a Plasticizer. Distilled water was obtained from Iraqi markets, It was added as a plasticizers materials for starch.

B. Preparation of Plasticized Starch

Plasticized Starch (PS) was prepared from starch using a mechanical stirrer model (RZR2021), Mixing conditions of starch, water, and glycerol was at 70˚C and 50 rpm, Mixing time was reduced to the minimum where the blend could be homogeneous, The PS obtained was oven dried at 90˚C for 24 h to reduce its moisture content (MC) [15].

C. Preparation of polymer blend

Plasticized Starch (PS) blended with different polypropylene ratio (20%,30%,40%,50%,60%,70%,80%, 90% and 100%) (prepared in twin – screw extruder with 50 rpm at 160-190 °C. electrical saw with very soft teeth used to cutting test sample According to standard ASTM D 638 IV sample tensile and ASTM D570-98 sample water absorption.

D. Tests

1. Soil Burial Test

To examine the biodegradability of the PP/ starch blend, soil burial test was carried out on a laboratory scale. Dumbbell shaped specimens of definite sizes were cut from each of the blend. Moist soil was placed into plastic containers with tiny holes was perforated at the bottom and on the body of the container to increase air, and water circulation. The test was carried outside the room and lasted for 90 days. The specimens were buried in the soil at a depth of 10 cm from the surface and thus subjected to the action of microorganisms in which soil is their major habitant. After the test, the blend samples were removed, washed with distilled water and dried in an oven at 70˚C for 24 h and then kept in a desiccator. Figure (1) show the soil burial test samples before and after the test [16].

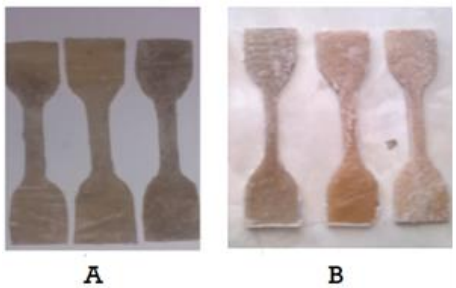

Fig.1: The soil burial test samples a) before and b) after the test.

Fig.2: Tensile test device.

2. Hydrolysis Test

The purpose of this test is to study the response of samples to water and influenced its and the impact of hydrolysis on the samples.

Weight loss of the samples were assessed by weighing the sample before and after biodegradation testing at every regular time interval (15 day). The weight loss of the Samples with time was used to indicate the amount of biodegradation in water environment. The percentage weight loss of samples in the water environments were obtained by deducting the observed weight at each interval from the original weight to its original weight. Dried samples before and after test at 80 degree to ensure the accuracy of results. weight loss, surface examination and mechanical properties such as hardness and flexural properties determined as a function of water immersing time .

3. Water absorption Test

Water absorption test is the most important properties of biodegradable based plastic. The purpose of this test was to study the effect of immersion in water on the polypropylene/starch blend samples. The water absorption test was carried out according to ASTM D570-98 specification[17], in the following manner:

The blend samples were dried at 80 0C for 30 min and cooled to room temperature before subjecting to a water absorption test. The dried samples were immersed in distilled water at for specific time (one hour) interval. The samples were removed from the water, blotted with tissue paper to remove excess surface water, and then weighed. The water absorption (WA) was determined gravimetrically from the weight difference of the sample at a given immersion time and the initial weight (before immersion in water) enter the initial weight [18].

4. The Morphology Test

The Morphology of the polypropylene/starch blend films before and after biodegradation was investigated with a (Dino-Light-Digital-Microscopy) made in (Kyoto Japan), operating at (200 X magnification). Each sample was washed with distilled water and dried in convection oven model (DZ-2BC),made in China, which is available in laboratory of Materials Engineering college /University of Babylon, at 50 0C until a constant weight before testing .

Fig.3: The Digital Microscope device.

III. RESULTS AND DISCUSSION

A. Soil burial test Result

Figures (4) and (5) showed the effect of soil burial tests on the tensile properties of polypropylene/starch blend that were exposed to soil environment for the periods of 30, 60 and 90 day. Tensile strength and elongation percent decrease with increase the starch content and burial time.

Decrease in mechanical properties with increasing the proportion of starch due to the dispersion the starch molecules between the polypropylene chains leading to increase chains spacing thus, the secondary bonding strength between them will decrease and which reflect negatively on those properties. As well as the presence of starch, especially in the surface of samples serve as stress concentration which helps emergence of notch and thus, the crack propagation with load increasing.

Absorption of moisture from the soil during the burial and the emergence of micro-organisms leads to reducing in mechanical properties such as tensile strength (see figure. 4) and elongation percent shown in figure (5).

The moisture absorption of the samples is mainly due to the starch. the blend with higher moisture absorption is usually more prone to microorganism attack. this is likely to allow microorganisms, such as bacteria and fungi, access to the inferior of the polymer using water as a medium; this suggests that the microorganisms consume starch and create pits and voids on the surface of polymer and weaken the structure of the polymer to work it's as centers for the beginning of the incision and thus spread, therefore decrease the tensile properties of the blend [16,18], all the blend films showed a reduction in tensile properties with increase in starch content as burial progressed [16] .

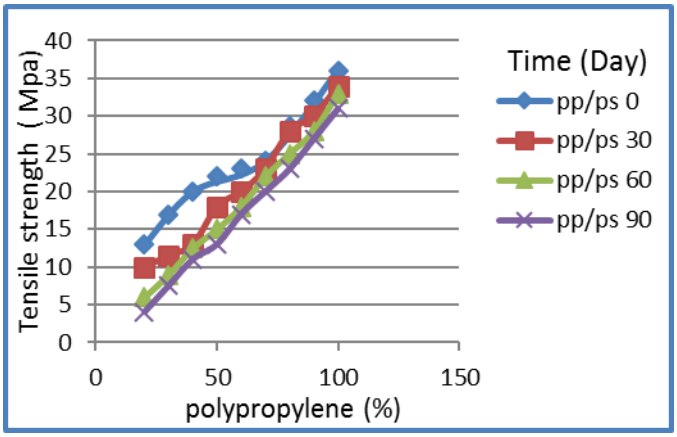

Fig. (4): Tensile strength of Polypropylene/starch blend after soil burial test

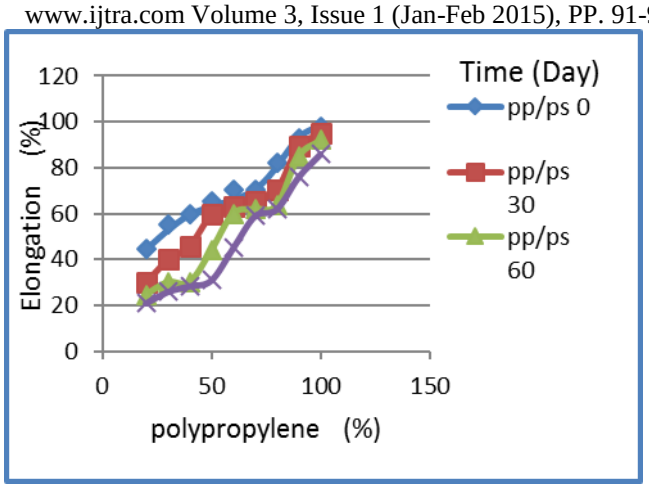

Fig.5: Elongation of Polypropylene/starch blend after soil burial test

B. The Hydrolysis Test

Figure (6) shows weight loss (%) of Polypropylene / starch blend against degradation time in water environment.

Results showed that Pure polypropylene Sample revealed no weight loss and no surface deterioration in water environments within the 90-day study period, On the other hand the weight losses increase with the amount of starch increase. these results reveal that higher starch content enhances the degradation kinetics and thus increases mass loss. this could be due to the hydrophilic nature of starch. the starch being hydrophilic in nature retains moisture that contributes to the degradation of the polymer. The higher the starch content in the blend, the higher the moisture content that renders faster degradation. these results corroborates the works of [19],wherein the amount of biodegradation recorded for these works were between 40 and 100 % .

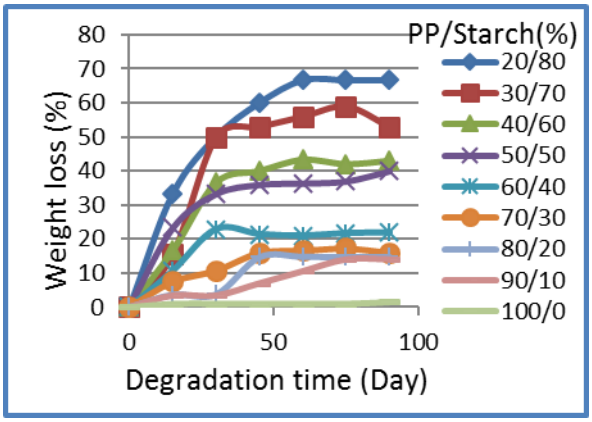

Fig.6: Weight loss (%) of polypropylene/starch blend against degradation time (Day) in water environment.

Figure (7) and (8) shows the variation of bending strength and hardness with polypropylene percentage of polypropylene/starch blend after degradation in water-environment. The results from the bending strength and hardness tests after exposure to water environment indicated that the blend exhibited a decline in the investigated properties with the increase in degradation time and increase in starch content for all the blend films. So, polypropylene - mixed starch degrade by loss of structural integrity and this renders it advantageous in terms of environmental protection. this is in good agreement with the result of soil burial test described earlier.

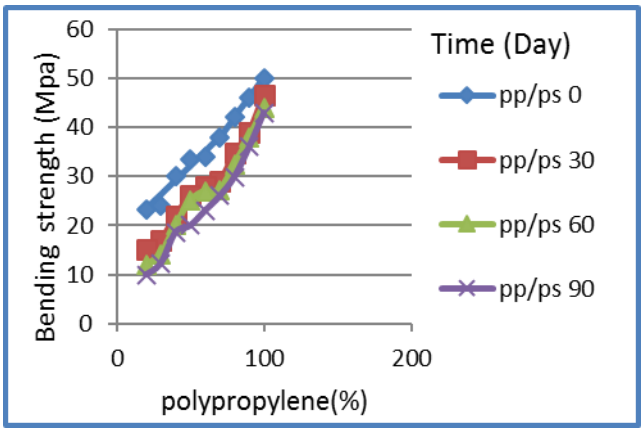

Fig. (7): Bending strength of Polypropylene/starch blend after hydrolysis

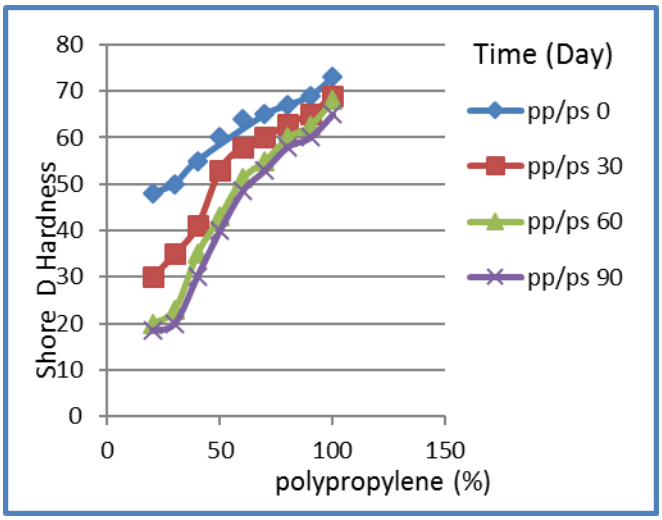

Fig. (8): Hardness of Polypropylene/starch blend after hydrolysis

C. The water absorption (WA):

Figure (9) show the water absorption of polypropylene/starch blend against time (one hour) in water environment.

Results showed that the water absorption (WA) decrease with the increase in the polypropylene percent in the blend. This is completely logical since Polypropylene is hydrophobic and Starch is hydrophilic.

When the amount of starch is increased in the blend, its polar character increases and hence the water retention increases[20] .

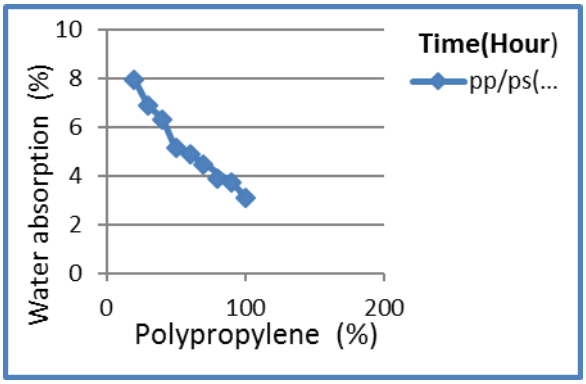

Fig.9:The water absorption (WA) (%) of polypropylene/starch blend against time (One hour) in water environment.

D. The Physical Appearance:

Figures (10)and (11) shows the Physical appearances of starch samples containing various percentages of polypropylene levels of degradation in soil and water environment during periods of 30, 60 and 90 day. the polypropylene samples before burial test in soil and hydrolysis in water environment were smooth. It can be seen that the polypropylene samples after biodegradation test remained unchanged, without any alteration in the original shape. this result indicated the stability of polypropylene samples, which cannot be degraded easily in soil burial condition and water environment.

As a result, the decrease in tensile properties of polypropylene samples might be occurred from some structural deformation and initial degradation of molecular chains due to moisture and microorganisms in soil.

The photographs of polypropylene /starch blend at different ratio of polypropylene are displayed in figures (10) and (11). All the blend films deformed and distorted as degradation processed, whereas the polypropylene samples remained unchanged in their shape. Nevertheless, there were differences in the degree of degradation between the blend ratio. that is, the loss of surface and shape occurred slower in the blend with low starch content than those with high starch content.

As a result, the physical appearance of all blend films was obviously changed after 90 day of burial test in soil and hydrolysis in water environment. For example, some of black and yellow stains were noticed on the film surface, associating with a microbial growth or morphological alterations. Normally, natural materials such as starch and cellulose initially promote microbial growth, appearing as discolorations or stains on the materials due to high organic components. many microorganisms will alter the pH of materials causing color changes and promoting damage on material properties by hydrolytic reaction [21]. Besides, these small stains still evolved to form the holes and sometimes led to the partial or total disappearance of the sample. The blend films after 90day of burial test in soil and hydrolysis in water environment showed the distorted shape and film deformation compared to the original blend films, affecting to their mechanical properties.

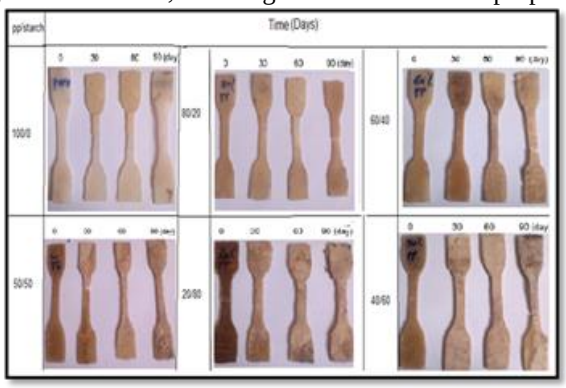

Fig. (10): Physical appearances of starch samples containing various percentages of polypropylene levels of degradation in soil.

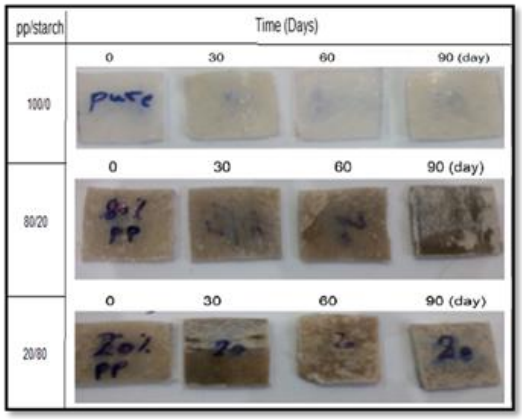

Fig. (11): Physical appearances of starch samples containing various percentages of polypropylene levels of degradation in water environment.

E. The Morphology test:

Figures (12) and (13) Shows the surface morphology for pure polypropylene and polypropylene/starch blend before and after degradation for 3 month (200X).

The influence of degradation time on the biodegradability of the polypropylene/starch blend films was obviously seen in the digital microscope.

Before burial test in soil and hydrolysis in water environment, the smooth surface of pure polypropylene and the blend films was observed. In contrast, the films after burial in soil and hydrolysis in water environment were rough and had a lot of small holes on the surface, whereas the polypropylene samples remained unchanged. The existence of holes can be noticed on the surface of both films in soil and in water environment. However, the blend with 20 % starch seemingly showed less amount of the holes compared to the blend with 80 % starch.

The polymer sample's gross morphology was observed to be changed physically; for example, the surface holes over the degradation period the increased starch content resulted in higher surface holes of the samples due to increased degradation. the change in physical appearance (surface holes) of the sample in the soil and water environment could be considered as an evidence of biodegradation of this polymer in the landfills or natural environment. the results indicate that the incorporation of hydrophobic polypropylene with hydrophilic starch enhances the hydrophilicity and degradability of the overall polymer. Therefore, the degradation characteristic of the starch-mixed polypropylene polymer could be modulated by manipulating the starch content in the polymer. Indeed, the polymer should be developed with essentially a controlled degradation characteristic while maintaining the required strength of the polymeric object during its designed life time for a particular application [19].

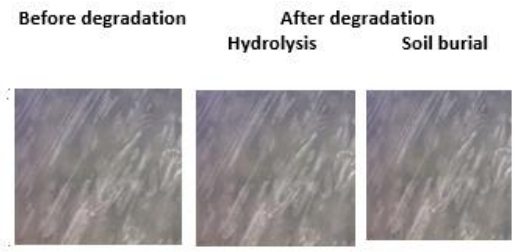

Fig.12: The surface morphology for pure Polypropylene before and after degradation for 3 month (200X).

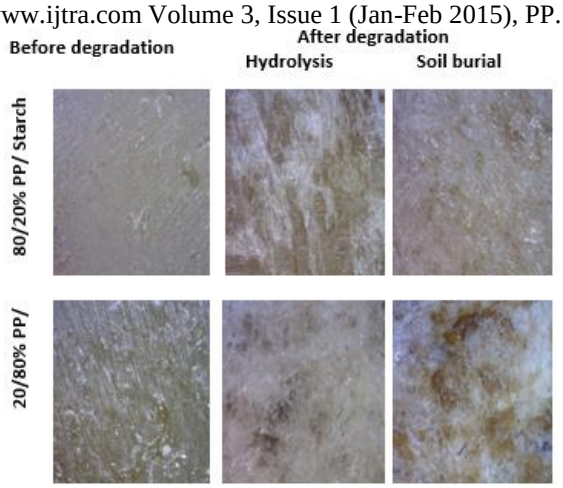

Fig.13: The surface morphology for polypropylene /Starch blend before and after degradation for 3 month (200X).

IV. CONCLUSIONS

1. Results of soil burial test showed that tensile strength and percentage of elongation of Polypropylene/starch blend decrease with increase the starch content and burial time.
2. The hydrolysis of Polypropylene/ starch blend showed that, polypropylene sample showed no weight loss and no surface deterioration in water environments within the 90-day study period. On the other hand the weight losses increase with the amount of starch increase.
3. The water absorption (WA) decrease with the increase in the polypropylene percent in the blend of Polypropylene/starch. This is completely logical since Polypropylene is hydrophobic and Starch is hydrophilic.
4. The physical appearance studies of Polypropylene /starch blend after burial test in soil and hydrolysis in water environment showed that all blend films was obviously changed after 90-day study period, whereas the pure polypropylene samples remained unchanged.
5. The morphology test result showed that voids and pitting are formed after burial in soil and hydrolysis and increased with increasing the time which indicates clearly the prevalence of degradation process.

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