

**STUDIES ON DEVELOPMENT OF
ENVIRONMENTALLY DEGRADABLE POLYETHYLENE**

by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

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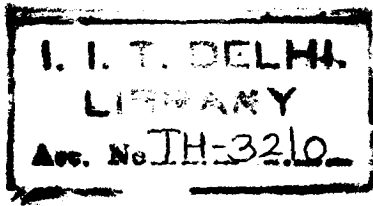


INDIAN INSTITUTE OF TECHNOLOGY, DELHI

March, 2005

polythene - Environmental degradation

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CERTIFICATE

This is to certify that the thesis entitled “**Studies on Development of Environmentally Degradable Polyethylene**” submitted by **Mr. Jaykisor Pal** to the **Indian Institute of Technology, Delhi** for the award of degree of Doctor of Philosophy, in Polymer Science and Technology is a record of bonafide research work carried out by him. Mr. Jaykisor Pal has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis.

The results contained in this thesis are original and have not been submitted in partial or full, to any other university or institute for the award of any degree (or) diploma.



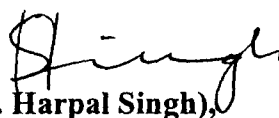
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MY PARENTS

ACKNOWLEDGEMENT

It is my great pleasure to express my profound gratitude to my thesis supervisors Prof A.K Ghosh and Prof H. Singh, for their guidance, constant inspiration and invaluable suggestion for carrying out this work. The discussions held with them were very much enlightening and motivated me to work with greater zeal and enthusiasm.

I am grateful to Prof Veena Chaudhary, Head, Center for Polymer Science and Engineering and to Prof S.N. Maiti, Ex-Head, Center for Polymer Science and Engineering, for providing the facilities and guidance required to carry out the experiments.

I am indebted to Prof A.K. Gupta, and Prof A.K. Ray for their concern to my work. I would also like to express my gratitude to Prof I.K. Verma for her invaluable suggestions during the analysis of my results

My special gratitude to Prof A.K. Misra, Director, I.I.T Bombay and Prof D. Khakkar, Head, Dept. of Chemical Engineering, I.I.T Bombay, for extending their co-operation by providing the film blowing facility for the experimental work

I am highly obliged to Prof D.D. Kale, U.I.C.T, Mumbai for extending his co-operation by providing the experimental facilities for film blowing and rheological characterization.

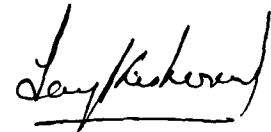
Thanks are also due to Gas Authority of India, Noida for providing raw material and partial financial support.

I wish to acknowledge the support extended by all the staff members of CPSE and Dept. of Textile Technology, especially to Mr. Ashok Kapoor, Mr. Devinder Singh, Mr. Surinder Sharma and Mr. Shiv Kant for their help during the work

I am thankful to Mr. Anantha Padmanabha, Ms MuthuLaxmi RJS, Ms Pramila, Mr. Shaunak Dey Roy, Mr. Milind Mhalgi, Dr. Sandeep Tyagi, Dr Bhawna Kulshreshtha Mr. Rakesh Kumar, Mr. Senthil Kumar, Ms. Sangeeta Sen, Dr. Madhumita Swaroop,

Ms. Ritimoni Rajkhowa Ms. Supriya and Ms. Nimisha Aggarwal for their constant help, technical support and keeping me cheerful during my hard days throughout the entire period of my work. My special word of thanks to Mr. Anup Das, Mr. Dilip Koluri, Ms. Deepti, Ms. Rashmi, Ms. Chaitra Mahesh, Mr. Bandeep Singh, Ms. Sonia Oberoi, Ms. Neetu Tomar, Ms. Bimlesh Lochab, Mr Venkatesh, and all other friends, and colleagues for their forbearance and the mutual help provided by them, which was a must for the successful completion of this work.

Above all, I am grateful to my parents without whose blessings and constant help this work would not have been possible. Last but not the least, I am grateful to my sister Antara for her constant moral support throughout my academic career.



(Jaykisor Pal)

ABSTRACT

Polyethylene is a commodity thermoplastic used widely in various applications such as home appliances, construction, electronics, packaging etc. Their widespread use in packaging sector, especially in the form of lightweight thin film packages, has resulted in generation of huge amount of plastic waste. Due to non-degradability of PE, these wastes remain in environment for longer time, causing severe waste disposal problems. Development of environmentally degradable PE offers the best route to tackle this crisis. The objective of the present study is to modify a film grade LLDPE in such a way that it will fragment and subsequently degrade on disposal. Further, study of their rheological behavior, film blowability, morphology, mechanical properties etc is also carried out.

In the present study, styrene-maleic anhydride based polymeric derivatives were chosen as degradation promoter for LLDPE. SMA derivatives are chosen because of their low cost, easy availability, high functionality, good solubility in alkaline medium (and thus also in soil media), low photostability and nontoxicity. SMA was modified into two forms; (i) Esterified SMA (ESMA) (ii) Iron-SMA complex. Esterification of SMA was done by using n-decanol, with an aim to enhance compatibility of SMA with PE. Iron-SMA complex was developed to impart photodegradability to PE. SMA was synthesized by free radical precipitation polymerization, under nitrogen atmosphere, at 80°C using benzoyl peroxide as initiator. SMA was esterified by n-decanol using methyl ethyl ketone (MEK) as solvent. Iron-SMA complex was prepared from the reaction of ferric chloride and aqueous solution of sodium salt of SMA. The synthesized compounds were characterized by FT-IR, ¹H-NMR, DSC, and TGA techniques.

Blends of LLDPE/ESMA were made by melt mixing in an extruder varying ESMA concentration from 20-40 wt%. To enhance the compatibility of LLDPE/ESMA further LLDPE grafted with glycidyl methacrylate (LLDPE-g-GMA) was used as compatibilizer in 70/30 LLDPE/ESMA blend composition. In a separate study, LLDPE was also mixed with iron-SMA complex, varying latter's concentration from 0.1-0.5 wt%. Rheological studies showed lower viscosity for ESMA as compared to LLDPE. The zero shear viscosity (η_0) and the viscosity at higher shear rates was observed to decrease with the increase in ESMA content in the blend, indicating lowering of melt strength of blends on ESMA addition. Storage modulus (G'), loss modulus (G'') and first normal stress difference coefficient (N_1) also decreased on addition of ESMA which indicates that melt elasticity is also compromised. Addition of LLDPE-g-GMA resulted in an increase in η_0 and as a result the melt strength. However, G' , G'' and N_1 showed insignificant change on addition of compatibilizer, indicating negligible effect of compatibilizer on the melt elasticity. Such an increase in η_0 is due to interfacial reaction between LLDPE-g-GMA and ESMA. Blends were blown using tubular film blowing technique. Film blowability was studied in terms of blow up ratio (BUR) and draw down ratio (DDR) and was analyzed as a function of ESMA and compatibilizer content. The blowability was observed to decrease with the increase in ESMA fraction in the blend. This observation was concurrent with the reduction of zero shear viscosity with the ESMA content in the blends. However, blowability of films improved on addition of LLDPE-g-GMA, which can be explained by the increase in zero shear viscosity due to reactive compatibilization occurring in the compatibilized blends during melt processing.

Morphological studies of all LLDPE/ESMA blends showed a two-phase morphology. The nature of two-phase morphology was dependent on the ESMA and compatibilizer content in the blends. It was observed that LLDPE/ESMA are immiscible/incompatible. The addition of LLDPE-g-GMA resulted in a finer morphology, which is attributed to interfacial reaction between the compatibilizer and ESMA domains, resulting in lowering of interfacial tension and increase in interfacial adhesion. Studies on tensile properties of blend films showed that the tensile strength of films decreased while modulus increased with increase in ESMA content. The tensile strength of blend films increased by ~17 % on addition of compatibilizer. Tensile strength of the films measured along longitudinal direction of processing was always higher than transverse direction in all blend films. The tensile strength data of LLDPE/ESMA blends were analyzed by different theoretical models, such as first power law model, Nielson's model, porosity model etc. It was found that experimental tensile strength of blends were comparable with the theoretically predicted value upto 30 wt% of ESMA content, while at ESMA content more than 30 wt% the value deviate significantly. This indicates presence of high stress concentration in blends with high ESMA content due to large size of ESMA domains.

LLDPE/ESMA blend films were exposed to distilled water, buffer solution of different pH (4, 8, and 9), soil, accelerated and outdoor natural weathering. Films kept in buffer solution underwent initial weight gain (due to absorption of water) and subsequent weight loss (due to dissolution of ESMA). The weight loss was more in alkaline medium and for the blends with higher ESMA content. The dissolution of ESMA from blends in alkaline medium is due to ionization of ESMA and formation of sodium carboxylate salt.

Addition of compatibilizer further facilitated the loss of ESMA from the Blend films. Upon burial in soil, a similar trend in weight change was observed. Surface morphology of the films exposed to buffer solution of pH at 9 and soil, as observed by SEM, showed prominent signs of roughness and deterioration. The level of deterioration was observed to be more in blends with higher ESMA content and in compatibilized blends. Accelerated and outdoor natural weathering studies of blend films resulted in fragmentation of samples. Fragmentation of compatibilized blend films started first (within 250 hours in accelerated condition and within 110 days in outdoor natural weathering) followed by the uncompatibilized blend films. LLDPE remained flexible throughout the experimental period. FT-IR spectra of xylene extracted blend films showed formation of carbonyl group, indicating photooxidation of LLDPE. LLDPE/ESMA blends showed higher carbonyl index compared to virgin exposed LLDPE. The degradation in LLDPE phase of LLDPE/ESMA blends occurred due to photooxidative degradation of ESMA and subsequent transfer of active radical from ESMA domains to LLDPE. Uniform distribution of ESMA in compatibilized resulted in further enhancement of photodegradation rate. Thermal analysis of degraded films by DSC showed that photodegradation has resulted in an increase in crystallinity of LLDPE due to preferential degradation of amorphous phase and subsequent secondary crystallization of low molecular weight segments. The higher increase in crystallinity was recorded for compatibilized blend films compared to virgin LLDPE films

Accelerated and outdoor weathering studies of LLDPE / iron-SMA complex showed faster embrittlement of films compared to virgin LLDPE films. The degradation was quantified by periodic determination of carbonyl index, which showed rapid

increase, in case of films containing iron-SMA complex. Increase in percentage crystallinity was also observed in the films. Iron-SMA complex is believed to act by catalyzing the hemolytic cleavage of hydroperoxide groups present in the LLDPE films.

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