

# Study of Biodegradation on Packaging Films Derived from Potato Starch and Maleic Anhydride Grafted LDPE and LDPE Polymer

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**Abstract:** Maleated low density polyethylene (with 0.5% grafted maleic anhydride) & low density polyethylene have been mixed (1:1) to prepare base material, which has been further mixed with Potato Starch (0-15%) in single step through commercial grade twin screw extruder. Using prepared material packaging films were blown and thus prepared samples were tested for its strength following standard biodegradation testing methods for tensile strength, percentage elongation and for melt flow index. Prepared system should have comparable mechanical strength (tensile and %age elongation which gets severely affected by mixing natural polymer) to that of synthetic polymers like LDPE and should be degradable. Hence, tensile strength, percentage elongation study was conducted and since MFI is indirect indicator biodegradability, MFI study was also conducted to find level of biodegradation among samples. Observations are, after degradation i) 40% tensile strength reduction was found in 15% starch mixed samples during composting study and at the same time 68% percentage reduction in elongation at break was found. MFI study carried out on samples also indicated that MFI has increased in samples of higher starch contents and indirectly indicating the higher possibility of degradation. 20% Weight loss observed indicating the degradability enhanced and probably synthetic polymer backbone got involved in the process for which starch is responsible. It could have been due to chemical reactivity between hydroxyl group of starch and maleic anhydride group of LDPE backbone at molecular level.

**Keywords:** LDPE: Low Density Polyethylene; LDPE-g-mA: Low Density Polyethylene-grafted-maleic Anhydride; Biodegradable Polymer.

## 1. Introduction

Large scale commercial use of synthetic polymers and their eco-friendly disposal is a critical phenomenon, which is more than a half century old. The need of biodegradable plastics has significantly increased, not only due to increasing environmental concerns but also due to depletion of petroleum resources likely to be exhausted within 70 years from now, as per recent survey.

Biodegradation is one of the simplest processes, which take place in normal environmental conditions and can be of immense use for degradation of polymeric materials. It is one of the 12 Principles of Green Chemistry which can be implemented through use of natural phenomenon of biodegradation, accordingly study presented here has been planned. The present work aims at preparing a cost effective biodegradable polymer, meeting desired properties requirements, and naturally bio-degradable.

Considering practical approach, natural and synthetic polymers were mixed to create systems. Since, polar and non polar components cannot be mixed directly, starch was chemically treated with glycerol (up to 30%)[1], and low density polyethylene was grafted with 0.5% maleic anhydride. Grafted LDPE and LDPE mixed in a ratio of 1:1 and then mixed with starch (0-30%) (system-I) for preparing the system and its physiochemical characteristics were analysed [2]. Conceptually maleic anhydride present in LDPE shall provide reactive sites for the reaction in between hydroxyl group of starch with anhydride group of LDPE to form ester bond in between polar and non polar components. Thus created system showed improved chemical reactivity

in between synthetic and natural polymer immiscible compounds.

Prepared systems (in different combinations) then have been characterized though, Morphological study, Mass Flow Index, Mechanical testing[2] & weight loss study. Confirmation of chemical reactivity in between maleic anhydride containing low density polyethylene and starch had been done by FTIR:ATR analysis. DSC & XRD analysis indicated that crystallinity decrease linearly with the linear increase in starch contents. XRD confirmed the increase in crystal size of the system which may be attributed to the development of secondary bonds (H-bonds / Vander wall's forces) between the carbonyl group of LDPE & hydroxyl group of starch. Thermal stability of the prepared system did not had any impact of the starch up to 30%. The maleic anhydride group present in the LDPE played a key role in reducing the interfacial energy and thereby promoting the interfacial adhesion between the starch and LDPE-g-mA and the uniformity in the system has been observed through SEM analysis. Study of mechanical properties of prepared system show that the tensile strength and percentage elongation have been decreased with the increase in starch contents. At 5% starch mixing these properties have been decreased marginally while up to 15% the decrease was significant after that these have decreased drastically.

Considering the practical utility as packaging applications and observations as above, in search of finding optimization level of starch in the composition, system has been prepared[3,4]. Accordingly, the starch concentration varied with an interval of 2.5% up to 15% (called as System-II) to

enhance the accuracy of the system where the acceptable level has been obtained.

The system thus prepared from practical application point of view, has been exposed to compost environment under controlled aerobic conditions for biodegradation testing for a

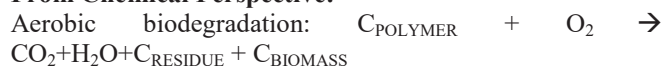
period of one year and then testing of decomposed samples for weight loss, strength & Melt Flow Index has been conducted. The results of this study are presented here. The Sample compositions being referred as System –II are tabulated in Table1.

**Table 1: Sample Compositions**

S. No. (Films)	LDPE composition	Starch composition	S. No.	LDPE composition	Starch composition
Sample 1	LDPE-g-mA + LDPE	0%	Sample 5	LDPE-g-mA + LDPE	10.0%
Sample 2	LDPE-g-mA + LDPE	2.5%	Sample 6	LDPE-g-mA + LDPE	12.5%
Sample 3	LDPE-g-mA + LDPE	5.0%	Sample 7	LDPE-g-mA + LDPE	15.0%
Sample 4	LDPE-g-mA + LDPE	7.5%			

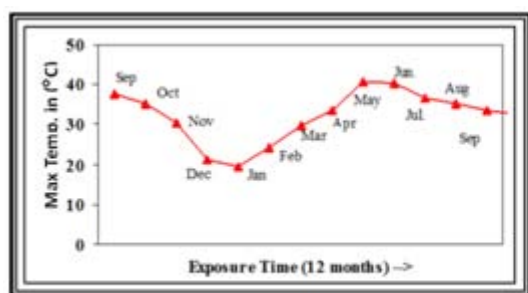
## 2. Biodegradation of Polymeric Material

### From Chemical Perspective:

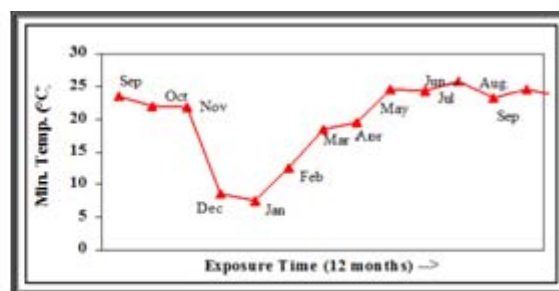


## 3. Biodegradation Methodology

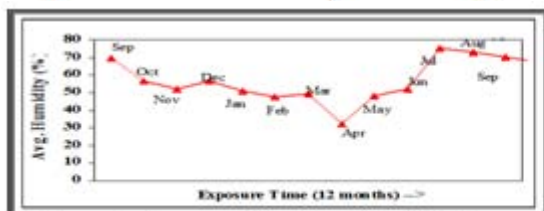
Composting site have been selected at Nursery in Delhi College of Engineering located at latitude 28°45'N and longitude 77°07'E. During sampling, ambient conditions and compost conditions have been monitored. The variation of Average, Minimum, and Maximum Temperatures recorded at the same location in ambient and in compost have been shown in figures 1 to 5.



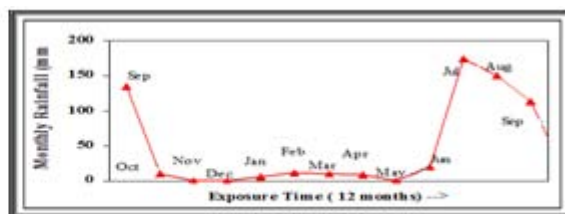
**Figure 1: Max ambient temperature changes**



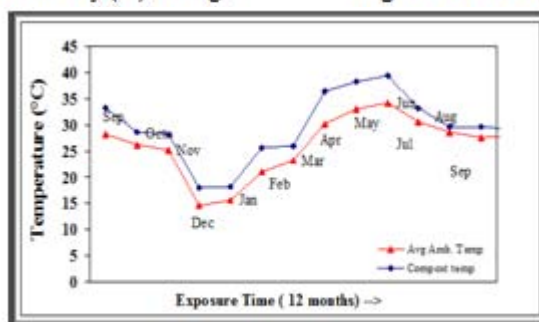
**Figure 2: Min ambient temperature change**



**Figure 3 : Avg. ambient humidity (%) change**



**Figure 4: Monthly Rainfall (mm) changes**



**Figure 5: Average Temp variation in ambient and compost**

Compost has been prepared as prescribed in the study by Eldsater & Karlsson(1999) [5,6]. The biodegradability test was performed in a laboratory scale composter of 4' x 3' x 6' size. Compost had been prepared more than six months before the sampling. The moisture content was maintained by periodic addition of water in the compost. The composting bin was covered by small fragments of green

grass. For maintaining aerobic conditions in the composting, network of perforated pipes laid down in the bin and have been pumped with normal air compressor.

### 3.1 Sampling Procedure

- Sample Size: Films of size 5x5 cm in 3 replicates have been used.
- Samples placement: The all samples with three replicates placed in approx. 30cm distance vertically and horizontally in between samples and such kind of 5 layers were made.
- Samples removal: After composting, samples were removed for testing at defined intervals of 1, 3, 6, 9, 12 Months.
- The samples were washed in the distilled water, dried, wrapped in a clean paper and stored at 25°C.

### 3.2 Constitution of Compost

The biodegradability tests were performed in a laboratory scale composter and the size of films was 5X5 cm. (5 replicates). The constitution [7,8,9] of solid waste mixture (compost) used for biodegradability testing was as follow: (dry 51 weight): 40.8 % shredded leaves, 11.4 % cow manure/ dung, 15.8% newspaper and computer paper, 2% white bread, 7.8 % saw dust, 19.2 % food waste (dry milk, potato, carrot, banana and other vegetables) and 3.0 % urea. Total dry weight was ~5 kg. The moisture content was maintained by periodic addition of water and temperature profile of the compost during testing is shown The composting bin was covered by small fragments of green grass and moisture content was maintained by periodically spraying of water. To avoid anaerobic conditions, the bin was constantly aerated with oxygen through a hollow tube. Composting temperature varied with the temperature of the surrounding atmosphere.

### 3.3 Evaluation of polymer degradation

The biodegradation levels in the samples were evaluated by measuring the weight loss, tensile properties & Melt Flow Index of the blown film samples at different intervals, so that comparison of properties could be done through the results obtained.

### 3.4 Biodegradation Assessment:

- a) **Weight Loss:** Weight loss of the films was determined by weighing the samples before and after biodegradation in compost. The percentage weight loss the film samples calculated by following equation (1).

$$\text{Weight Loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \dots \text{Equation (1)}$$

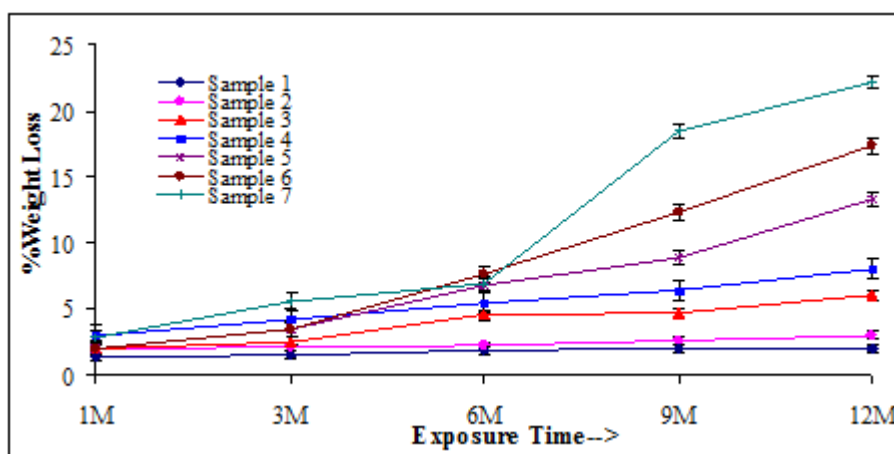
Where  $W_i$  is the initial weight of the sample before degradation (g). And  $W_f$  is the final weight of the sample after degradation (g)

- b) **Tensile Properties (ASTM D-882):** Tensile test of rectangular film specimen (10x180) mm have been conducted using Universal Testing Machine at a crosshead speed of 50 mm/ min and a gauge length of 10 cm according to ASTM D882. At least (05) five specimens of each sample were tested.
- c) **Melt Flow Index (MFI) (ASTM D-1238)** The MFI of biodegradable samples calculated using instrument M/s Rosand UK make. The working capacity of the instrument is in the range of 0-325°C with an accuracy of  $\pm 0.1^\circ\text{C}$ . ASTM D 1238 method has been adopted for the testing.

## 4. Results and Discussion

### 4.1 Weight Loss study

The variation of %Weight loss in samples having starch composition up to 15% during composting is shown in figure 6.



**Figure 6:** Variation of %Weight loss in Samples of 15% Starch during composting

It may be seen that the percentage weight loss of the biodegradable films increased with increasing potato starch incorporation in agreement to the result obtained by Pranamuda [8]. The percentage weight loss of the samples takes place by the hydrolysis mechanism. Hydrolysis occurs at the ester linkages, which allows the molecular weight of

the samples to be decreased by fungi and bacteria in the compost.

Weight loss increases with the increase of exposure duration. Weight loss within the period of investigation has ranged from 1.3 to 3% in the first month of degradation

which have gone up from 1.96 to 22.1% in 12 months. However, other studies have indicated weight loss of maximum 2% in 12 months for starch- polyethylene composites having 25.0% starch in LLDPE [9]. Observation of weight loss during the study period shows that weight loss was highest during 6-9 months duration (summer season). The weight loss was 11.56% for the sample No.7 having 15% starch. The increased rate of degradation may be attributed to the environmental conditions during this period. Since, Delhi is very close to semi arid zone the maximum ambient temperature shooted up to 38.8°C during winter months and relative humidity have gone up to 75.3 % (%RH) during monsoon season. At this point of time the temperature and humidity inside the compost remains even higher. Ishak et al. [10] have suggested that attack of micro-organisms is high during warm and humid climatic conditions causing degradation of properties and product failure.

Microorganisms attack on samples and liberate enzymes that breakdown potential food into assimilable chemical fragments. Here, in the samples degradation humid and warm environment might have facilitated the enzymatic attack, where micro-organisms have attacked the polymer films samples and liberated more and more enzymes. Because of which highest weight loss in the study duration have been recorded. The micro-organisms attack here on the samples of biodegradable polymer composition (LDPE grafted with maleic anhydride / LDPE (1:1) in various compositions of potato starch contents) have not only break down the potato starch but also attacked on the LDPE backbone which is rich in oxygen containing ester group. Hence, total 22.1% degradation of the samples having maximum starch contents of 15% show that the degradation in the LDPE backbone has also taken place. This is inline to the expectations considered for selection of materials and grafting with maleic anhydride for preparing biodegradable polymer.

## 4.2 Mechanical Properties Study

The degradation of mechanical properties of samples of 15% starch contents during composting has been studied with respect to tensile strength and percentage elongation.

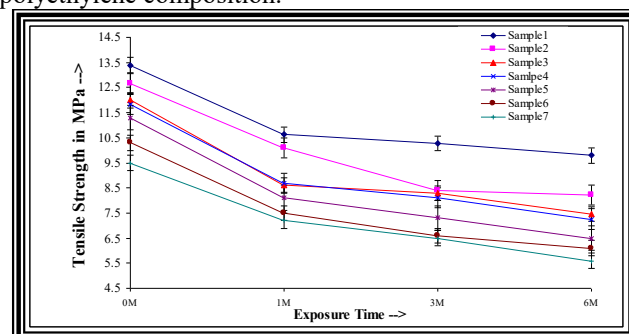
### a) Tensile Strength and Percentage Elongation

Figure 7 and 8 show the loss in tensile strength and percentage elongation of blown film samples (LDPE grafted with maleic anhydride / LDPE (1:1) in various compositions of potato starch 15% contents) plotted against exposure time during composting. As the micro-organisms consumed starch, the plastic matrix loses its structural integrity which is reflected in the decline of tensile properties. After six month's exposure of film samples in compost, tensile strength of the film samples has reduced up to 42% while elongation at break has reduced up to 69% of the corresponding initial values.

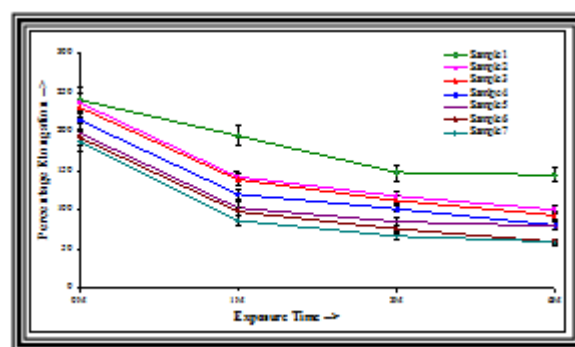
The elongation at break is the most affected parameter and it is observed to be more sensitive measure to the extent of degradation than the tensile strength. It is clear from the results that the decline of elongation is greater in film sample having higher starch contents. This is because the

elongation at break of LDPE depends on its density and hence on its degree of crystallinity, [11-13] the denser and hence the more crystalline material, less ductile it becomes.

This decrease in mechanical properties may be attributed to the phenomenon of moisture absorption inside the compost. Water has plasticization effect on starch based plastics. The absorption of water by film, due to hydroxyl group of starch, decreases H-bonding between the polymer chains resulting in plasticization of the sample. This leads to swelling of starch and likely to weaken the interface in the starch polyethylene composition.



**Figure 7: Variation of Tensile Strength**



**Figure 8: Variation of Percentage Elongation**

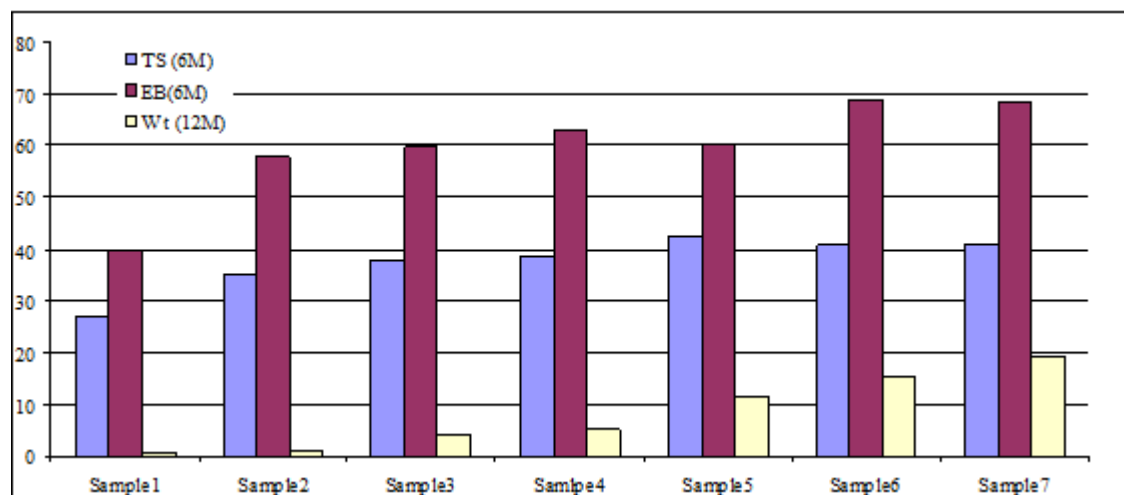
## 4.3 MFI : Melt Flow Index (MFI) (ASTM D- 1238)

Melt flow index measures the rate of extrusion of plastic materials passing through specific length and diameter under prescribed conditions of temperature and load. The different grades of same polymers have different MFI value, which is used to characterize them. MFI gives the idea about the uniformity of the flow rate of the plastic. MFI is indirect measurement of degradation. The MFI study is the macroscopic study of the plastic material, which is directly related to the molecular weight of the test specimen of that polymeric material. MFI of all samples have increased with the exposure time of the compost. Initially it was having no significant impact, however after three months this has increased significantly and after six up to 12 months it has increased more than two folds. Which indicate the continuous degradation of samples.

## 5. Percentage Reduction

Percentage reduction in properties of LDPE/LDPE grafted maleic anhydride/starch biodegradable polymer films with time of composting have been given in figure 9 which have been observed during composting of prepared samples of biodegradable polymer blown films.





**Figure 9:** Percentage reduction in properties of LDPE/LDPE grafted maleic anhydride/starch biodegradable polymer films with time of composting

**TS – Tensile Strength EB – Elongation at Break, Wt – Weight Loss**

## 6. Conclusion

These 15%starch content based blown film samples were exposed in compost environment for the biodegradation study. The degraded samples over the span of 12 months were analyzed through Weight loss analysis, Mechanical properties analysis and MFI.

The biodegradation study indicated that the overall percentage reduction in tensile strength was nearly 40%, percentage reduction & in Elongation at break was nearly 68% and percentage reduction & in weight loss of the degraded film samples was near 20%. The weight loss of nearly 20% indicates that the introduction of maleic anhydride group in the LDPE, which formed the ester bond with hydroxyl group of starch, has helped in the degradation of film samples.

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## ASTM Methods

- 1) ASTM D-882: Standard Test Method for Tensile Properties of Thin Plastic Sheeting
- 2) ASTM D-1238: Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer.