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Novel biodegradable packaging materials based on recycled polyethylene waste

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ABSTRACT

Plastics packing material are collected, separated, cleaned from solid impurities, washed and polyethylene wastes are recycled by solvent-recrystallization method using xylene and methanol. Recycled polythene was blended with starch, sodium salt of partially carboxymethylated starch (Na-PCMS) and starch acetate (SA) in different amount by using Bra bender mixer. The resulting blend, were tested for Melt Flow Index, Flexural Strength, Tensile Strength, % elongation and Durometer hardness. Also tensile properties of recycled polyethylene were analyzed. Properties of recycled blend composition were found better compare to recycled polyethylene and virgin Low density polyethylene. Biodegradation of blend composition was carried out by Bacillus species. After regular interval blend composition were analysed for % weight loss, total cellular protein and tensile properties. After thirty days 46% blend composition were consumed by Bacillus species. Further, Surface morphology of blend composition before and after degradation was studied by scanning electron microscopy (SEM).

KEYWORDS

Recycle polyethylene;
Polymer blends;
Biodegradation;
SEM;
Starch derivatives;
Packaging materials.

INTRODUCTION

Over the last 50 years, synthetic plastics have become the major new materials replacing the traditional once such as paper, glass, steel and aluminium in many applications. Thus, the total volume of plastics production now a day exceeds that of steel[1]. Their main advantages are they can be easily formulated producing materials with desirable properties that are light in weight, cheap to produce and with low energy requirements for their transport and especially for their production. But plastics also have some disadvantages, mainly, the non-biodegradability of most of them causing many environmental problems associated with plastics disposal after their usage. Plastics are a visible part of the problems because of their extended use in daily life. Some polyolefin such as polyethylene and polypropylene have excellent physical properties and therefore they are produced in higher and higher quantity every subsequent year. But unfortunately they are resistant to degradation.

The organic matter in municipal waste is systemati-

cally fragmented by microorganisms into CO2, H2O, NH3 or similar low molecular weight compounds, imparting fertility to the soil[2]. The accumulated plastics waste in soil can neither add to the fertility of soil nor improves its firmness in landfill operations. Many solutions have been operated for soil waste management of plastics, like incineration, landfill disposal, degradable plastics and recycling. Incineration of plastics will release toxic gases and vapours, which could prove to be a serious health hazard. Use of plastics in landfill operation is least preferred because of space constraints.

The polymer recycling and use of recycled polymer becomes one of the most important aspects to overcome the problem of environmental pollution. Recycled plastic is considered to be a source of new materials with an economic impact. A mixture of post-consumer polyethylene waste (HDPE/LDPE) was pyrolyzed over various catalysts using a fluidised-bed reactor[3].

Polyethylene production/ consumption are increasing day by day. Polyethylene is generally not affected by microorganisms. But PE is susceptible to heat and light in presence of oxygen, it undergoes thermo oxidative and photo oxidative degradation[4-14]. This affects some of its useful properties. The stability of PE depends on trace amounts of impurities such as hydro peroxide carbonyl and metallic compounds[15,16]. Thermo-oxidative degradation of PE is a free radical chain reaction where peroxy [O2*] and alkyl [R*] radicals are formed during the degradation process, which further propagate the degradation reaction. These reactions cause deterioration in useful physical and physico mechanical properties i.e. tensile strength, solution viscosity etc[17–21]. Since oxidative degradation is a deleterious process[22,23].

The effect of non-degradability of Polyethylene can be minimized by recycling but the results in a worldwide scale have not been too successful so far. The biggest percentage of recycling has been achieved in India and some European countries. India is leading country for plastics recycling in the world. About 60% of plastics are recycled in India. The recycling of plastics requires efficient combination of mechanical and chemical methods. A variety of mechanical methods for recycling plastics have already been developed and a large portion of recycled plastic can be used for energy production[24,25] . Significant progress has been achieved in the last few years in the technology of plastics as well. This includes mixing and depolymerisation of plastics into their corresponding monomers, which can be reused.

It is calculated that worldwide, only 1% of the produced plastics is recycled as in[26]. whereas remaining part, especially of plastics used for packaging materials, are up in municipal burial sites. It is estimated that plastics compose approximately 7.2wt% (20% by volume) of the total filler, contributing significantly to the problem of filler management[27].

Thus, in the last one or two decades, there has been an increased interest in the production and use of fully biodegradable polymers with the main goal being the replacement of non-biodegradable plastics, especially those used in packaging materials. But the fully biodegradable polymers are estimated to be four to six times more expensive than PE or PP, which are the most widely used plastics for packaging applications.

Falling in the above areas of research goal of 100% biodegradability within a few months is not a wise choice. But a controlled period of biodegradation spanning from months to years depending on the application is a wise choice.

So, in the present work both recycling of used polyethylene and it's blending with natural and modified natural polymer has been attempted.

Many research and industrial attempts have been focused on the use of natural biopolymers such as starch, cellulose, lignin, chitin and chitosan, which are fully biodegradable. In addition these materials are very cheap and they are produced from renewable, natural sources. But the use of these polymers in pure form (natural forms) leads to poor physical properties in final product. Some approaches to overcome these problems include chemical modification by changing their hydrophilic character to hydrophobic such as starch and cellulose esters[28–32].

Starch having higher degradation rate, it was used in additives in synthetic polymers in order to decrease their cost as well as non-biodegradability of polymers like PE, PP, PVAc, ABS, EAA and EVA[2,27, 33–36]. However most of the starch applications are focused in polyethylene. The later is widely used as packaging materials and as mulch film in agricultural application. In both cases recycling is very important, but are not widely

employed.

Several commercial products have been developed, most of them containing low amount of starch[30]. Increasing the amount of starch causes a decrease in both TS and %elongation. As a result, the materials lose their ability to produce blown films. This decrease arises from poor adhesion between LDPE and starch due to the different polar character of LDPE and starch.

For better compatibility and biodegradability in the present work starch is modified to Na-PCMS and starch acetate.

Polyethylene waste from packaging industries, pharmaceutical industries etc. are collected. These wastes are separated according to their nature, use and colour. These waste are recycled by dissolving them into xylene and precipitated out using methanol. These recycled PE is tested for tensile properties. These polyethylene were blended with starch, Na-PCMS and starch acetate in different amount by using Bra bender mixer. The resulting blend, were tested for MFI, FS, TS, % elongation, Durometer hardness and tensile strength. The resulting blends were used for biodegradation using Bacillus species and properties after degradation were measured. Also, the surface morphology of blends before and after degradation was monitored by scanning electron microscopy.

MATERIALS AND METHODS

Starch, monochloroacetate (MCA), was purchased from national chemicals. Solvents and other chemicals are of LR grade. They were used after routine purifications.

Preparation of sodium salt of partially carboxymethylated starch (Na-PCMS)

Na-PCMS was synthesized by standard slurry method as reported by N. K. Patel et al[37].

Starch and isopropanol were stirred vigorously, while required amount of 30% (w/v) aqueous NaOH were added drop-wise during 10minutes at room temperature. Stirring was continued for 1 hour to activate the starch. Then sodium monochloroacetate was added. The mixture was placed on a water bath at 55^{0}C for 5 hours with stirring. Then product was filtered, suspended in methanol and neutralize with acetic acid. Then washed with ethanol and dried at 60^{0}C.

Preparation of starch acetate (SA)

Starch acetate was prepared by using the method as described by N. K. Patel[38].

Required amount of pyridine and starch were refluxed at 115^{0}C for 1 hour. The suspension was cooled to about 60^{0}C and required amount of acetic anhydride was added slowly with continuous stirring. The mixture was then maintained at 100^{0}C for 2.5 hr. (150minutes). Then cooled to room temperature and starch acetate was precipitated using large quantity of distilled water. The product was filtered, washed with water and dried.

Recycling of plastics

Polyethylene, which are separated and cleaned from the waste and xylene, were taken into three-neaked flask equipped with stirrer, thermometer and water condenser. The mixture was heated at 100^{0}C with constant stirring for 2hrs. The solution was cooled to room temperature and precipitated in methanol. Product was filtered and dried in vacuum to constant mass.

Preparation of blend composition

Polyethylene was melt blended with starch, Na-PCMS and starch acetate in different composition using Brabender having twin screw and mixing head with a capacity of 200gms.

Polymers were vacuum dried at 60^{0}C prior to mixing. The components were physically premixed before being fed into the Brabender. Mixing was performed at 110^{0}C, 70rpm for 15 minutes to maximum torque of 20Nm. Moisture gain by the blend was restricted by placing them into vacuum desiccators immediately after preparation.

Preparation of polymer sheets

Sheets of specified thickness were prepared by sandwiching the blend between mould plates of laboratory compression moulding machine at 110^{0}C for 15 minutes. The sheets were held under 60 kg/cm^2 pressure for 5 minutes and then taken out of mould and cooled to room temperature.

Melt flow index (MFI)

The measurement of MFI was carried out as per

the process described in ASTM D1238-53T. The weight of polymeric blend flowed in 10 minute under a 2160gm load (approximately 43.25psi pressure) at 190^{0}C was measured by melt indexer.

Durometer hardness (DH)

Durometer hardness measurements were done as per the process described in ASTMD 2240-75. Hardness is measured in terms of shore A and shore D. They represent the hardness of the material when it is subjected to a certain force through a penetrating object of well defined dimension.

Flexural strength (FS)

The measurement of flexural strength was done as per the procedure described in ASTMD 790. A three point loading system utilizing Central loading on a single supported beam was used for the measurement. Across head speed 2.5 cm/min. was used for all the specimens.

Tensile strength and % elongation

Tensile strength and % elongation measurements were conducted by using a tensile tester at room temperature following the process described in ASTMD 638. Across head speed of 10 cm/minute was used in all measurement.

Isolation of blend degradation culture

Organisms capable of degradation blends were isolated by enrichment culture technique using Na -PCMS (1.1 w/v) as a sole source of carbon.

Medium employed for isolation of bacteria consisted of

Ingredient	gms/lit
Magnesium Sulphate	0.2
Calcium Chloride	0.02
Monopotassium phosphate	1.0
Dipotassium phosphate	1.0
Ammonium Nitrate	1.0
Ferric Chloride	0.05

Suspend 3.27gms of medium in 1000 ml distilled water 50 ml of above medium was dispersed in 250ml Erlenmeyer flasks. The medium was autoclaved at 121^{0}C for 15 minutes Na-PCMS was added upon sterilization to each flask and these flasks were inoculated with 5ml of 10% (w/v) soil suspensions prepared using garden soil. These flasks were then incubated on rotating shaker (150 rpm) till visible turbidity and disappearance of insoluble Na-PCMS particles were observed. Loop fall of these enrichment cultures were streaked on starch agar plates in order to isolate amylase producing bacteria. Around five different amylase producing bacteria spp. were obtained viz. isolate BS_1 to BS_5. Amongst, these five isolates, isolate BS_2 was selected for further study as it showed maximum amylase production on solid medium.

Degradation of blend composition

50gm of above blend was taken in each 1000ml flask containing sterile mineral medium (pH7). To it 10%v/v of culture suspension of isolated BS_2 was added. All the flasks were kept on shaker (150rpm) and every alternate day one flask was removed and analyzed for dry weight of blend, total cellular protein, tensile strength and percent elongation. A biotic control included blend in medium without culture. Above sets were in duplicate and results are the average of reading obtained.

Weight loss

Blends were filtered through whatmann filter paper no. 1. The residue was washed with ethanol and dried at 40^{0}C in vacuum oven till constant weight. The filtrate was used for determined total cellular protein.

Total cellular protein

1 ml liquid full suspension was centrifuged at 4000rpm for 15 minutes and cells were washed with normal saline (N-Saline) and re centrifuged the cell pellet was than suspended in 1 ml. of 1N NaOH and cells were lysed by incubating the suspension in boiling water bath for 10minutes. It was recentrifuged for 10 minutes and supernatants were analyzed for protein content by method of Lowary et al. (1951)[39].

Scanning electron microscopy

The test sample of blend composition before and after degradation was examined with ESEM TMP, Philips model electron microscope.

RESULTS AND DISCUSSIONS

Optimization of blend compositions was carried out

with respect to Recycled polyethylene, Na – PCMS, Starch acetate and starch. Properties of optimum composition are tabulated in TABLE 1.

TABLE 1 : Properties of LDPE, recycled polyethylene and blends

Blend Composition	Properties					
	MFI	Durometer Hardness		Flexural Strength	Tensile Strength	% elongation
		Shore A	Shore D	Kg/ Cm^2	Kg/ Cm^2	%
LDPE (Virgin)	0.5	90	40	69.63	31	100
Recycled Polyethylene – (A)	0.4	85	35	60.00	28	90
A: NaPCMS (70:30)	1.11	88	39	70.20	35	145
A:NaPCMS:SA (60:30:10)	1.23	90	41	67.89	36	135
A:NaPCMS:SA:Starch (55:30:10:5)	1.25	89	40	67.80	37	140

Melt flow index

MFI values of the blends at 190^{0}C are tabulated in TABLE 1. Addition of Na-PCMS, starch acetate, and starch increase the melt flow index. Which indicates that decreased in resistance to flow that lowers the melt viscosity and is advantage out from processing points of view.

Durometer hardness

DH was measured in terms of shore A and shore D. The DH values are tabulated in TABLE 1. DH showed two different trends. Addition of Na-PCMS and starch acetate increased, while starch addition lowered the DH values. The overall effect in DH was either increase or it remained nearly same as virgin polyethylene.

Flexural strength

Flexural strength values of the blends are tabulated in TABLE 1. Addition of Na-PCMS increased and starch acetate (SA) lowers the FS, while there was nearly no change observed in FS due to addition of starch.

Tensile strength and % elongation

Tensile strength and % elongation at room temperature are tabulated in TABLE 1. Addition of Na-PCMS, starch acetate and starch increased tensile strength, while % elongation was increased on addition of Na-PCMS and starch. Addition of Starch acetate lowers the % elongation.

% Weight loss after biodegradation

The samples were incubated for 30 days, and one sample was removed after every three days and analyzed for weight loss. The results are tabulated in Table 2. Maximum 46 % of weight loss was observed after 30 days. It conclude that BS_2 utilized starch, starch acetate, Na-PCMS as well as recycled polyethylene

Total cellular protein

Total cellular protein was estimated by Lowary's method. The results are tabulated in TABLE 2. Total cellular protein was increased up to 18 days for the blend composition. Which reflects increase in biomass after which growth was found to cease. This indicates that extra cellular enzymes are involved in the degradation of blends.

TABLE 2 : Properties of blend after biodegradation

Time (Days)	A:NaPCMS:SA:Starch (55:30:10:5)			
	Weight loss	Total Cellular protein	Tensile strength	% elongation
	%	µg/ml	Kg/cm^2	%
0	0	136	37	140
3	3.5	180	----	----
6	4.0	207	36	130
9	11.0	293	----	----
12	19.0	299	34	120
15	26.0	350	----	----
18	32.0	565	30	100
21	35.0	460	----	----
24	39.0	430	28	90
27	45.0	400	----	----
30	46.0	290	27	85

Tensile properties after biodegradation

Tensile strength and % elongation of blends were measured after every six days of incubation. The results are tabulated in TABLE 2. Both tensile strength

and % elongation were decreased as the degradation time progresses. After 30 days tensile properties was lower than that of polyethyle. So, it may conclude that some amount of polyethylene was utilized by BS3

Scanning electron microscopy

The microphotographs of before and after degradation of 30 days time are shown in Figure 1-2 respectively. Before the attack of BS2, the overall surface of the blend is clear and homogeneous. After thirty days large holes appeared suggesting more and more consumption of NaPCMS, starch acetate and starch by

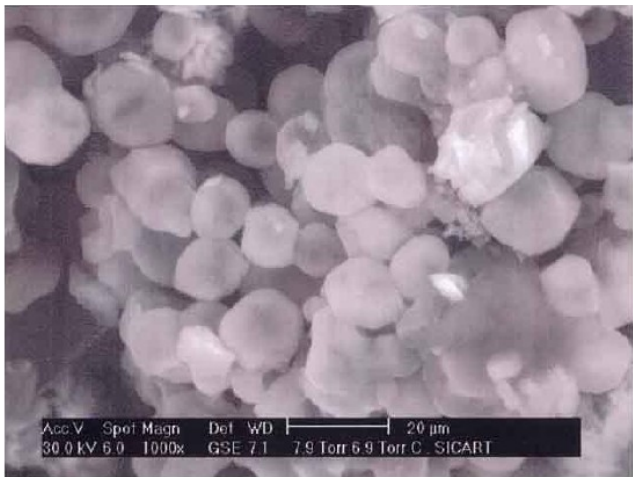

Figure 1 : Blend composition before degradation

Figure 2 : Blend composition after degradation (30days)

BS2.

CONCLUSION

In an attempt to prepare cost effective biodegradable plastics having optimum mechanical properties, First starch was modified to starch ether and starch acetate. Polyethylene were recycled and blended with natural and modified natural polymers. This gives the advantage of recycling as well as preparing plastics, which has biodegradation characteristics without hampering the optimum mechanical properties. Biodegradation of the blend composition results in 46% degradation after one month. This may conclude that the aim of preparation of degradable plastics having good characteristics properties was achieved. Blends can be used where ever Biodegradable polymers are required as well as in the packaging application and wherever polyethylene and polypropylene used.

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