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Environmentally Degradable Blends of Low Density Polyethylene (LDPE) and Partially Carboxymethylated Starch (PCMS)

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Sodium - salt of partially carboxymethylated starch (Na-PCMS) with degree of substitution (DS) 0.21 and 0.58 was synthesized by etherification of starch. These starch ethers and low density polyethylene (LDPE) were mixed with and without poly(vinylacetate) (PVAc) in various proportions using Brabender mixer. FTIR confirmed the etherification reaction of starch and blending. Positive changes in the mechanical properties as a function of blending, and environmental degradation have been observed. Addition of 5 wt% PVAc improves the blend quality. Samples were exposed to direct sunlight for one month and environmental degradation was measured in terms of change in tensile strength and per cent elongation.

Keywords: Carboxymethylated starch; Polyethylene; Blends; Environmental degradation; Compatibility

INTRODUCTION

Degradable polymers are desirable for variety of applications, such as in packaging, agriculture and medicine.

Polyolefins covers almost 90% of the world plastic market with excellent performance properties. Polyolefins fail to provide biode-

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gradation character. Thus, in the absence of knowledge to handle the plastic waste, it has become an environmental threat [1]. In an attempt to synthesize a cost effective biodegradable plastics, starch filled polyethylene is one of the best alternatives [2-5]. Starch and polyethylene blend is non compatible at micro level and often leads to poor performance [6]. In order to overcome this drawback, either polyethylene or starch needs to be modified. The aim of this study is to modify starch to Na PCMS form and blend with LDPE. Small amount of poly(vinylacetate) (5%) was added for improvement in film quality. In order to examine the effect of the degree of substitution of carboxymethyl group on the properties of the LDPE/Na-PCMS blends, (Na-PCMS) of two different DS 0.21 and 0.58 were selected.

The sheets of the various sets of the blends were prepared exposed to sunlight for one month period. Mechanical properties like tensile strength and % elongation were evaluated in order to study the performance of the blends.

EXPERIMENTAL

Materials

LDPE from Indian Petrochemicals Ltd. (IPCL) Baroda, Gujarat, India, PVAc, Starch, monochloroacetic acid from National Chemicals, Baroda, Solvents of laboratory grade and other laboratory chemicals were used after routine purification.

Synthesis of Na-PCMS

Na-PCMS of different DS was synthesized by method as reported elsewhere [7].

Blending

Na-PCMS was melt blended with LDPE in Brabender having twin screw and mixing head with capacity of 200 gms. Polymers were vacuum dried at 60°C prior to the mixing. The components were physically premixed before being fed into the Brabender. Mixing was

performed at 110°C 70 rpm for 15 minutes up to a maximum torque of 20 Nm. For both types of (Na PCMS) (DS – 0.21 and 0.58). moisture gain by the blend was restricted by placing them into vacuum desiccator immediately after preparation.

Preparation of Polymer Sheet

Sheets of specified thickness were prepared by sandwiching the blend between mould plates of laboratory compersion molding machine at 110°C for 15 minutes. The sheets were held under 60 kg/cm² pressure at 110°C for 5 minutes and then taken out of the mould for cooling at room temperature [8].

RESULTS AND DISCUSSION

Melt Flow Index

The measurement of MFI was carried out as per the procedure described in ASTM D 1238–53 T. Melt flow measures the amount of material which flows through the orifice at 190°C under load of 2.16 kg during a period of 10 minutes. High values of MFI indicates better flow at processing temperature leading to perfect molding and ease of processing at relatively low temperature. MFI results are tabulated in Table I.

All the MFI values for the blends were greater than LDPE. This indicates the lower melt viscosity of the blend which is advantageous from processing point of view.

TABLE I Melt flow index

Composition	Melt flow index gm./10 min.	
	DS–0.58	DS–0.21
LDPE/CMS		
100/0	0.5	0.5
90/0	0.55	0.55
85/15	0.76	0.61
80/20	0.82	0.78
75/25	0.91	0.85
70/30	1.04	0.99

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Tensile Strength (TS)

Tensile strength measurement were conducted by using tensile tester at room temperature following the process described in ASTM D638. A crosshead speed of 10 cm/min. was used in all measurements.

Three measurements were conducted for each sample and the results were averaged to obtain mean value. Tensile strength and per cent elongation of both the blends are tabulated in Table II.

The higher values of % elongation is attributed to addition of Na-PCMS in the blends. Tensile strength showed different trends. There was raise in the TS upto 25% addition of Na-PCMS (DS – 0.58) and thereafter it declined. While in case of Na-PCMS (DS – 0.21) even 20% addition caused reduction in TS. This may be due to the lower degree of substitution.

Durometer Hardness (DH)

Durometer hardness measurements were done as per the procedure described in ASTM D2240–75. DH measurements represents the hardness of material which is subjected to a certain force through a penetrating object of well defined dimensions. DH is measured in terms of shore A and shore D. Results are tabulated in Table III.

All the DH values for the blends were lower than LDPE, and it was almost the same for both types of Na-PCMS (DS 0.58 and 0.21).

Environmental Degradation

From the earlier discussion on mechanical properties of polymer blends it is concluded that optimum properties were observed for 25%

TABLE II Per cent elongation and tensile strength

Composition	% elongation (%) (mean)		Tensile strength kg/cm ² (mean)	
	DS – 0.21	DS – 0.58	DS 0.21	DS 0.58
100/0	100	100	31	31
90/0	110	110	31	32
85/15	118	125	32	32
80/20	128	133	32	34
75/25	131	150	30	35
70/30	138	160	28	30

TABLE III Durometer hardness

Composition	Shore A		Shore D	
	DS - 0.21	DS - 0.58	DS - 0.21	DS - 0.58
LDPE/PVAc				
100:0	90	90	40	40
90:0	89	89	39	39
85/15	88	88	38	37
80/20	87	88	37	36
75/25	87	86	36	36
70/30	86	85	36	35

and 20% composition of Na-PCMS DS 0.58 and 0.21 respectively. So we preferred these two compositions of blends for degradation. Also, addition of 5 wt% of PVAc improved the tensile properties. All the films were exposed to sunlight for one month to observe the degradabilities. All the films lost about 4% weight. Results observed in terms of TS and % elongation are tabulated in Table IV.

A decrease was observed in TS and % elongation for all the blends composition after exposure of sunlight up to 1 month.

Infrared Spectroscopy

Infrared spectroscopy helps in confirming the etherification reaction of starch and of the blending. The spectra of Na-PCMS and LDPE, Na-PCMS and PVAc blends were taken in KBr pellets using FTIR, inkjet nicolet 400 D spectrophotometer. Figures 1 and 2 represent the IR spectra of Na-PCMS and LDPE, Na-PCMS, PVAc blends respectively.

TABLE IV Comparison of % elongation and tensile strength before and after environmental degradation

Composition	% Elongation (%)		Tensile strength (kg/cm ²)	
	Before	After	Before	After
(CMS - 0.21 DS)				
LDPE/CMS/PVAc				
80/20/0	128	78	32	25
75/20/5	145	81	33	26
(CMS - 0.58 DS)				
75/25/0	150	90	35	25
70/25/5	160	93	37	28

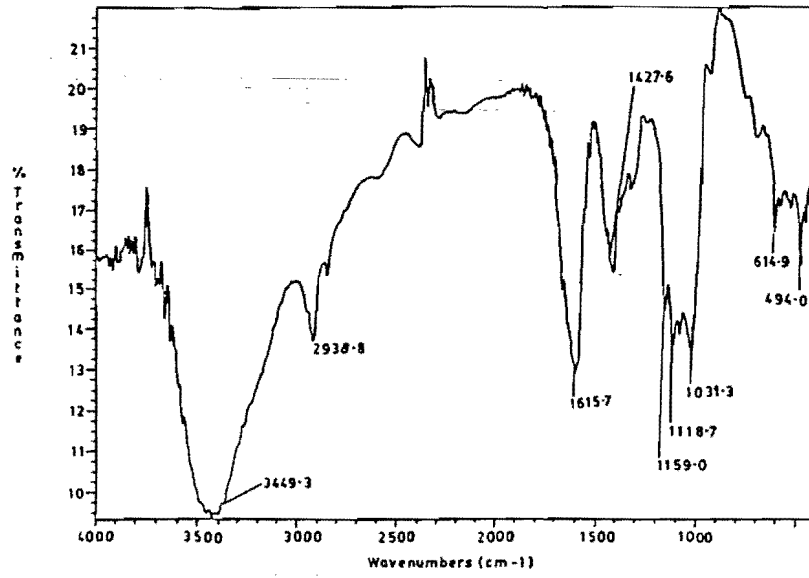


FIGURE 1 IR Spectrum of Na-PCMS.

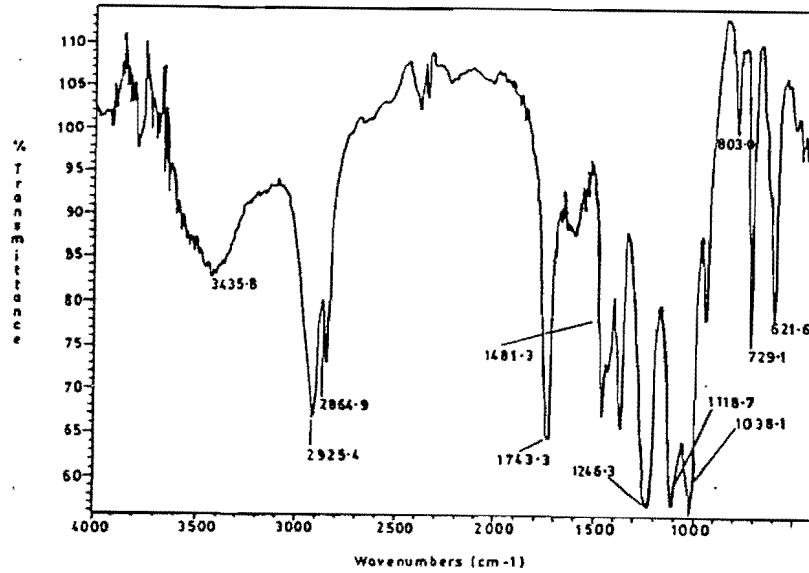


FIGURE 2 IR Spectrum of Blend of LDPE NAPCMS and PVAC.

It has been observed that the Na-PCMS showed an absorption band at, 1615 cm^{-1} and 1427 cm^{-1} , characteristic bands of Na-PCMS. From the persual of Figure 2, IR spectra show sharp peak around 1743 cm^{-1} confirming the ester linkages in PVAc in the blend. A sharp absorption band at 1038 cm^{-1} is attributed to the aliphatic olefins $(-\text{CH}=\text{CH}-)_n$, present in the blend based on LDPE. C—O stretching band is observed at 1246 cm^{-1} , sharp band around 2925 cm^{-1} determines the vibrational stretching of $(-\text{C}-\text{H}-)_n$ and $(-\text{CH}_2-)$ present in LDPE. The presence of above key peaks in IR spectra supports the preparation of LDPE, Na-PCMS and PVAc blend.

CONCLUSION

Ease of processing of LDPE and Environmental degradability is achieved by incorporation of sodium salt of partially carboxymethylated starch (DS = 0.21, 0.58) and 5% by wt of PVAc in all the blend preparations. The performance properties measured were TS, DH MFI and, % elongation MFI and, % elongation values were higher due to incorporation of Na-PCMS up to 30% wt. Increase in TS for DS = 0.21 up to 20% wt is observed and for DS = 0.58 upto 25% wt. It decreases after further addition of Na-PCMS. General trend for DH is downward for all the Na-PCMS % wt addition. Due to Environmental degradation, a reduction in the TS and % elongation is noted. The resulting blends may be used for such application as agriculture, packaging *etc.*

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