STUDIES ON DEGRADATION OF LDPE BLENDS IN PRESENCE OF METALLIC ADDITIVES

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CERTIFICATE

This is to certify that Ms. Priyanka Singh has carried out her major project entitled “Studies on degradation of LDPE blends in presence of metallic additives” under our joint supervision and guidance during the session 2006-2007. To the best of our knowledge and belief, this work has not been submitted to any other university or institution for the award of any degree or diploma.

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Abstract

Plastics are the source of rising environmental problems since most of them are not used for long-lived applications and find their way into the solid fraction of the municipal solid waste. Most countries are facing difficulty in managing the problems resulting from continuously increasing amounts of plastic wastes. An acceptable solution to this problem is to use degradable plastics, which enter the biological cycle after completing their lifecycle. In this connection, the formulation of environmentally sound degradable polymeric materials and relevant plastic items constitute a key option among those available for the management of plastic waste.

In the present study, we have attempted to investigate the degradation behaviour of blown films of LDPE, LLDPE and its blends in the presence of metal stearates, namely iron stearate and manganese stearate. For this purpose, the metallic stearates were synthesized, characterized and compounded with the polyolefins at appropriate levels to control the lifetimes of plastic films. Multiple extrusion experiments were performed to check the processing stability of developed formulations.

The effect of additive has been investigated on the thermo-oxidative, photo-oxidative and natural weathering. The thermo-oxidative test was conducted by placing films in an air oven at 70^0C for extended periods. For photo-oxidative studies, LDPE films containing pro-oxidants were exposed to xenon arc lamp at 550 W/m^2 and 63^0C temperature. FTIR spectroscopy, mechanical testing, thermal analysis, MFI measurement was performed to monitor the degradation behaviour. Both the metallic stearates were found to be capable of initiating degradation in LDPE and blends.

CHAPTER-1

Introduction

Plastics have become an important part of modern life and are used in different sectors of applications like packaging, building materials, consumer products and much more. Every year about 100 million tons of plastics are produced worldwide. Demand for plastics in India has reached about 4.3 million tons in the year 2001-02 and would increase to about 8 million tons in the year 2006-07 (1). Currently, however, the per capita consumption of plastics in India is only about 3 kg compared to 30-40 kg in the developed countries.

Most countries are now facing tough solid waste management challenges as in how and where to dispose of the garbage that is piling up each passing year. Landfill capacity is declining and finding new sites is often met by communities with fears and objections. Consequently, local solid waste management officials are faced with collecting more and more garbage to be disposed off in fewer and fewer landfills. But this is not to say that the packaging industry is producing more wastes relative to the national economic growth. In fact, the ratio of packaging production relative to GNP growth exhibits decreasing trend as a country improves from being least developed to become an industrialized one (2).

Packaging, particularly plastics packaging, has always been charged as a major culprit in the mountain-sized solid waste disposal problem. As a result, the packaging industry faces increased public and legislative pressures, which may be politically expendient, but do little to truly reduce the amount of solid waste generated. Thus, the packaging industry should bring to the fore technology breakthroughs and sound information that will be helpful in the formulation of solid waste disposal blueprints, which is a complex problem. A simplistic solution may do more harm than good. In their own home-grounds, packaging users and suppliers can begin to share in minimising the negative impact of packaging in the environment by incorporating environmental factors (e.g., ultimate disposal of used or empty packages) into the packaging designs. This will have real and positive impacts on both the amount of solid wastes and the methods utilised to manage it.

In this connection, the formulation of environmentally sound degradable polymeric materials and relevant plastic items will constitute a key option among those available for the management of plastic waste (3). The technologies based on recycling, including also the energy recovery by incineration, will be flanked by the increasing option of environmentally degradable plastics. These should be designed to replace the conventional commodity plastics in those segments in which recycling is difficult and labor-intensive with hence a heavy penalization on the cost-performance of "recycled" items. A downgrading of the original material properties is indeed occurring both during the lifetime of the items meant to be recycled and their reprocessing stages once they reached the recyclable item rank.

The position held by environmentally degradable plastics would be outlined in terms of the development levels so far reached and of the future perspectives. It is worth mentioning that a major aspect that has attracted the attention of plastic manufacturers, polymer scientists, and public officers, is represented by the establishment of definitions comprising all the possible categories of environmentally degradable polymers and plastics, together with suitable standards and testing protocols. The nature and fate of the degradation products constitute another crucial point for the acceptance of environmentally sound synthetic polymeric materials undergoing degradation under specific environmental conditions.

An excellent way to make polyethene degradable is to blend it with pro-oxidant additives, which can efficiently modify the degradation behaviour of these materials. Common pro-oxidants include metallic soaps like transition metal salts with higher fatty acids. Transition metals specially Mn, Fe, Co, possess a remarkable ability to decompose the hydro-peroxides formed during oxidation process. Cobalt stearate has been reported to be an effective photo and thermo-oxidative initiator for degradation (4).

This study is concerned with degradation behaviour of formulations containing manganese stearate and iron stearate in concentration range (0.5-1%w/w).

CHAPTER-2

Literature survey

2.1 Overview of degradable polymers

Degradability of a polymeric material is its ability to break down, by bacterial (biodegradable), thermal (oxidative) or ultraviolet (photodegradable) action. For degradable polymers to be made into functional plastic bags, they must meet the following criteria.

- Be able to be formed into film
- Have adequate tensile strength and elongation
- Have adequate puncture resistance
- Have adequate tear resistance
- Generally possess properties that resemble low-density polyethylene (LDPE) or high-density polyethylene (HDPE) in overall physical properties and rheological characteristics.

It is also evident that degradable plastics for bags are required to degrade rapidly at the end of their useful life, while it is equally important that their mechanical properties remain essentially unchanged during use. In general, it is essential that the polymer retains its useful properties through one or more of a variety of fabrication procedures, e.g., blending, pelletizing, extrusion, film blowing or cast film fabrication. The final product film/bag must have a reasonable storage life. Additionally, the customer expects to have functional bags that serve a useful purpose under a variety of circumstances. It is only at the end of the service life, that the polymer must degrade in the disposal environment. In summary, there are three essential criteria for degradation of plastic.

- They must disappear and leave no visible trace
- This disintegration must occur in a reasonable timeframe
- They must not leave behind any toxic residues.

2.2 Types of degradable plastic

Degradable plastics can be classified according to the way that they degrade. For example, whether they require the actions of microorganisms, or whether they require heat, ultraviolet light, mechanical stress or water in order to break down.

- **Biodegradable polymers** are those that are capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standardized tests, in a specified time, reflecting available disposal conditions.

- **Compostable polymers** are those that are degradable under composting conditions. To meet this definition, they must break down under the action of microorganisms (bacteria, fungi, algae), achieve total mineralization (conversion into carbon dioxide, methane, water, inorganic compounds or biomass under aerobic conditions) and the mineralization rate must be high and compatible with the composting process.

- **Oxo-degradable polymers** are those that undergo controlled degradation through the incorporation of pro-oxidants additives (additives, that can trigger and accelerate the degradation process). These polymers undergo accelerated oxidative degradation initiated by natural daylight, heat and/or mechanical stress, and embrittle in the environment and erode under the influence of weathering.

- **Photodegradable polymers** are those that break down through the action of ultraviolet (UV) light, which degrades the chemical bond or link in the polymer or chemical structure of the plastic. This process can be assisted by the presence of UV-sensitive additives in the polymer.

- **Water-soluble polymers** are those that dissolve in water within a designated temperature range and then biodegrade in contact with microorganisms.

Apart from the above, plastics can also be classified according to the material they are manufactured from, (for example whether they are made from natural starch polymers, from synthetic polymers or from a blend of a conventional polymer with an additive to facilitate degradation)

2.3 Mechanisms of plastic degradation

Polymeric materials degrade during manufacturing, processing, and long-term use. Degradation can be any destructive change, either in the chemical structure and physical properties, or in the appearance of a polymer.

Organic polymers contain bonds that are mainly of the C-C, C-H, C-Cl or C-O type. These bonds can be broken if the polymer is exposed to energy corresponding to their bond energy values. Exposure of polyolefin's to oxygen, particularly at elevated temperatures or in sunlight will lead to degradation of the polymer. Degradation of polyolefins in the presence of oxygen is an autocatalytic process commonly referred as auto-oxidation.

Auto-oxidation is a free radical reaction, where the initiating step occurs when the chemical bonds in the molecules are broken. The scission preferentially occurs at weak links, where the bond energies are lower and leads to the formation of radicals (equation-1). The cleavage can occur by e.g. exposure to UV-radiation, heat, ionizing radiation and mechanical stresses. These radicals can react with atmospheric oxygen and start the auto-oxidation of the polymer (equation1-6).

Initiation: $RH \longrightarrow R\bullet + H\bullet$ (1)

Propagation: $R\bullet + O_2 \longrightarrow RO_2\bullet$ (2)

$RO_2\bullet + RH \longrightarrow ROOH + R\bullet$ (3)

Termination: $R\bullet + R\bullet \longrightarrow R-R$ (4)

$RO_2\bullet + R\bullet \longrightarrow ROOR$ (5)

$RO_2\bullet + RO_2\bullet \longrightarrow \text{Products}$ (6)

The hydroperoxides (ROOH) have a key position in the auto-oxidation reactions, since they are very unstable compounds and further decompose to new radicals when exposed to heat or irradiation (equation 7-8).

$$ROOH \xrightarrow[\Delta]{h\nu} RO\bullet + \bullet OH \quad (7)$$

$$2ROOH \longrightarrow RO\bullet + ROO\bullet + H_2O \quad (8)$$

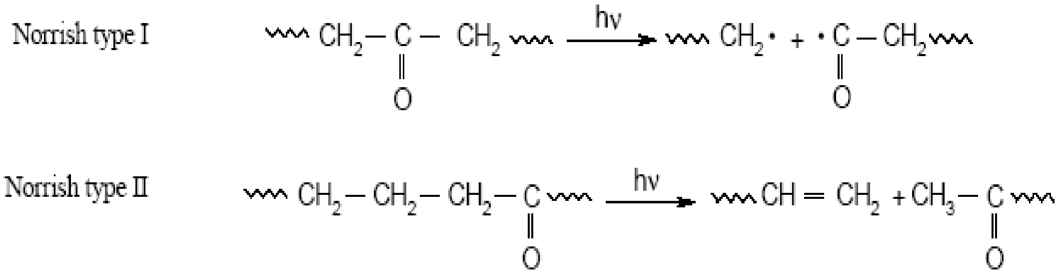
The decomposition of hydroperoxides is catalysed by transition metal ions, particularly cobalt, iron, manganese and copper. It has been reported that metal ions reduce the activation energy of the hydroperoxide decomposition (equation 9-10).

$$ROOH + M^{n} \longrightarrow RO\bullet + OH^{-} + M^{n+1} \quad (9)$$

$$ROOH + M^{n+1} \longrightarrow ROO\bullet + H^{+} + M^{n} \quad (10)$$

Besides these reactions, additional reactions also take place during photo-oxidation. The carbonyl groups which are formed during photo-oxidation, and are reported to be effective UV absorbers undergo photolysis by the Norrish type I and type II reactions resulting in chain cleavage.

The Norrish type I reaction is a free radical reaction where cleavage occurs adjacent to the carbonyl group to generate radicals. The type II process is an intermolecular re-arrangement resulting in scission of the main chain to give a methyl ketone and a terminal double bond (5-6).



2.4 Critical factors affecting degradation of polyethylene films

The degradability of any polymeric material depends primarily on two factors; polymer characteristics and environmental factors.

2.4.1 Polymer characteristics

2.4.1.1 Chemical structure

It is primarily the chemical structure, which decides the degradation mechanism for any polymer and dictates its degradation characteristics. For example, the presence of hydrolysable linkages in a polymer will make it degradable by hydrolytic and/or enzymatic process. Most of the biodegradable polymers therefore contain easily hydrolysable linkages. These polymers act as a source of carbon and hydrogen for the microorganism and are utilized by the enzymatic process. Similarly a polymer undergoes photo-degradation, when it has suitable chromophoric groups in its structure capable of absorbing UV light. This leads to the formation of free radicals on the surface, which results in the propagation of photo-oxidation in presence of atmospheric oxygen, resulting in the formation of oxidation products, finally leading to the degradation of the polymer.

2.4.1.2 Molecular size

Initiation of degradation (particularly photo degradation) takes place due to the presence of end groups in the form of unsaturation, hydro-peroxides or any other functional groups on the polymer structure(7). High molecular weight polymer has lesser concentration of these chain end functionalities and is therefore more resistant to degradation.

2.4.1.3 Hydrophilicity

Polymers that are more hydrophilic, such as poly (vinyl alcohol), poly (acrylic acid), and polyether tend to be more biodegradable than hydrophobic polymers of comparable molecular weight. Also, increasing the hydrophilicity of a polymer by chemical modification increases its biodegradability (8). Hydrophilicity in polymers not only helps in better penetration of microorganism in the polymer but also induces the production of necessary enzymes within the microorganism relatively more easily compared to hydrophobic polymer.

2.4.1.4 Crystallinity Crystallinity also decides the degradation characteristics of a polymer. Crystalline regions of a polymer are more difficult to penetrate and are inaccessible to microbes as well as to abiotic agents. Amorphous regions are preferentially degraded in synthetic polymer as well as in biopolymers (9).

2.4.2 Environmental factors

The critical factors affecting degradation include total solar radiation, air temperature, relative humidity, mechanical stress, agrochemicals, air pollutants and critical combinations of the above factors (10).

2.4.2.1Total solar radiation

The exposure of many plastic materials to solar irradiation (with wavelengths of 290–2500 nm) affects the chemical structure and consequently their mechanical properties. Such degradation occurs by a free radical mechanism, which includes initiation, chain propagation, chain breaking and termination steps. In order to start the photo-degradation process, the UV radiation has to be absorbed by the plastic film. PE itself (without any chromophores) cannot absorb UV radiation above 290 nm. The first step initiated by external impurities or catalyst residues with chromophoric groups, which are present in the polymer or by hydroperoxide or ketone groups, introduced during processing. Once free radicals are formed in the initiation step, the photo-oxidation process propagates, giving rise to various oxidation products, finally leading to disintegration of the PE film. Photo-oxidation depends on the diffusion of oxygen into the polymer, the material geometry (film thickness), the pollutants diffusion and the presence of additives. Thus, the critical factors related to the effect of the total solar radiation on the degradation of PE films may be summarized as follows.

(a) Ultraviolet radiation: Although the most energetic part of the solar spectrum is the UV radiation (wavelengths of 290–400 nm), the greatest sensitivity for LDPE is confined at 300–310 and 340 nm.

(b)Photo-absorbing chromophores: As mentioned already, absorption of UV radiation by the PE films is only possible in the presence of photo-absorbing chromophores. Photo-absorbing chromophores may be developed during manufacture ,use and also as photo-degradation byproducts. This last group of chromophores (containing carbonyls) may be used as indicators of degradation (i.e., by monitoring changes of carbonyl groups in the film).

(c) Diffusion of oxygen: Photooxidation of the outer layers of the PE film is the combined action of the UV radiation absorbed by photo-absorbing chromophores (which were developed in the PE material during manufacture and/or use) and the direct contact with the atmospheric oxygen. The free radicals produced in this way may then react further with the atmospheric oxygen (the free radicals acting as new chromophores) and lead to further degradation of the plastic. Photo-oxidation of the inner layers is possible only up to the depth where oxygen can diffuse, depending on thickness, percentage of crystalline phase and tensile stresses

2) Air temperature: This is particularly important in green houses where the influence of air temperature is a critical factor in degradation as it increases the rate of various chemical reactions associated with degradation. Relatively high temperatures are reached at the metal parts of the greenhouse construction. The difference between high temperatures during the day and low temperatures during the night can also lead to increased degradation. Also the influence of the construction (wood backing, aluminum backing, stainless-steel backing) is an important parameter in this respect.

Thus, the critical factors related to the air temperature effect on the degradation of PE films may be summarized as follows.

(a) Rate of photo-oxidation increasing with temperature and

(b) Degradation increasing with cyclic temperature changes.

3) Relative humidity and water condensation: Water condensation can lead to the gradual wash-out of some additives leading to loss of their properties. Humidity can more easily permeate the amorphous regions of the polymer and modify its original properties. The critical factors related to the water condensation and relative humidity effects on the degradation of PE films may be summarized as follows.

(a) Photo-chemical generation of hydroxyl radicals and other reactive species (chromophores) which can promote various free-radical reactions

(b) Influence of the duration of wetness

(c) Influence of pH and composition (e.g., contaminants) of the precipitation.

4) Mechanical stress

In general, the mechanical properties of polymers depend on molecular weight, crystallinity, presence of branches and cross links. Some of the most dramatic changes that occur in an irradiated polymer are in its mechanical properties. However, these properties do not change at the same rate as the chemical reactions (photo-oxidation) take place in the polymer. Wind loads can impose increased tensile and shear stress on the greenhouse plastic film leading to premature failure of the film. In addition, friction and abrasion are important degradation enhancing factors due to wind action. Also, accumulation of snow for prolonged period can lead to problems of creep and possible failure due to constant loading. Hail may result in puncturing of the films (impact failure) and then tear propagation. Not only do the externally imposed stresses influence directly the mechanical degradation of the plastic film, but they can also indirectly accelerate the photo-degradation process. In particular, degradation due to mechanical loading is related to slippage of chains (more frequently) and bond scission (direct effect) and increased chemical reactivity (indirect effect). Thus, the critical factors related to the mechanical stress effect on the degradation of PE films may be summarized as follows:

(a) Direct mechanical degradation process i.e., bond scission or slippage of chains

(b) Indirect effect of stress on the rate of the photo-degradation process

(c) Indirect effect of abrasion and/or friction of the film with other elements (e.g. greenhouse structural elements) on the rate of the photo-degradation process (localized effects; possibly direct degradation due to friction)

(d) particular effects of the various film installation procedures (clipping system, wire-supporting system, etc.) on tearing or yielding or rupture of the film and possibly on local oxidation/degradation effects

(e) Effect of impact (e.g. hail) on degradation.

5) Agrochemicals and air pollutants

Sometimes the environmental pollution and/or the use of agrochemicals in the greenhouse affect the lifetime of the polymers due to possible chemical reactions. Due to chemical interaction, additives can modify their chemical structure and, consequently, exhibit reduction in activity.

Pollutants, such as polycyclic aromatic hydrocarbons, nitrogen oxides, sulphur oxides, ozone and hydrocarbons, can be absorbed by the film and can generate chromophoric groups that, by absorbing UV radiation can accelerate the photo-oxidation process. Thus, the critical factors related to the chemical degradation of PE films may be summarized as follows.

(a) Effect of agrochemicals-Various drastic agrochemicals and the techniques of application (direct contact or vapours), effect directly the degradation and indirectly on the rate of photo-degradation .
(b) Effect of solvents
(c) Effect of air pollutants (Air pollutants like NO, NO_2, SO_2, O_3) can cause damage due to acceleration of the photo-oxidation process and possible chemical reaction with film additives

.

6) Critical combinations

Combination of several of the above parameters can lead to increased degradation rates. Any critical combination will include:
(a) Basic combination (a high UV dose in combination with high temperatures or cycles of high temperature in the presence of oxygen and chromophores)
(b) PE reacting with NO_2 at elevated temperatures due to the presence of impurities agrochemicals (Cl and/or S containing agrochemicals) combinations of them limiting the lifetime of the plastic film by interacting with certain classes of stabilizing additives (relative humidity and water condensation) combination of high temperature and humidity (and/or water condensation depleting UV stabilisers) possibly increasing the photo-oxidative degradation.

2.5 Criteria for characterization of degradation

Based on the analysis of the critical ageing factors it is clear that various interacting ageing factors and degradation mechanisms are responsible for the final degradation of the plastic films. As a consequence, combination of quantitative criteria rather than a single criterion should be considered for the monitoring the film degradation. Representative qualitative criteria for the same are presented below.

2.5.1 Carbonyl groups

The rate of carbonyl growth is an indication of oxidative reactions. As a result of degradation, significant changes in carbonyl groups absorbance of the PE are observed, by means of IR spectroscopy. An increase in carbonyl groups absorbance is observed in the cases of natural weathering, thermal ageing or accelerated photo-irradiation. The relative magnitude of carbonyl groups absorbance measured in each case varies depending on several interacting factors. The more amorphous the polymer material, the easier is the diffusion of oxygen. This implies more intense oxidation, combined with the exposure to UV radiation and so faster growth of carbonyls.

2.5.2 Crystallinity

Crystallinity changes during the degradation of polymers are particularly important in relation to other chemical changes, such as oxidation, chain scission, cross-linking and hydrolysis. The gradual increase in percent crystallinity is linked to the formation of oxygen containing groups. High initial crystallinity makes structural changes during photo ageing of PE difficult. Techniques like X-ray diffraction and Differential Scanning Calorimetry (DSC) may be used to estimate the change in the degree of crystallinity by measuring changes in enthalpy. Crystallinity changes may also be evaluated indirectly by IR spectroscopy

2.5.3 Molecular weight

High molecular weight and low degree of branching lead to polymers with a longer life because mechanical properties such as elongation at break and tensile strength are improved. Degradation is usually accompanied by a decrease of molecular weight of film. The molecular weight can be determined by various techniques like gel permeation chromatography, osmometry and viscosity measurement method etc. Change in MFI is also an indication of molecular weight change.

2.5.4 Mechanical properties

Tensile strength and elongation is quite sensitive to the changes in the molecular weight of the polymer. Thus, changes of the molecular weight during degradation affect directly these properties. Degradation can be roughly evaluated from loss of mechanical strength. The mechanical properties which may be measured include elongation at break, tensile strength, modulus of elasticity, etc, tear resistance (initial tear resistance and tear propagation resistance), impact resistance and creep.

2.5.5 Density

Degradation of polyethylene is generally accompanied with an increase in density. Increased density results in reduced diffusion, probably as a result of PE cross-linking and increased crystallinity. Density changes depend on temperature and some competing processes such as the formation of double bonds during irradiation and cross-linking.

2.6 Environmentally degradable polyethylene and photosensitizing additives

Environmentally degradable polyethylene are those polymers which degrade by a combined and cumulative effect of heat, sunlight, oxygen, water, pollution, micro-organisms (bacteria, fungi, alga, etc.), macro-organisms (insects, crickets, woodlice, snails, etc.), mechanical action, wind, and rain and so on. The main mechanisms of environmental degradation are photolysis, thermolysis, oxidation, hydrolysis and biological attack. The overall environmental degradation of polymers can thus be divided into biocatalytic processes involving enzymes (biodegradation); and pure chemical and radical processes (physical-chemical degradation) such as oxidation, irradiation and hydrolysis. Oxidative degradation and biodegradation are the most important processes involved in the environmental degradation of polyolefins.

Photosensitizing additives in the degradable plastics include additives based on transition metal ions (Mn, Cu, Fe, Co, Ni, Ce) and metal complexes (e.g., cobalt stearate, cerium stearate), which render conventional polyethylene susceptible to hydroperoxidation. The critical point is that only trace quantities of Mn, Cu, Fe, Co, Ni and Ce are added to the polymer and these concentrations mimick the trace elements present in most soils. These transition metal compounds are typically incorporated into the final formulation as additives at levels of a few percent. They are proprietary combinations of additives, which, with appropriate compositional adjustments, allow for a wide range of storage, use, and degradation times, depending on the end use and the environment. Polyolefin pellets, which have been compounded with these additives, are processed on conventional equipment at normal speeds. An important feature of these additives is that they are activated both by the action of sunlight and by heat.

CHAPTER-3

Experimental

3.1 Materials

Manganese acetate, ferric nitrate, sodium hydroxide and stearic acid (AR grade E.Merck) were used for the synthesis of metallic additives. Low-density polyethylene (LDPE) of grade (Indothene24FS040) and linear low-density polyethylene (LLDPE) of grade (GleneF20009) have been used for the preparation of films.

Property	*LDPE Indothene24FS040*	*LLDPE Glenef20009*
Melting point (^{0}C)	110	120
Density (g/cm^3)	0.92	0.95
MFI (g/10min)	4	1.09

3.2 Preparation of metallic additives

3.2.1 Synthesis

Metal stearates, namely manganese stearate and iron stearate were obtained by the reaction of sodium stearate with manganese acetate and iron nitrate respectively according to the procedure (11) reported below. The general reaction scheme for the preparation of metal stearate is shown as below in reaction

$$CH_3(CH_2)_{17}COOH \ +NaOH \longrightarrow CH_3\ (CH_2)_{17}COONa$$

$$2\ CH_3\ (CH_2)_{16}COONa + Mn(ac)_2 \longrightarrow [CH_3\ (CH_2)_{16}COO]_2Mn$$

$$3CH_3\ (CH_2)_{16}COONa + Fe(NO_3)_3 \longrightarrow [CH_3\ (CH_2)_{16}COO]_2\ Fe$$

Scheme3.1: Double decomposition technique for the synthesis of Metal stearates

Procedure: A typical procedure for the preparation of metal stearate is as follows. 1.4g of NaOH was dissolved in 500ml distilled water. This was followed by the addition of 10g (0.1mol) of stearic acid at 90 ^{0}C for 0.5h to form sodium stearate. Subsequently, a 10% w/v solution of 4.74g of ferric nitrate and 4.47g of manganese acetate was added dropwise with continuous stirring to prepare ferric stearate and manganese stearate respectively. Addition of the salt led to immediate precipitate of the stearate which was filtered and washed repeatedly with water till the effluent showed absence of metal. The metallic soap was vacuum dried prior to blending with polymer.

3.2.2 Physico-chemical characterization of metallic additives

3.2.2.1 Physical properties

The solubility of additives was checked in various solvents. The solvents chosen included polar/ non-polar and protic/ non-protic solvents. Table 3.1 represents the solubility behaviour, ash content and non-volatile content of metallic additives.

Table 3.1 Physical properties of metallic additives

Metallic additive	Non Volatile content	Ash content	Colour	Solubility			
				water	toluene	acetone	DMSO
Iron stearate	99.3%	8.42	red	Insoluble	soluble	insoluble	insoluble
Manganese stearate	99%	10.6	pink	insoluble	soluble	insoluble	Partially soluble

3.2.2.2 Non-volatile content

A weighed amount of sample was placed in a drying oven maintained at a temperature of 105^{0}C. After 3 h, the sample was removed from the oven, cooled in dessicator and reweighed. The weight of the residue, consisting of solid and non-volatiles, was calculated as a percentage of initial sample weight.

3.2.2.3 Ash content

For determination of ash content, the sample was heated in a crucible over a hot plate to drive out all volatile solvents and moisture. It was subsequently transferred to a muffle furnace where the temperature was maintained at 550^{0}C for 2 h to ensure final ignition. The remaining ash was weighed and reported as ash content.

3.2.2.4 Free fatty acid content

It was determined chemically by titration of the unreacted carboxyl groups against a standard base. For this purpose, a known amount (~1g) of metal complex was hydrolyzed and then immersed in acetone for swelling/dissolution. After equilibrium swelling, the solution was titrated against previously standardised methanolic NaOH using phenolphthalein as indicator. The carboxyl-content was then calculated using the following equation.

$$\text{Carboxyl content} = \frac{(V_1 - V_2) \times N_1}{W \times 1000}$$

Where V1 and V_2 are the volume (mL) of NaOH consumed by additive and blank respectively, N_1 is the normality of methanolic NaOH and W is the weight (g) of cobalt carboxylate. In all the samples of metal carboxylates, free fatty acids were absent thereby indicating that all the acidic functionalities were consumed during the preparation of metal carboxylates.

3.2.2.5 Elemental analysis

An elemental analyzer (Elementar, Vario EL) was used to determine the percentage of C, H, N, and S in various additives. These studies were aimed at determining the molecular formula of the additives.

Table 3.2 Results of Elemental Analysis and Metal Content

Cobalt carboxylate	**Experimental (%)**				**Formula predicted from elemental analysis**
	C	**H**	**O**	**metal**	
Iron stearate	66.45 [67.82]	11.17 [12.4]	22.38 [15.07]	5.31 [4.71]	$Fe(OOCC_{17}H_{35})_2.2H_2O$
Manganese stearate	65.4 [65.75]	10.99 [12.02]	15.2 [14.61]	8.41 [7.62]	$Mn(OOCC_{17}H_{35})_2.2H_2O$

3.2.2.6 FTIR

The structural characterisation of additives was done using FTIR spectroscopy. FTIR spectra were recorded using KBr pellets in the region of 400-4000 cm^{-1} using a BIORAD (FTS-40) spectrophotometer. The FTIR spectra of stearic acid exhibited characteristic (C = O) and (C-O) absorption bands at 1714 cm^{-1}, 1409 cm^{-1} due to the presence of carboxylic groups. An absorbance band at 1560 cm^{-1} was observed in iron and manganese carboxylates, which was due to the asymmetric vibration stretching of the carboxylic group coordinated to the metal ion (Figure 3.1).

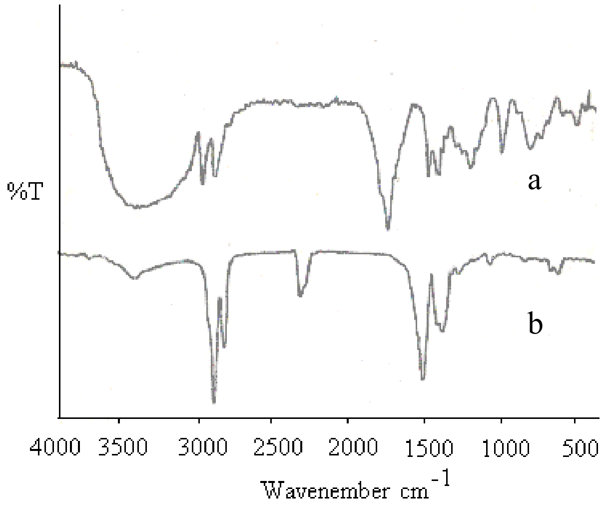


Figure 3.1:FTIR Spectra (a) Stearic acid (b) Manganese Stearate

3.2.2.3 Thermal characterization

In the DSC scans of metallic salts, a sharp endothermic transition due to melting was observed. The DSC traces are shown in Figure 3.2 below. The melting point was noted as peak of the endothermic transition which is found to be 120 and 90^{0}C for manganese stearate and iron stearate, respectively. The thermogravimetric (TG) traces of iron and manganese stearate in the temperature range of 50-475^{0}C (N_2 atmosphere) indicate that these additives are stable under the processing conditions.

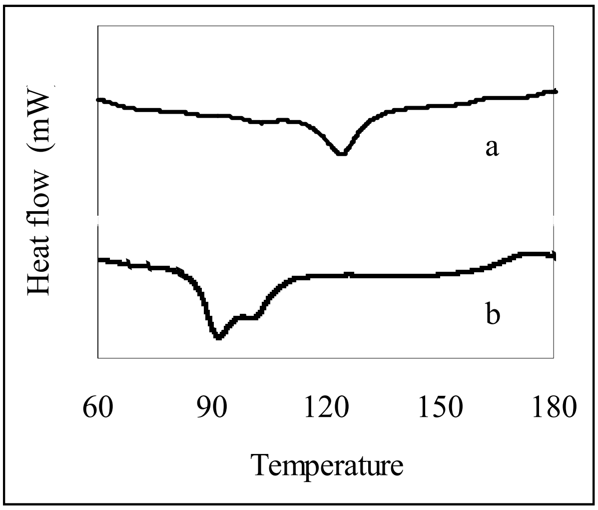


Figure 3.2 DSC traces of (a) Manganese Stearate (b) Iron Stearate

3.3: Preparation of films

LDPE was blended with varying amounts of metal stearate (0.5-1%w/w) using an extruder attached with film blowing die to prepare film of 70 ± 5μ thickness. The temperature in the barrel zones were maintained at 120^0 C (feed zone), 130^{0}C (compression zone) and 140^{0}C of die section (12). The details of formulation are presented in table 3.3.

Blown film extrusion is the process by which most commodity and specialized plastic films are made for the packaging industry. The film blowing process basically consists of a extruding a tube of molten thermoplastic and continuously plastic melt is extruded through an annular slit die, usually vertically, to form a thin walled tube

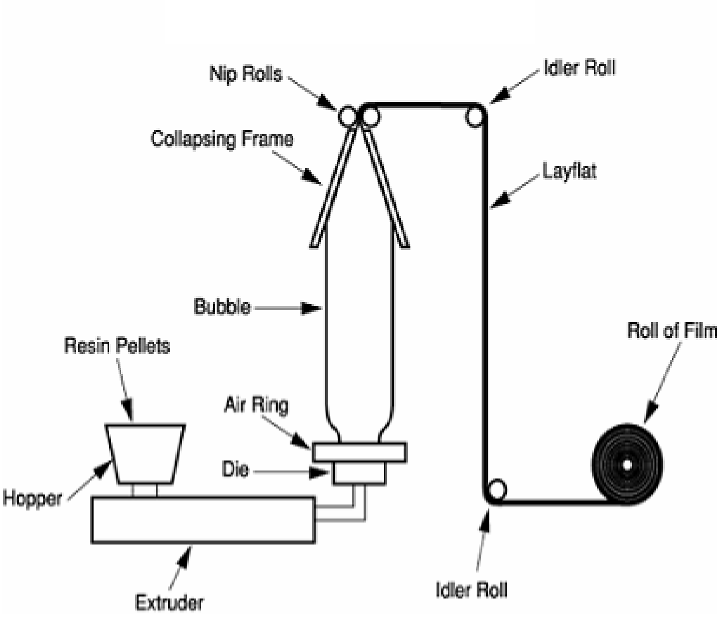


Figure 3.3 Blown film line

Air is introduced via a hole in the centre of the die to blow up the tube like a balloon. Mounted on top of the die, a high-speed air ring blows onto the hot film to cool it. The tube of film then continues upwards, continually cooling, until it passes through nip rolls where the tube is flattened to create what is known as a 'lay-flat' tube of film. This lay-flat or collapsed tube is then taken back down the extrusion ' tower' via more rollers.

Table 3.3: Details of formulations and their sample designation

Sample designation	Amount (g)				MFI (2.16kg 190^0C)
	LDPE	LLDPE	Manganese stearate	Iron stearate	
F1	300	_	_	_	3.6
F2	-	300	-	-	0.9
FMS1	300	_	1.5	_	3.6
FMS2	300	_	2.25	_	3.7
FMS3	300	_	3.0	_	3.7
FIS1	300	_	_	1.5	3.6
FIS2	300	_	_	2.25	3.6
FIS3	300	_	_	3.0	3.6
FMS4	225	75	2.25	–	2.8
FMS5	150	150	2.25	–	2.0
FMS6	75	225	2.25	–	1.4

3.4 Degradation studies

3.4.1 Thermal degradation

The degradation was carried out by placing the extrudate films of different composition in an air oven at 70^0 C for extended periods and the films were removed at regular time intervals. The degradation was assessed by monitoring change in mechanical properties, structure, MFI studies (13).

3.4.2 Photo-oxidative degradation (Accelerated weathering)

Accelerated photo degradation studies were carried out by exposing films to xenon arc lamp. Accelerated weathering simulates the damaging effects of long-term outdoor exposure of materials and coatings by exposing test samples to varying conditions of the most aggressive components of weathering - light, moisture, and heat. The Xenon-Arc lamp uses a long arc, air-cooled xenon lamp equipped with inner and outer filters as the light source. When borosilicate inner and outer filters are used, the irradiance spectrum closely resembles natural daylight, as shown in Fig. 3.4.

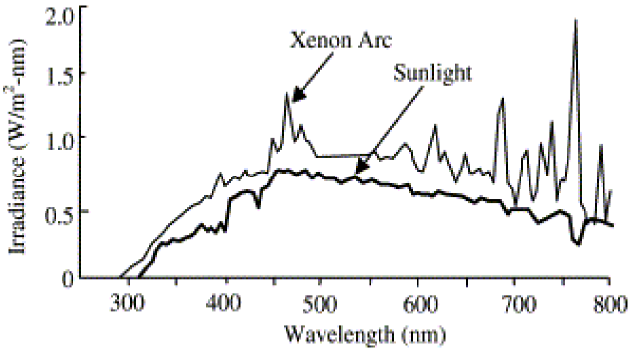


Figure3.4 Comparison of Spectra of xenon arc with borosilicate filters and sunlight.

Heaters control the temperature of cabinet. Microprocessors monitor and precisely control the radiation applied to the test samples. Films are exposed for the radiation of 550 W/m^2. Samples after irradiation was collected at regular time interval to evaluate the effect of irradiation time on degradation.

Figure3.5 Table top suntest apparatus used for accelerated weathering

A limitation of this device, however, is its high initial cost and maintenance. The filters and xenon lamps need to be replaced frequently to maintain a constant radiation spectrum.

3.4.3 Natural weathering

Natural weathering includes the action of any combination of atmospheric (natural) weathering conditions on polymeric films. Examples of natural weathering conditions include temperature variations, sunlight, moisture, salt, pollution, erosion, and corrosive chemicals.

Films were exposed at Delhi college of Engineering facing north east direction with an inclination angle 45^0. These experiments were started in month of March, 2007. Meteorological conditions for the site are presented in Table 3.4.

Table3.4 Meteorological conditions for the site (14-15)

	March	*April*	*May*	*June*
Average maximum temperature (^{0}C)	29	36	39	39
Average minimum temperature (^{0}C)	15	22	26	28
Average relative Humidity %	47	34	33	46
Daily Global solar radiation (kW/m^2)	6.34	7.14	7.51	6.76

3.4.4 Kinetics of degradation

The kinetics of degradation provides parameters, which can be used to deduce the lifetime of polymers at different temperatures. The thermal decomposition of linear polythene has been reported to occur by random chain scission yielding little or no monomer but many small fragments. However, LDPE contains short butyl branches, which can act as weak links causing initiation to occur adjacent to these sites. It is almost impossible to obtain the exact kinetic parameters for each reaction involved in the polymer decomposition and apparent kinetic parameters are often used to represent the behaviour of polymer decomposition in general. Actually these parameters rather represent the overall weight loss behaviour during the polymer thermal decomposition as a function of temperature.

The non-isothermal kinetics of degradation was performed on a simultaneous Perkin Elmer Diamond STG-DTA-DSC. The experiments were carried out in nitrogen at a purge rate of 100 ml/min. For each polymer, samples of 3.5±0.3 mg were equilibrated to 200^{0}C before being heated to 550^{0}C at different heating rates (3, 5 and 7^{0}C/min).

Multiple constant heating rates- Flynn- Wall –Ozawa method

The most commonly used approach to determine the apparent kinetic parameters is first to measure the weight loss behaviour during the material decomposition and then to employ the Arrhenius equation to fit this data.

$$\frac{d\alpha}{dt} = Ae^{-\frac{Ea}{RT}}(1-\alpha)^n \qquad \text{...3.1}$$

Where A is the frequency factor, n is the reaction order, E_a is the apparent kinetic energy of degradation reaction, R is the gas constant, α is the conversion and T is the absolute temperature. In thermo gravimetric analysis, the conversion rate of a reaction is defined as the ratio of actual mass loss to the total mass loss corresponding to the degradation process.

$$\alpha = \frac{M_0 - M}{M_0 - M_f} \qquad \text{...3.2}$$

Where M, Mo and M_f are the actual, initial and final mass of the sample respectively.

Flynn and coworkers derived a method for the determination of activation energy based on the following equation.

$$\log\beta = .457\left(\frac{-E_a}{RT}\right) + \left[\log\left(\frac{AE_a}{R}\right) - \log F(\alpha) - 2.315\right] \qquad \text{......3.3}$$

Where, β is the heating rate. Thus, at the same conversion, the activation energy, E_a is obtained from the plot of log β against 1/T.

3.4.5 Lifetime predictions

Lifetime estimations are very useful in the selection of polymers for different applications. The lifetime is usually determined by accelerated aging, like air oven aging studies, which require extended time periods. The apparent kinetic parameters calculated from this study can be used to arrive at the lifetime of the formulations. The estimated lifetime of a polymer to failure has been defined as the time when the mass loss reaches 5 wt%, from the integration of equation 3.3 the lifetime can be estimated as follows.

$$t_f = \frac{0.0513}{A} \exp \frac{E_a}{RT} \qquad \ldots\ldots 3.4$$

3.5 Evaluation of degradation

3.5.1 Mechanical testing

The tensile tests were performed on LDPE films according to ASTM 882-85 using a materials testing machine (Model JRI-TT25). Films of 100 mm length and 10 mm width were cut out from the exposed films and subjected to a crosshead speed of 200 mm/min (16). The tests were undertaken in an environment at 20^0C and with a relative humidity of 65%. Three samples were tested for each experiment and the average value has been reported.

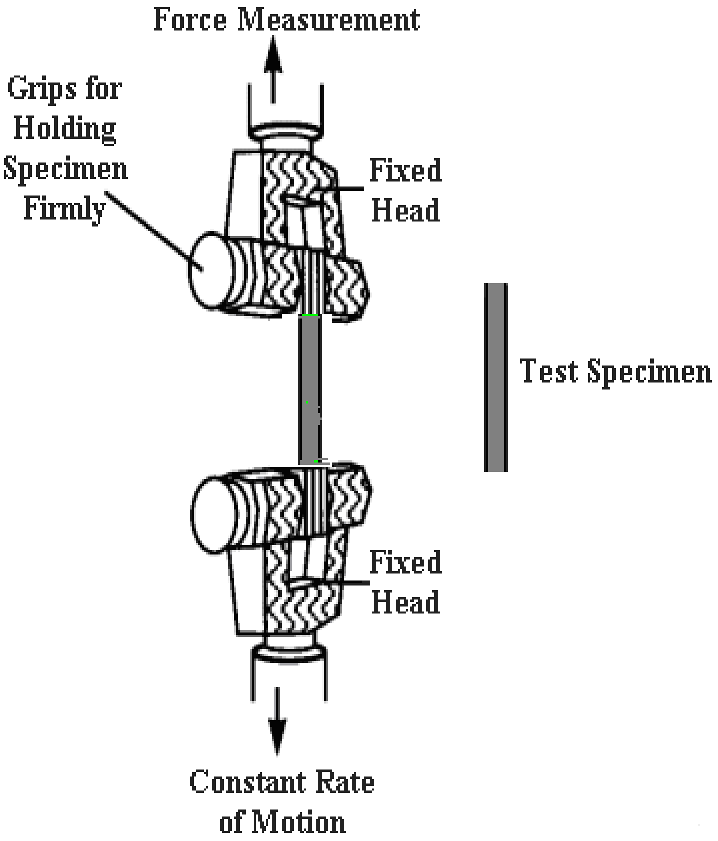


Figure3.6 Tensile test for films

3.5.2: FTIR spectroscopy

FTIR is one of the most powerful tool for identifying functional groups formed on the surface of polymer as a result of degradation. The wavelength of light absorbed is characteristic of the chemical bond.

The structural changes occurring in the LDPE films upon exposure were investigated using FTIR spectroscopy. Carbonyl Index (CI) was used as a parameter to monitor the degree of photo-oxidation of polyethylene and has been calculated according to the baseline method(17).

$$\text{Carbonyl Index (CI)} = \frac{\text{Absorption at 1740 cm}^{-1}\text{ (the maximum of carbonyl peak)}}{\text{Absorption at 2020 cm}^{-1}\text{ (internal thickness band)}}$$

3.5.3 Melt flow index

The Melt Flow Index is a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the weight of polymer in grams flowing in 10 minutes through a capillary of specific diameter and length by load of 2.16 kg as per ASTM D1238.

The melt flow rate is an indirect measure of molecular weight, high melt flow rate corresponding to low molecular weight. At the same time, the melt flow rate is a measure of the ability of the material's melt to flow under pressure. The melt flow rate is inversely proportional to the viscosity of the melt at the conditions of the test.

CHAPTER-4

Results and Discussion

4.1 Degradation studies of LDPE films with manganese stearate

4.1.1 Thermo–oxidation of LDPE films

LDPE films containing manganese stearate (0.5-1%w/w) were exposed in air oven at 70^0C. Samples were removed at regular time interval to monitor the degradation using various techniques.

4.1.1.1 Investigation of mechanical properties

One of the most widely recognized physical changes, known to result from ageing of polymer is the loss of mechanical strength. Table 4.1-4.2 represents the variation in tensile strength and % elongation due to thermal exposure. Figures 4.1-4.2 show the decrease in the mechanical properties of the films due to thermo-oxidation. As it is evident from the figures, the initial values of tensile strength and elongation were not affected by the incorporation of these additives clearly indicating that these additives do not lead to degradation in the processing stage. The initial tensile strength of all the samples was in the range of 8.50 $\pm$ 0.25 MPa. Tensile yield strength and percent loss in elongation at break have been reported here as they have been considered to be direct indication of degradation. Both tensile strength as well as elongation at break decreased because of thermo-oxidation, the decrease being more prominent in the films containing manganese stearate.

The decrease in these properties increased with concentration of the additive. Films containing manganese stearate show a rapid elongation loss of 68% within 24h of exposure at lower concentrations. At higher concentrations, i.e., $\approx$ 1%w/w of the additive, this loss in elongation increases to 78% within 24h of exposure and 96% within 200h of exposure. Films could not be tested further as they broke during handling as they broke during handling. LDPE films in the absence of additive however lost 25% of its elongation within 100h of exposure and retained 40% of its elongation even after 600h of thermo-oxidation.

Table 4.1 Effect of thermal exposure on tensile strength at yield (MPa) of different formulation

Sample designation	Effect of thermal exposure on tensile strength at yield (MPa) of different formulations			
	0 h	24 h	100h	200 h
F1	8.6	10.2	8.5	8.2
FMS1	8.5	10.0	8.3	8.0
FMS2	8.4	9.9	6.7	6.8
FMS3	8.2	8.3	4.6	3.4

Table 4.2 Effect of thermal exposure on % elongation at break of different formulations

Sample designation	Effect of thermal exposure on % elongation at break of different formulations			
	0 h	24 h	100 h	200 h
F1	883	810	723	465
FMS1	782	244	118	89
FMS2	751	169	64	44
FMS3	803	110	52	24

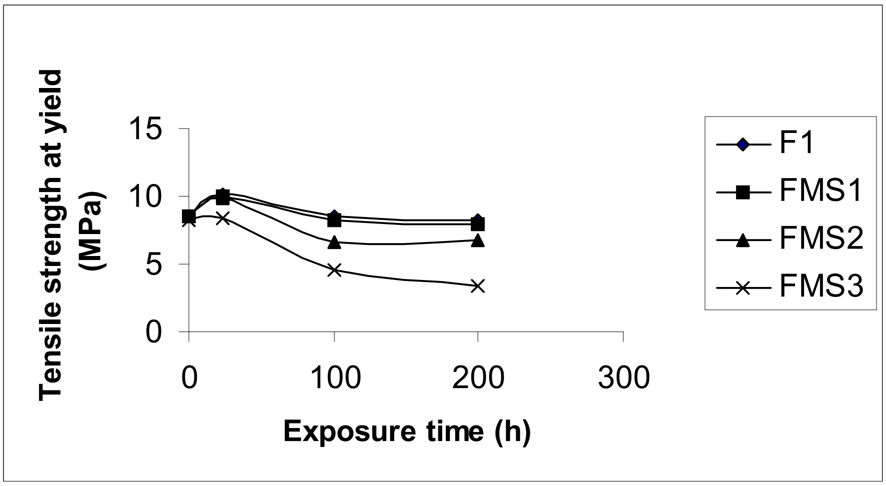


Figure4.1 Effect of exposure time on the tensile strength at yield of films with or without manganese stearate

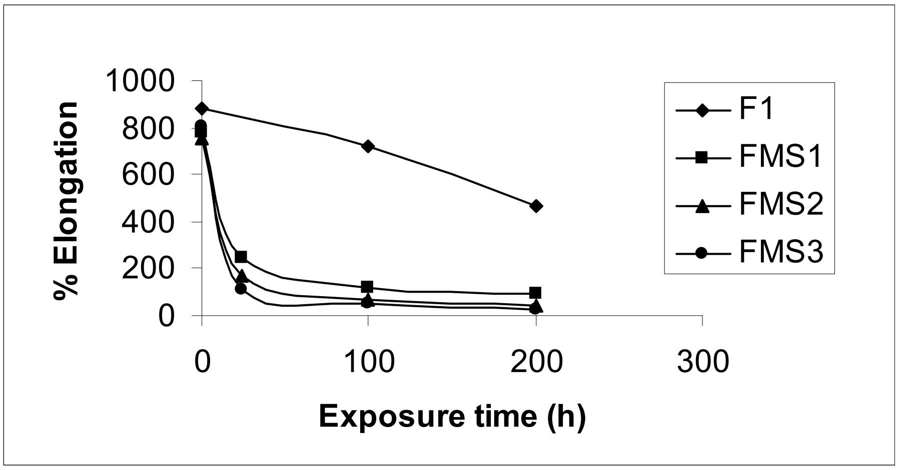


Figure 4.2 Effect of exposure time on the % elongation of films with or without manganese stearate

4.1.1.2 FTIR analysis

The change in FTIR spectra of F1, FMSI, FMS2 and FMS3 are presented in Figure 4.3-4.6. FTIR spectra of FMSI, FMS2 and FMS3 show evolution of various functional groups, especially absorbing in the carbonyl region (1785-1700 cm^{-1}). The carbonyl band can be assigned to C=O stretching vibrations in aldehydes and/or esters (1733 cm^{-1}) and carboxylic acid groups (1700 cm^{-1}) (18-20).

LDPE films containing manganese stearate exhibited similar changes in the spectra recorded for different formulation and the change was more pronounced at higher concentrations of the additive or after longer thermal exposure time. This change has been quantized in terms of carbonyl index (CI), which has been calculated by baseline method. The increase in CI with exposure has been depicted in Figure 4.7. The absorption due to other groups generated e.g. hydroxyl, vinyl, have been reported to follow the same trend as that of carbonyl. LDPE films however show very little change in these regions. It has been reported that films enter decay stage when the CI increases to 6 (21). The CI of virgin LDPE does not increase to 6 even after 600h of thermo-oxidation, while all the films containing manganese stearate reach this decay stage within 24h of exposure. Carbonyl index data have been reported in table 4.3. It is clearly seen from the data that samples undergo decay only when manganese stearate was present in different formulation.

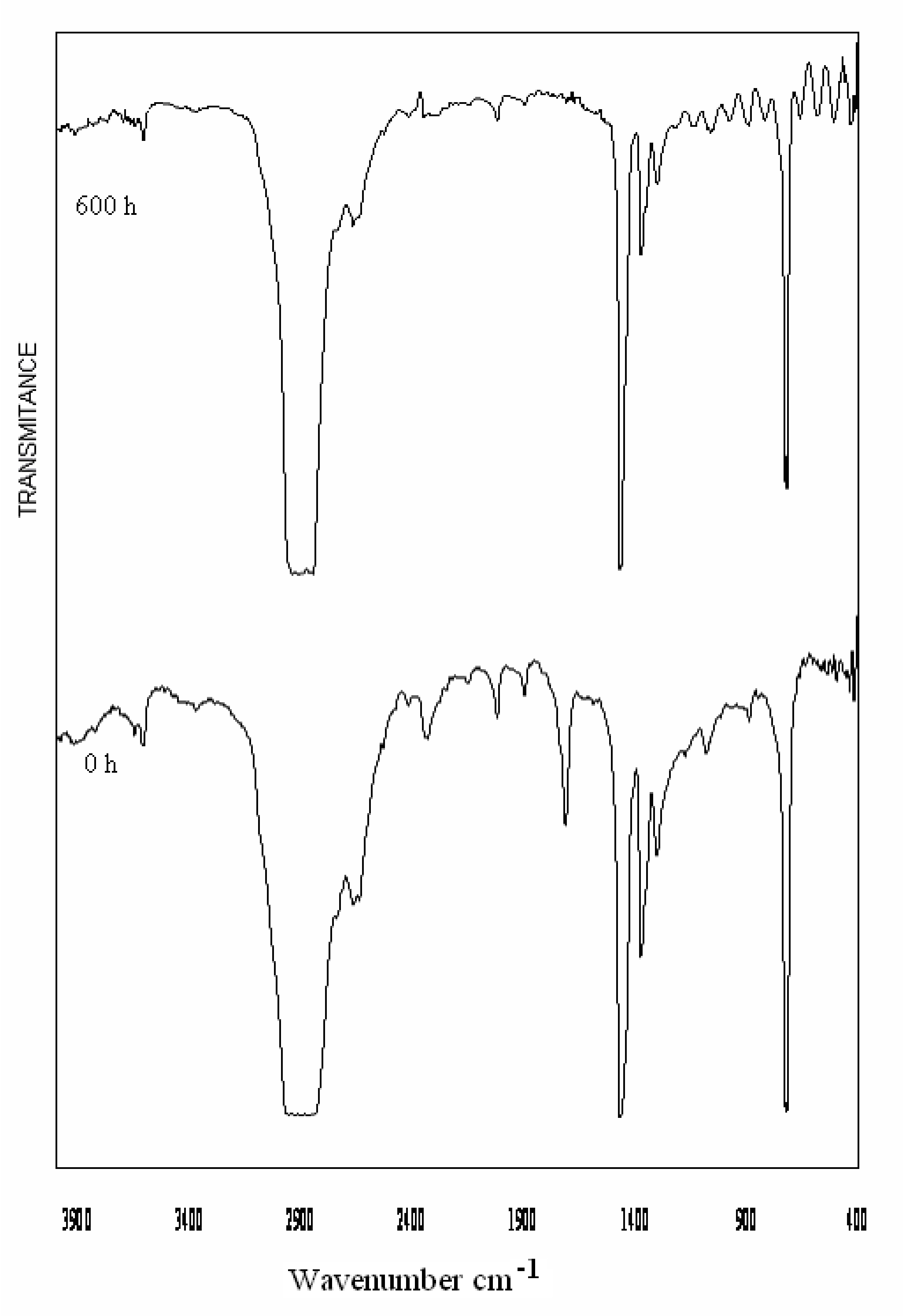


Figure4.3 FTIR spectra of F1 film before and after thermal exposure

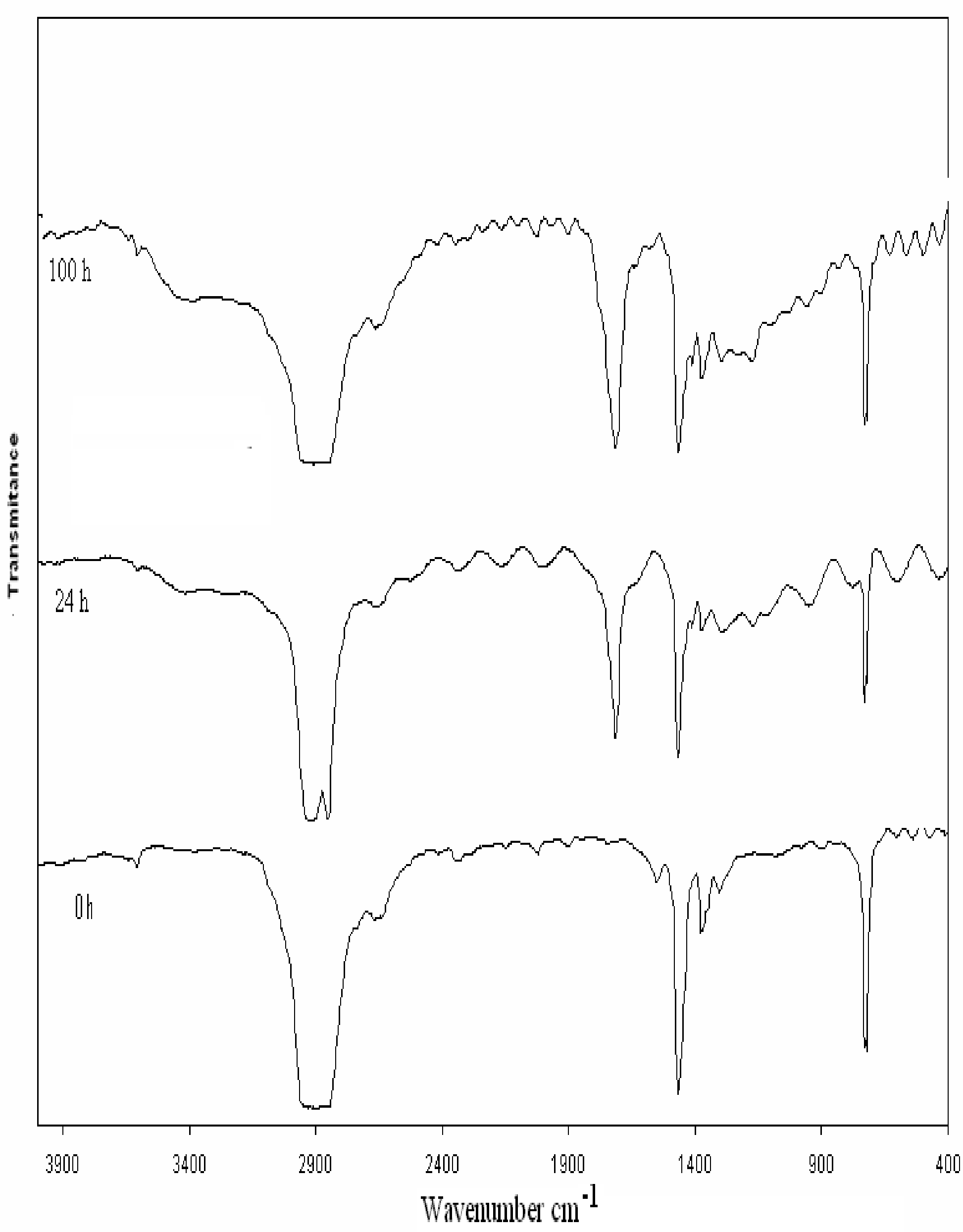


Figure4.4 FTIR spectra of FMS1 film before and after thermal exposure

Figure4.5 FTIR spectra of FMS2 film before and after thermal exposure

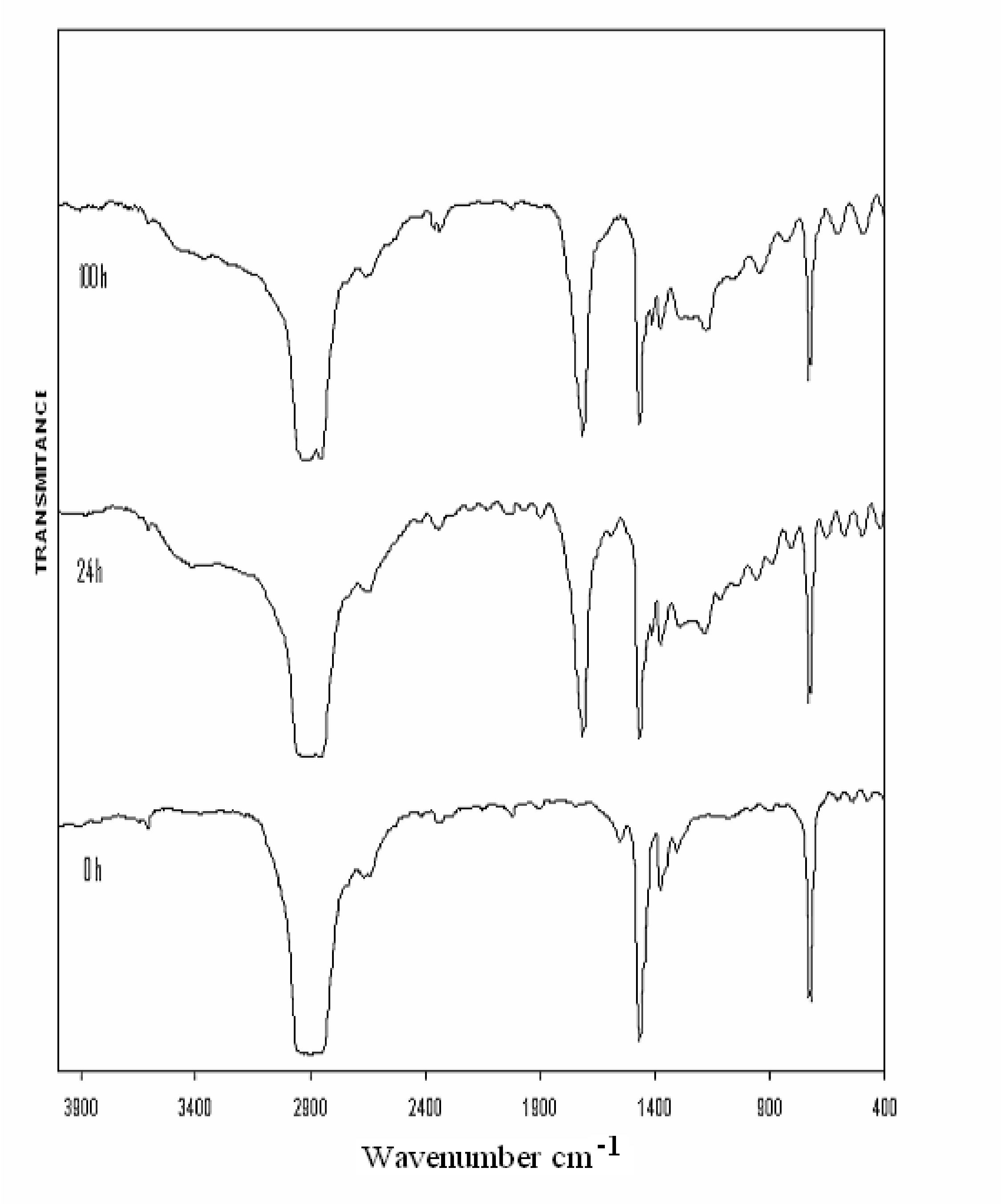


Figure4.6 FTIR spectra of FMS3 film before and after thermal exposure

Table 4.3 Effect of thermal exposure on carbonyl index (CI) of LDPE film with or without additive.

Sample	Carbonyl index after thermal exposure		
Designation	0 h	24 h	100 h
F1	0.87	1.23	1.32
FMS1	0.97	9.11	10.98
FMS2	1.05	10.8	12.06
FMS3	1.2	12.6	14.66

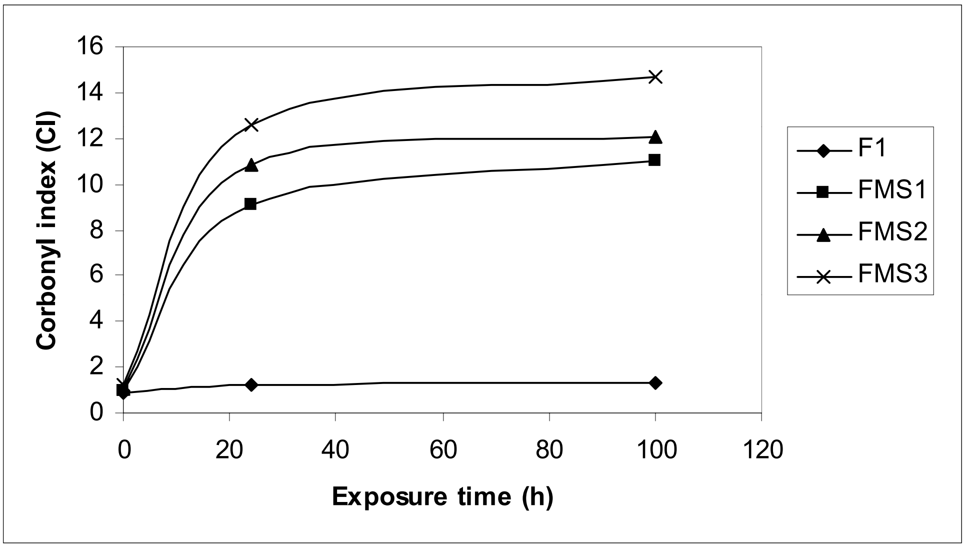


Figure 4.7 Effect of thermal exposure on carbonyl index (CI) of LDPE films with or without additive

4.1.1.3 MFI measurements

The decrease in the molecular weight was confirmed by investigating the increase in MFI with thermal exposure. Initial MFI of all the formulations was similar, indicating that the polymer does not undergo degradation during processing. The MFI of LDPE films increases from 3.6 to 4.5 after 400 h of thermal exposure while MFI of films containing manganese stearate could not be calculated due to free flow of samples. All the above results confirm that the degradation of the LDPE film containing manganese stearate starts within 24 hours of thermal exposure.

Table 4.4 Effect of exposure time (hours) and additive concentration on MFI of the films

Sample designation	Effect of exposure time and additive concentration on MFI of the films		
	0 h	24 h	400 h
F1	3.6	4.0	4.5
FMS1	3.6	*	*
FMS2	3.6	*	*
FMS3	3.7	*	*

* MFI could not be determined as samples flowed freely under test conditions.

4.1.2 Photo –oxidation of LDPE films

Films of different formulations containing manganese stearate were subjected to xenon arc exposure and removed at regular time intervals to investigate the degradation behavior.

4.1.2.1 Mechanical properties

Figures 4.8-4.9 depict the changes in mechanical properties of films due to photo-exposure. Unlike thermo-oxidation, some of formulation exhibited an increase in the tensile strength due to photo-oxidation. The photochemical degradation of LDPE results from competing reactions of cross-linking and chain scission. LDPE films containing manganese stearate show a loss in mechanical properties. The tensile strength at yield and % elongation data of different formulations are presented in Table 4.5-4.6.

Table 4.5 Effect of photo-oxidation on tensile strength at yield (MPa) of LDPE films of different formulations

Sample designation	Effect of photo-oxidative exposure on Tensile strength at yield (MPa) of different formulations.		
	0 h	40 h	76 h
F1	8.6	8.6	8.1
FMS1	8.9	8.9	4.3
FMS2	8.4	8.5	3.5
FMS3	8.2	7.7	3.0

Table 4.6 Effect of photo-oxidation on % elongation at break of LDPE films of different formulatios

Sample designation	Effect of photo-oxidative exposure on % elongation at break of different formulations		
	0 h	40 h	76 h
F1	85.8	59.7	40.5
FMS1	78.2	41.6	6.6
FMS2	75.1	27.6	3.6
FMS3	80.0	11.2	3.4

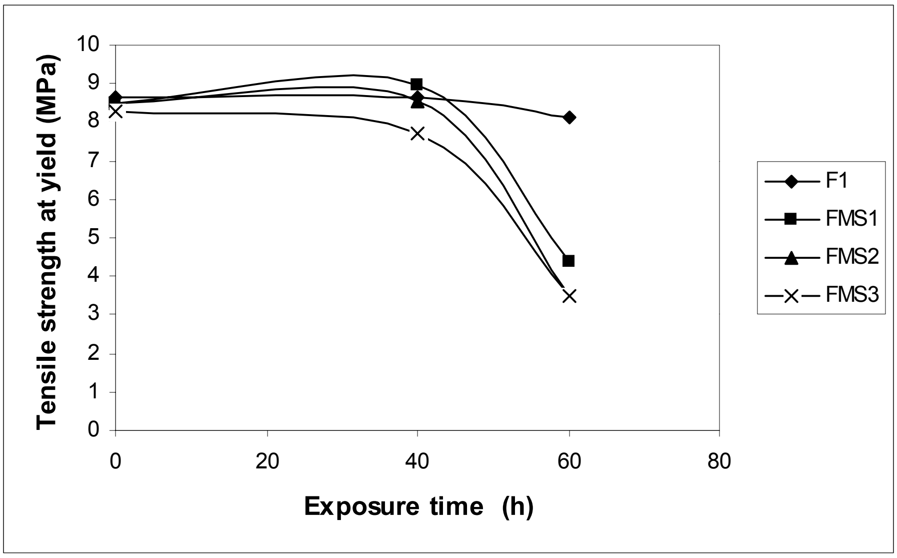


Figure 4.8 Effect of photo-exposure on tensile strength at yield (MPa) of different formulations

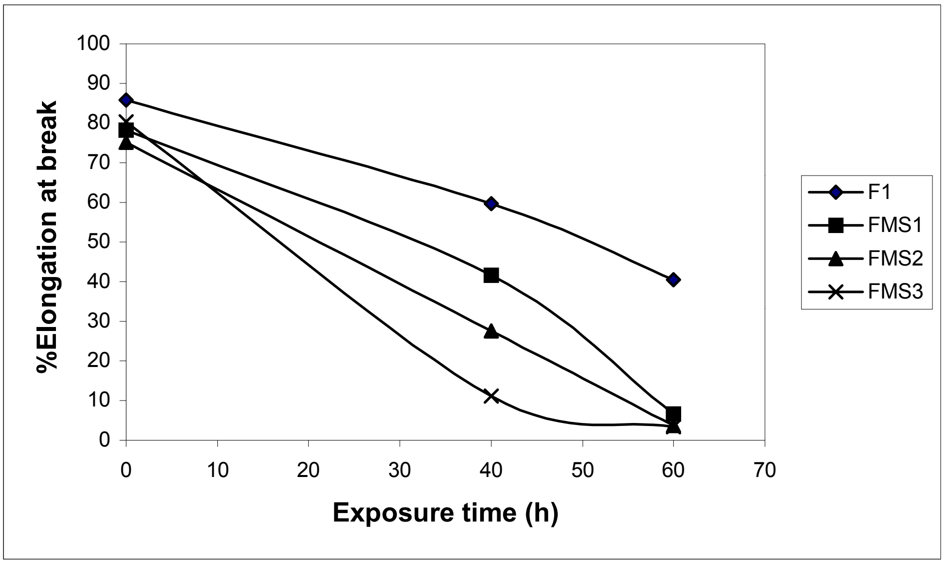


Figure 4.9 Effect of photo-exposure on % elongation at break of different formulations

4.1.3 Natural weathering of LDPE films

The natural weathering of any polymeric material generally depends on various parameters like UV content, temperature and humidity etc. The metrological and radiation data for the site are reported in Table 3.4.

4.1.3.1: Mechanical properties

Figure 4.10 and 4.11 represent the effect of exposure time on mechanical properties after being subjected to outdoor weathering. These factors determine the useful lifetime of a plastic product in outdoor applications. Tensile strength and % elongation was found to be sensitive to weathering. The yield strength for samples containing manganese stearate increased in the 20 days followed by a decrease in the subsequent month. Samples with 1% w/w manganese stearate show 82 % decrease in % elongation showing that manganese stearate is effective initiator for degradation.

Table 4.7: Effect of natural weathering on tensile strength at yield (MPa) of different formulations

Sample designation	Effect of natural weathering on Tensile strength at yield (MPa) of different formulations		
	0 days	20 days	30 days
F1	8.6	8.1	8.0
FMS1	8.9	9.9	8.4
FMS2	8.4	9.5	8.0
FMS3	8.2	8.1	6.7

Table 4.8: Effect of natural weathering on % elongation at break of LDPE films of different formulations

Sample designation	Effect of natural weathering on elongation at break of LDPE films of different formulations		
	0 days	20 days	30 days
F1	85.8	71.6	51.6
FMS1	78.2	65.6	23.6
FMS2	75.1	41.6	22.0
FMS3	80.0	30.4	14.2

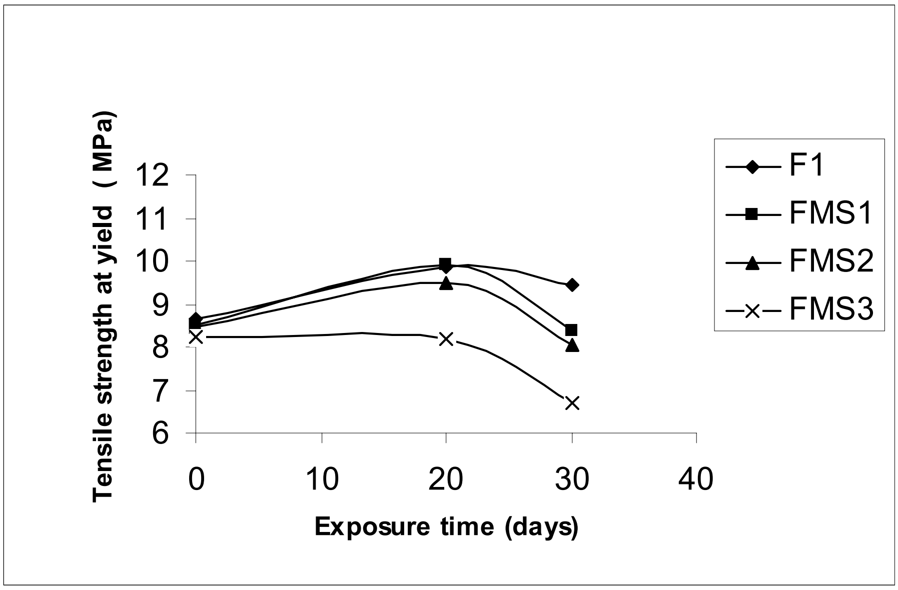


Figure 4.7: Effect of natural weathering on tensile strength at yield (MPa) of LDPE films of different formulations.

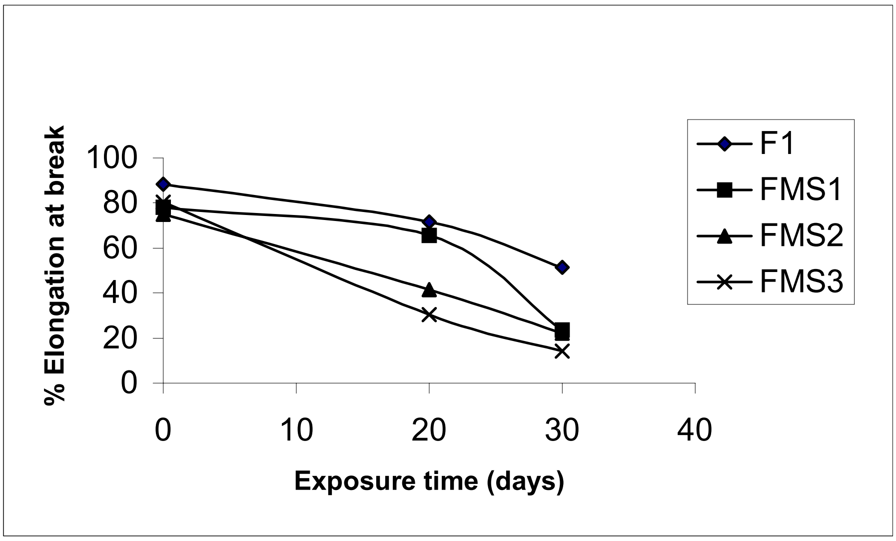


Figure 4.10: Effect of natural weathering on % elongation at break of LDPE films of different formulations

4.1.4 Lifetime prediction

The melting point of LDPE, as determined from DSC traces, was 110^0C. The thermogravemetric (TG) and DTG traces for F1 performed in nitrogen atmosphere at three different heating rates are presented in figure 4.11. It is evident from the figure that the sample exhibit single step decomposition in nitrogen atmosphere.

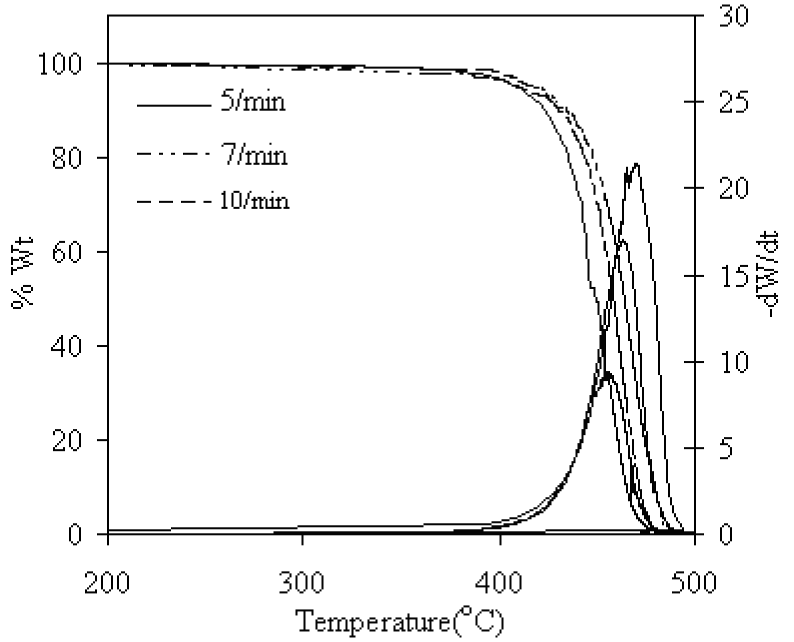


Figure 4.11 TG/DTG traces for F1 at different heating rates (nitrogen atmosphere)

Based on equation 3.3, the relationship between logarithm of heating rate (log β) and 1000/T for different values of percentage conversion for F1 in nitrogen atmosphere are shown in figure 4.12. The iso-conversion plots were found to be almost parallel straight lines in nitrogen atmosphere.

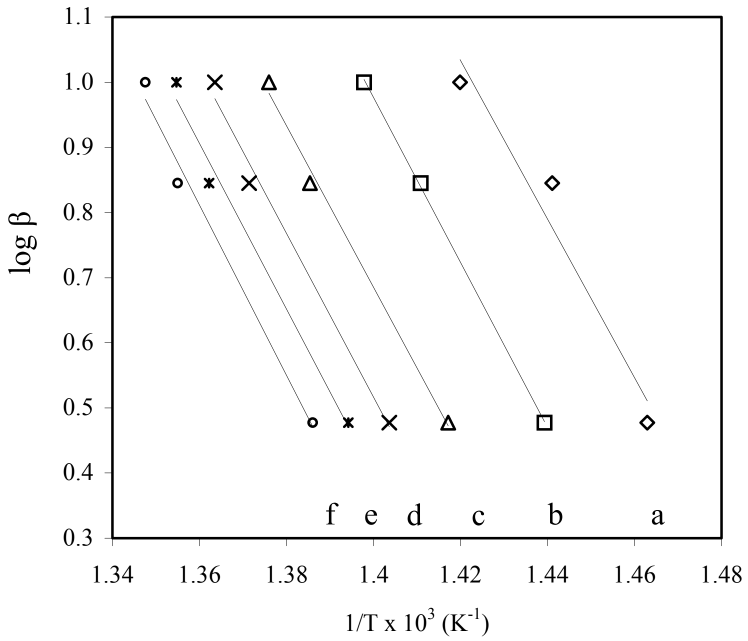


Figure 4.12 Plot of log β vs 1000/T (F1, nitrogen atmosphere, a=5%, b=10%, c=20%, d=30%, e=40%, f=50% conversion)

Lifetime estimation is very useful in development or selection of polymers for different applications. The lifetime is usually determined by accelerated aging, like air oven aging studies, which require long times. For a polymer, the lifetime can be estimated from equation-3.4. Degradation of polymer is first order reaction. The estimated lifetime at 5%, i.e., $\alpha = 0.05$ (24-26) weight loss at various temperatures are presented in Table 4.9. It can be seen that lifetime is strongly dependent on service temperature and decrease as temperature increases from 25 to 200^0C.

Table 4.9 Lifetime of various formulations at different temperature

Sample designation	Lifetime (minutes)				
	20^0C	75^0C	100^0C	150^0C	200^0C
F1	8.20E+26	7.50E+19	1.20E+17	2.70E+12	6.30E+08
FMS1	2.10E+10	2.91E+07	2.10E+06	2.77E+04	9.14E+02

4.2 Degradation studies on LDPE films in presence of iron stearate

4.2.1 Thermo–oxidation of LDPE films

LDPE films containing iron stearate (0.5-1%w/w) were exposed in an oven at 70^0C. Samples were removed at regular time interval to monitor the degradation.

4.2.1.1 Investigation of mechanical properties

Tensile strength and elongation is quite sensitive to the changes in molecular weight. These were found to be direct indicators of degradation as reported in the literature [27-29]. Thus changes of molecular weight during degradation affect directly the tensile strength. Fig 4.13-4.14 reveal that the changes in mechanical properties of film due to thermo-oxidative degradation. The initial tensile strength of films were in range of ≈ 8.50± 0.20 MPa. It is evident from the figures that initial values of tensile strength and % elongation were not affected by the incorporation of these additives. Table 4.10-4.11 represents variation in tensile strength and % elongation due to thermal exposure. It is clear from the table that film with iron stearate shows 46% loss in tensile strength after 300h of thermal exposure whereas it is only 19% in case of film in absence of pro-oxidants.

Table 4.10 Effect of thermal exposure on tensile strength (MPa) of LDPE films (iron stearate) of different formulations

Sample designation	Effect of thermal exposure on tensile strength (MPa) of different formulation			
	0 h	100 h	200 h	300 h
F1	8.6	8.5	8.2	8.3
FIS1	8.5	8.3	6.9	6.4
FIS2	8.4	8.0	6.2	5.7
FIS3	8.3	7.9	5.4	4.4

Table 4.11 Effect of thermal exposure on % elongation at break of LDPE films (iron stearate) of different formulations

Sample designation	Effect of thermal exposure on % elongation at break of different formulation			
	0 h	100 h	200 h	300 h
F1	85.8	72.5	46.7	27.7
FIS1	86.8	51.8	33.7	14.8
FIS2	88.5	33.0	13.7	8.3
FIS3	88.4	18.3	13.0	6.4

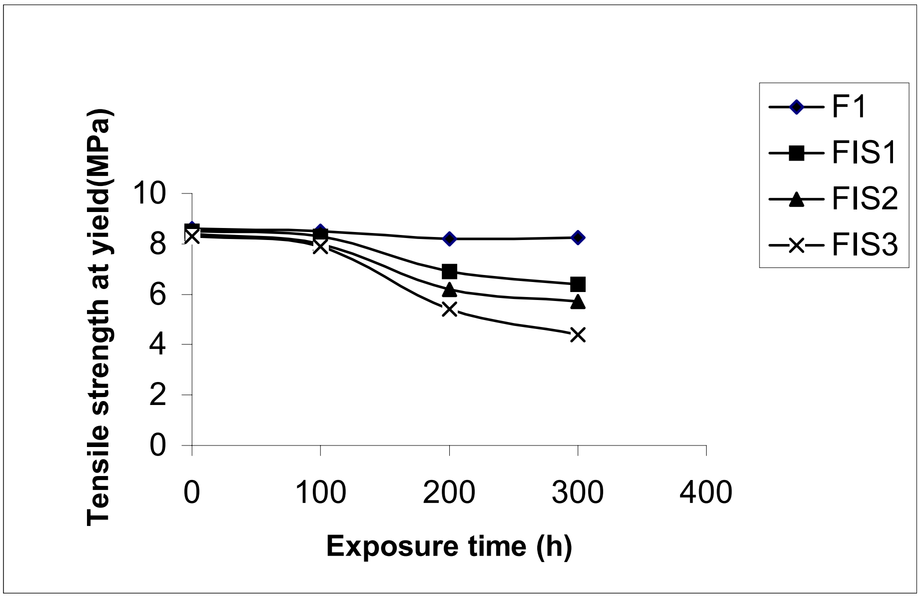


Figure4.13 Effect of exposure time on the tensile strength of different formulations

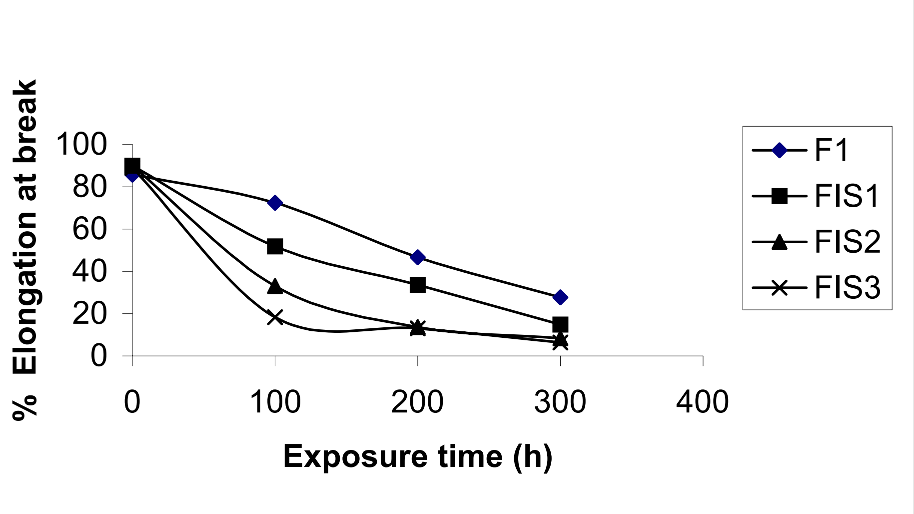


Figure4.14 Effect of exposure time on % elongation at break of different formulations

4.2.3 FTIR analysis

FTIR spectra of FIS1, FIS2, FIS3, before and after thermal exposure are shown in fig 4.15-4.17.The absorption band at ≈ 1740 cm^{-1} which can be assigned to the stretching of ketone group. The rate of carbonyl growth is an indication of oxidative reaction occured during thermal exposure.

The degradation was also monitored by the increase in the CI. In the FTIR spectra of LDPE film containing iron stearate, significant changes due to carbonyl group (1785-1700 cm^{-1}) were observed upon aging. The carbonyl band can be assigned due to the -C=O stretching vibrations in aldehydes and/or esters (1733 cm^{-1}), carboxylic acid groups (1700 cm^{-1}). The ratio of absorbance of carbonyl band and internal thickness band (2020 cm^{-1}) has been used to calculate the carbonyl index (CI). Increase in the CI of LDPE containing higher concentrations of iron stearate are shown in fig 4.18. It is believed that polyethylene films enter into the decay stage at CI greater than 6.

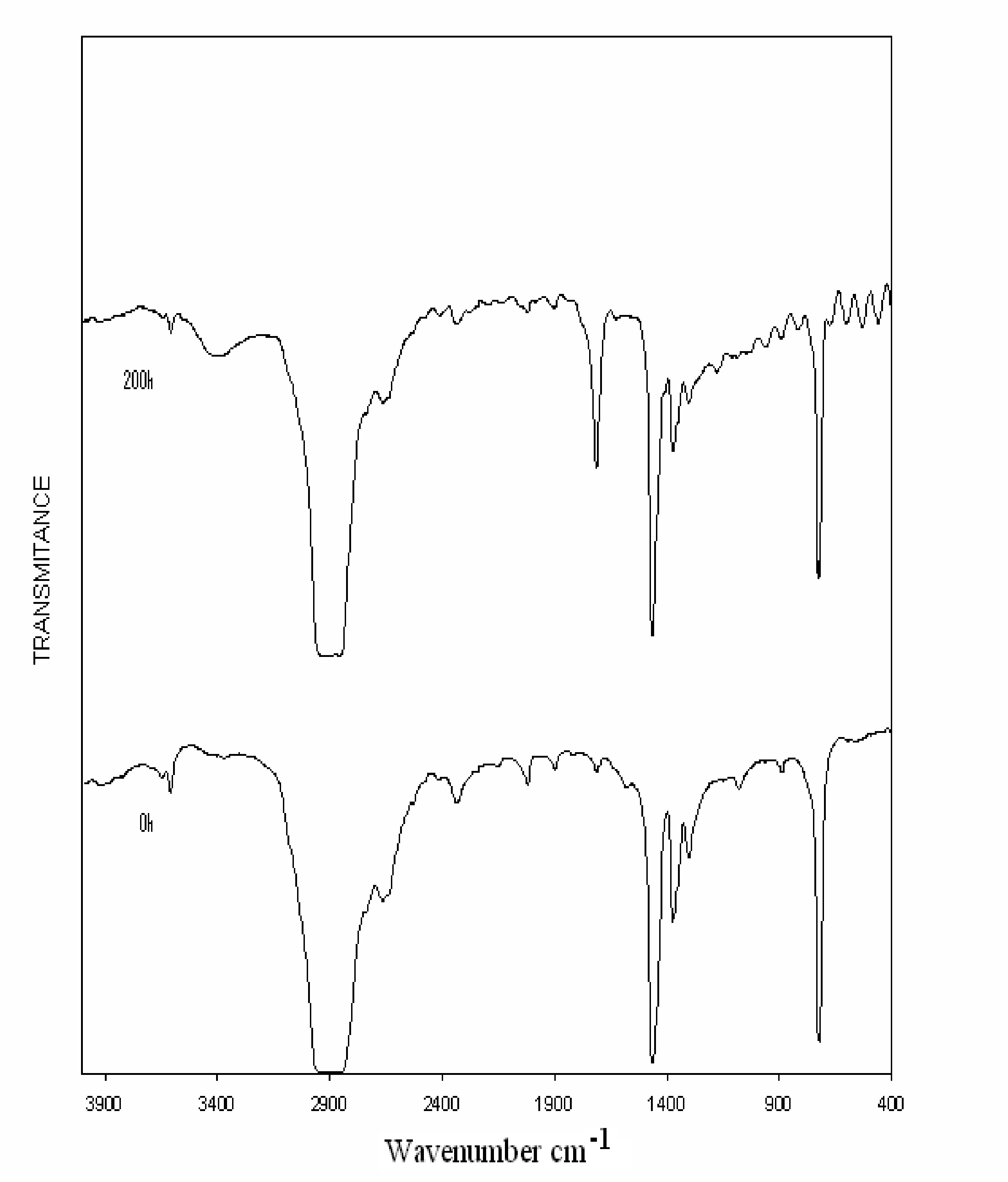


Figure 4.15 FTIR spectra of FIS1 film before and after thermal exposure

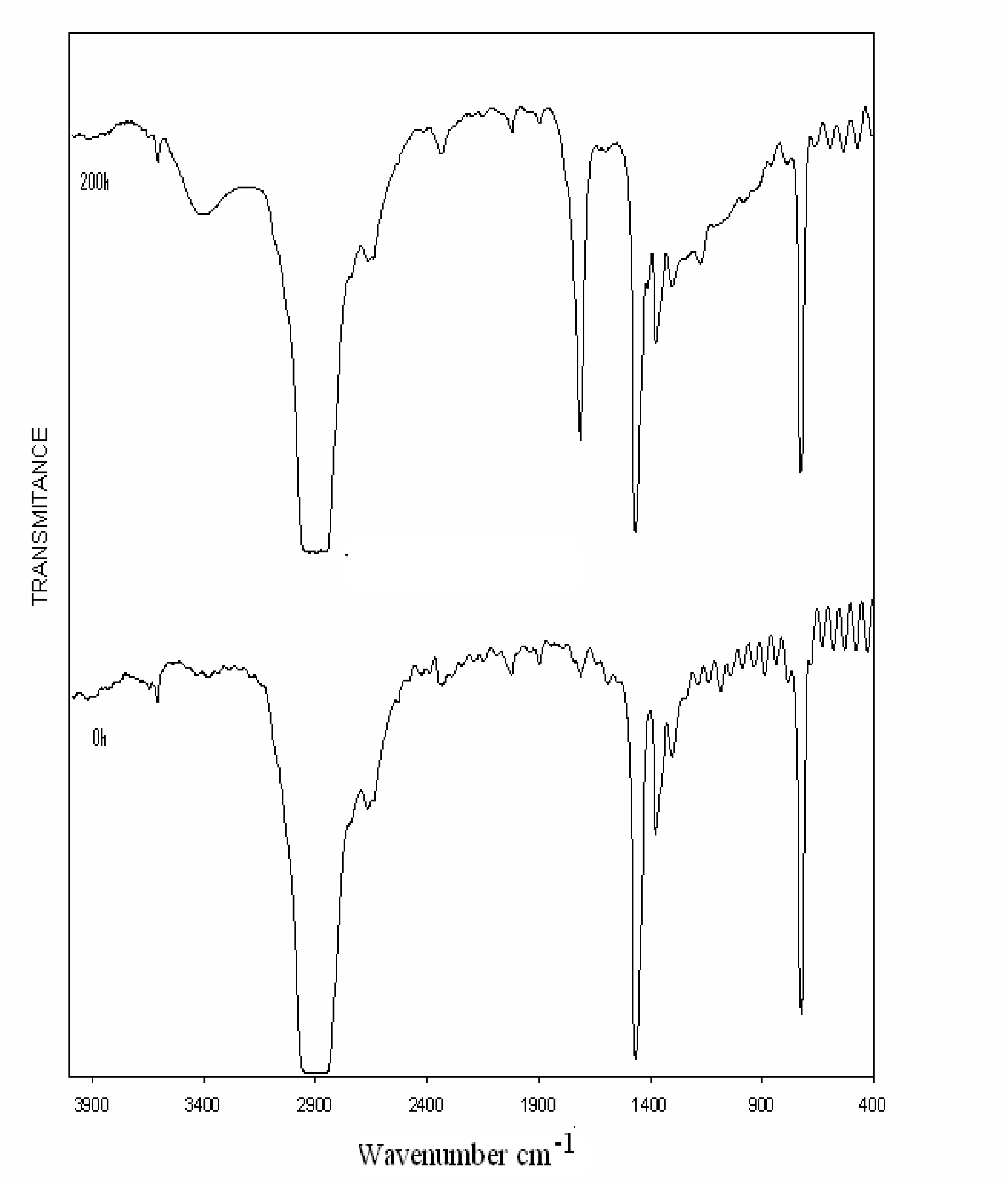


Figure4.16 FTIR spectra of FIS2 film before and after thermal exposure

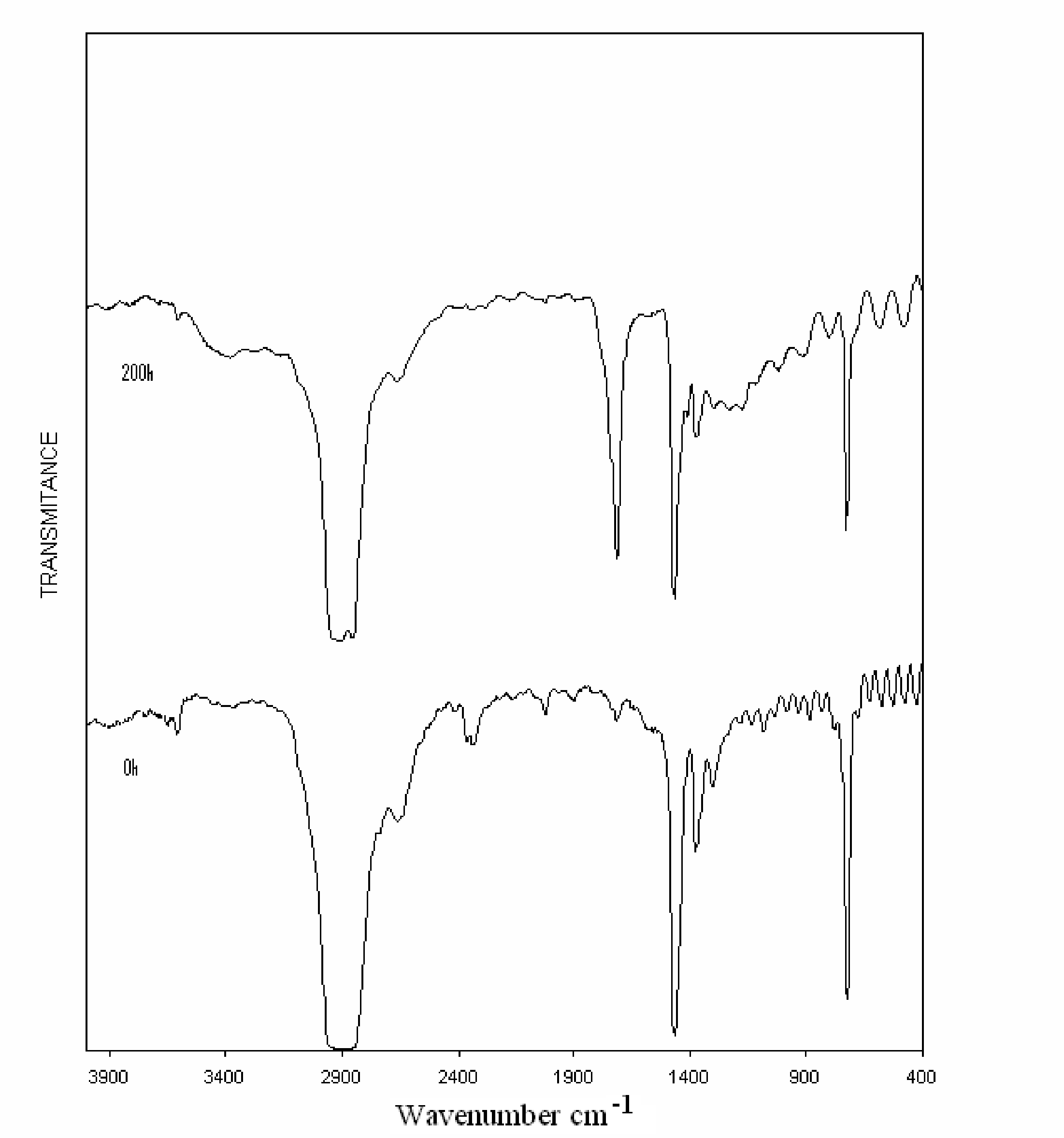


Figure 4.17 FTIR spectra of FIS3 film before and after thermal exposure

Table 4.12 Effect of thermal exposure on carbonyl index (CI) of LDPE film with or without iron stearate

Sample designation	Carbonyl index after thermal exposure	
	0 h	200 h
F1	0.87	1.44
FIS1	0.88	4.23
FIS2	0.99	7.22
FIS3	1.02	8.9

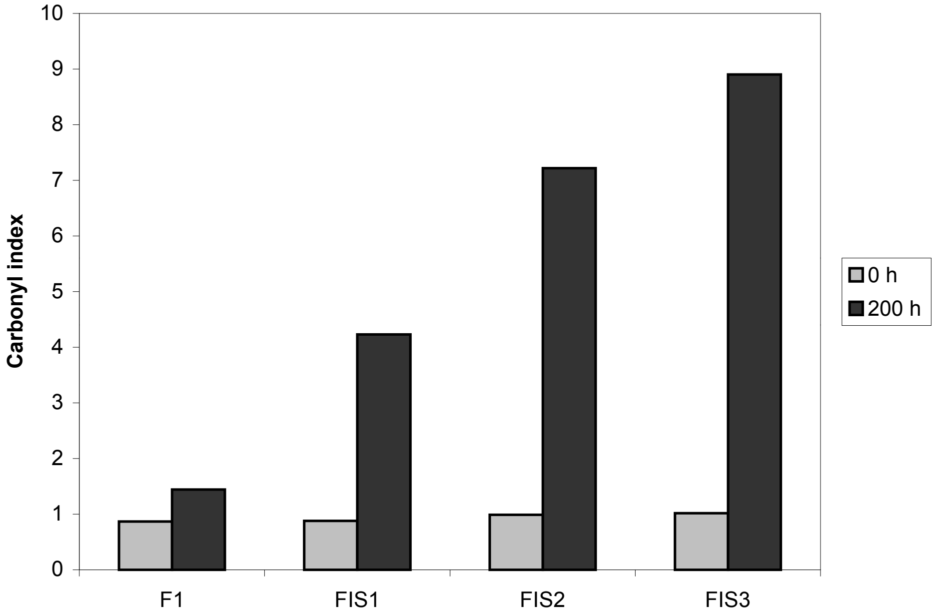


Figure 4.18 Effect of thermal exposure on carbonyl index (CI) of LDPE with or without iron stearate

4.2.2 Photo–oxidation of LDPE films

Films of different formulations containing iron stearate were subjected to xenon arc exposure and removed at regular time intervals to study the degradation behavior.

4.2.2.1 Investigation of mechanical properties

Figures 4.19-4.20 exhibit the changes in mechanical properties of films due to photo-exposure. As in the case of thermo-oxidation, LDPE films exhibited an decrease in the tensile strength and elongation due to the photo-oxidation. LDPE films containing iron stearate show a loss in the properties within 50 h of exposure. FIS2 and FIS3 samples got broken after 76h of exposure. The results of tensile strength at yield and the percentage elongation of films of varying concentration are presented in Table 4.13-4.14.

Table 4.9 Effect of photo-exposure on tensile strength at yield of LDPE films with or without iron stearate

Sample designation	Effect of photo-exposure on tensile strength at yield (MPa) of different formulation		
	0 h	40 h	76 h
F1	8.65	8.64	8.1
FIS1	8.52	7.3	5.2
FIS2	8.43	6.67	*
FIS3	8.3	4.29	*

* Films could not be tested because these were broken during handling

Table 4.10 Effect of photo- exposure on % elongation at break of LDPE films with or without iron stearate

Sample designation	Effect of photo-exposure on % elongation at break of different formulations		
	0 h	40 h	76 h
F1	85.8	59.7	40.5
FIS1	90.0	35.7	11.7
FIS2	90.0	22.4	*
FIS3	89.0	9.4	*

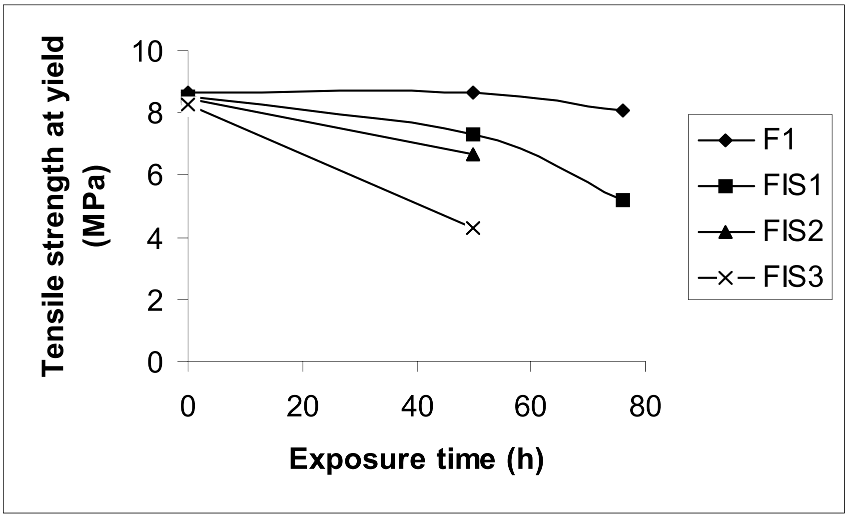


Figure4.19 Effect of exposure time on the tensile strength with or without iron stearate

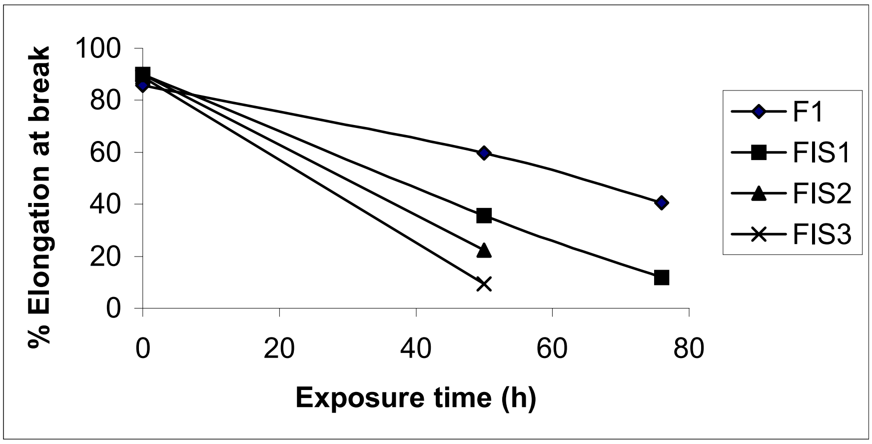


Figure4.20 Effect of exposure time on % elongation at break with or without iron stearate

4.2.3 Natural-weathering

Generally, the natural weathering of any polymeric material depends on various parameters like UV content, temperature and humidity.

Mechanical properties

The results of tensile strength at yield and the percentage elongation of films of different formulations are presented in Table 4.11-4.12. It is clear from the table and figures that the rate of degradation is less in case of natural weathering as compared to accelerated weathering and thermal exposure. It is also clear from the following table that the effect of natural weathering is more prominent with formulations having iron stearate

Table 4.11 Effect of natural weathering on tensile strength (MPa) of different formulations

Sample designation	Effect of natural weathering on tensile strength at yield (MPa) of different formulation		
	0 days	20 days	30 days
F1	8.65	8.17	8.06
FIS1	8.52	8.1	*
FIS2	8.43	8.036	*
FIS3	8.3	7.34	*

* Films could not be tested, as these were broken during handling

Table 4.12 Effect of photo-exposure on % elongation at break of different formulations

Sample designation	Effect of natural weathering on % elongation at break of different formulations		
	0 days	20 days	30 days
F1	85.8	71.6	51.6
FIS1	90.0	66.0	*
FIS2	90.0	33.6	*
FIS3	89.0	17.6	*

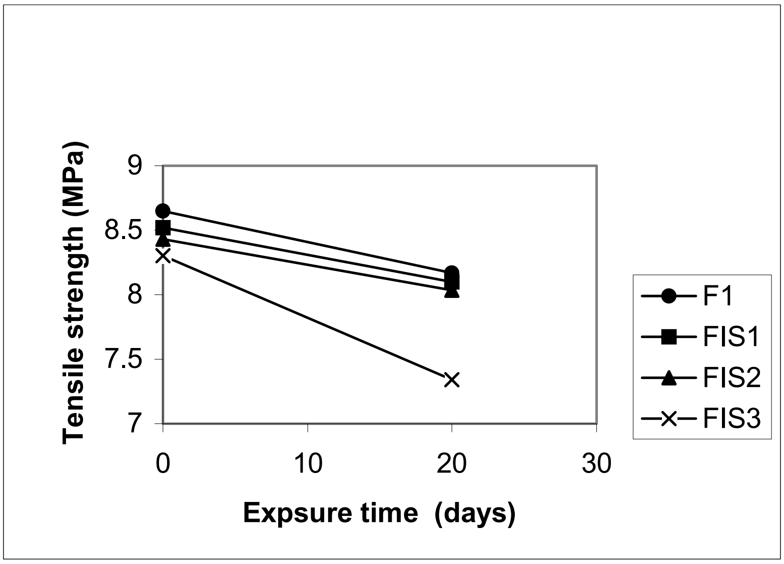


Figure 4.21 Effect of natural weathering on tensile strength (MPa) at yield of LDPE films with or without iron stearate.

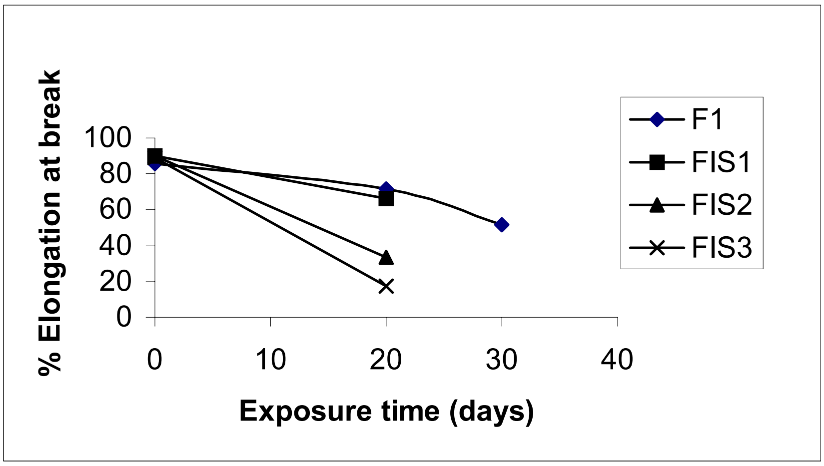


Figure 4.22 Effect of exposure time on % elongation at break of LDPE films with or without iron stearate

4.2.4 Lifetime prediction

Life-time estimation is very useful in development or selection of polymers for different application (24). The lifetime is usually determined by accelerated aging, like air oven aging studies, which require long times. For a polymer, the lifetime can be estimated from eq-3.4. Degradation of polymer is first order reaction. The estimated lifetime at 5% weight loss at various temperatures are presented in table 4.13. It can be seen that lifetime is strongly dependent on service temperature and decrease as temperature increases from 25 to 200 ^{0}C.

Table 4.13 Lifetime of different formulations at different temperatures

Sample designation	Lifetime (minutes)				
	20^{0}C	75^{0}C	100^{0}C	150^{0}C	200^{0}C
F1	8.20E+26	7.50E+19	1.20E+17	2.70E+12	6.30E+08
FIS1	1.80E+07	1.48E+04	8.70E+02	8.17E+00	2.06-01

4.3 Degradation studies of LDPE blends with manganese stearate

4.3.1 Thermo-oxidative degradation

4.3.1.1 Mechanical properties

Tensile strength and % elongation data have been reported in table 4.14- 4.15 for various formulations. The effect of exposure time on tensile strength at yield and % elongation of different formulations is clearly seen in figure 4.23 – 4.24. It is also clear from the table that the initial value of mechanical properties depend on the blending ratio. Tensile strength increases as the amount of LLDPE increases. Films containing manganese stearate, a significant loss in the mechanical property which is a direct indication of degradation. LDPE exhibited 67% loss in elongation after 400h of exposure which was only 18% in case of LLDPE. After blending and adding manganese stearate, 60% loss in elongation was observed after 70 h of exposure.

Table 4.14 Effect of thermo-oxidation on tensile strength (MPa) at yield of different films with or without manganese stearate

Sample designation	Effect of thermal exposure on tensile strength at yield (MPa) of different formulations			
	0 h	70 h	200 h	400 h
F1	8.7	8.6	8.3	7.1
F2	20.9	18.6	17.6	17.2
FMS4	10.7	11.0	6.9	3.5
FMS5	14.7	12.9	11.1	6.6
FMS6	18.3	17.3	11.7	8.3

Table 4.15 Effect of thermo-oxidation on % elongation at break of different films with or without manganese stearate

Sample designation	Effect of thermal exposure on tensile strength at yield (MPa) of different formulations			
	0 h	70 h	200 h	400 h
F1	85	72	46	27
F2	938	804	780	768
FMS4	682	271	236	12
FMS5	882	514	471	16
FMS6	900	800	674	73

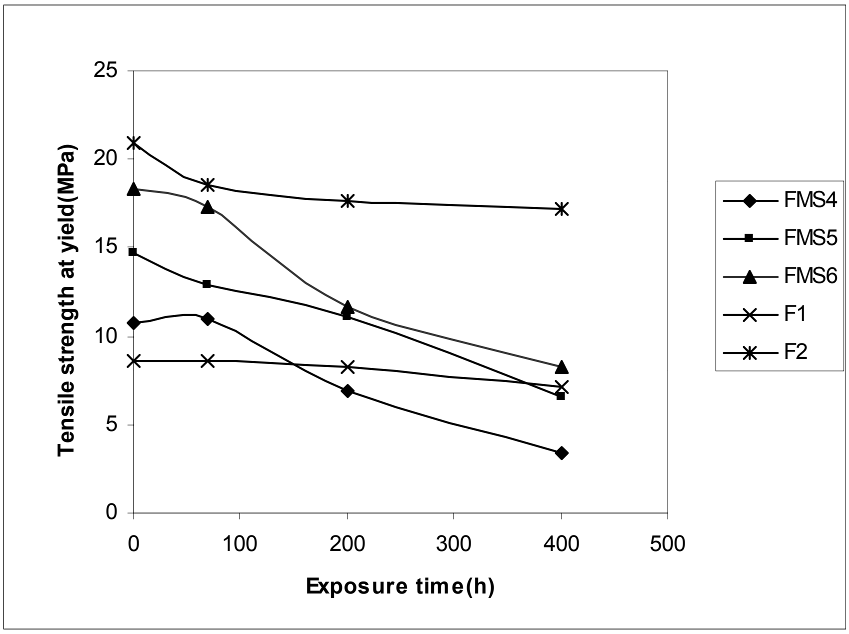


Figure 4.23 Effect of thermo-oxidation on tensile strength (MPa) at yield of LDPE films with or without iron stearate

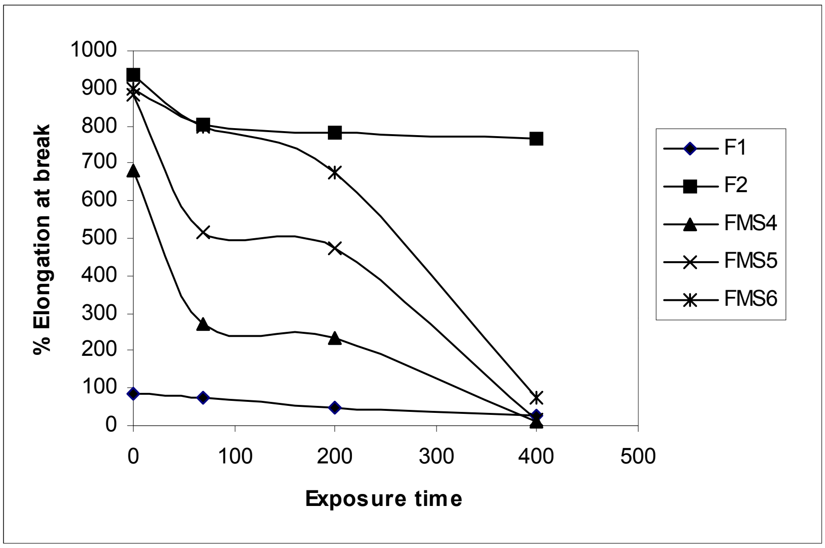


Figure 4.24 Effect of thermo-oxidation on % elongation at break of of LDPE films with or without iron stearate

4.3.2 Photo-oxidative degradation

4.3.2.1 Mechanical properties

Samples containing pro-oxidants broke on handling due to xenon arc exposure, and hence could not be tested for mechanical properties. The degradation was monitored by FTIR spectroscopy.

4.3.1.2 FTIR Studies

FTIR spectra of FMS4, FMS5, FMS6, before and after thermal exposure are shown in fig 4.25-4.27. The absorption band at ≈ 1740 cm^{-1} can be assigned to the stretching of ketone group. The rate of carbonyl growth is an indication of oxidative reaction.

The degradation was also monitored by the increase in the CI. In the FTIR spectra of film containing manganese stearate, significant changes in the carbonyl (1785-1700 cm^{-1}) were observed upon aging.. The carbonyl band can be assigned due to -C=O stretching vibrations in aldehydes, carboxylic acid groups (1700 cm^{-1}). The ratio of absorbance of carbonyl band and internal thickness band (2020 cm^{-1}) has been used to calculate the carbonyl index (CI). Increase in the CI of different formulations are shown in fig 4.28 It is believed that polyethylene films enter into the decay stage at CI greater than 6 .Change in carbonyl index with exposure time are shown in table 4.16.

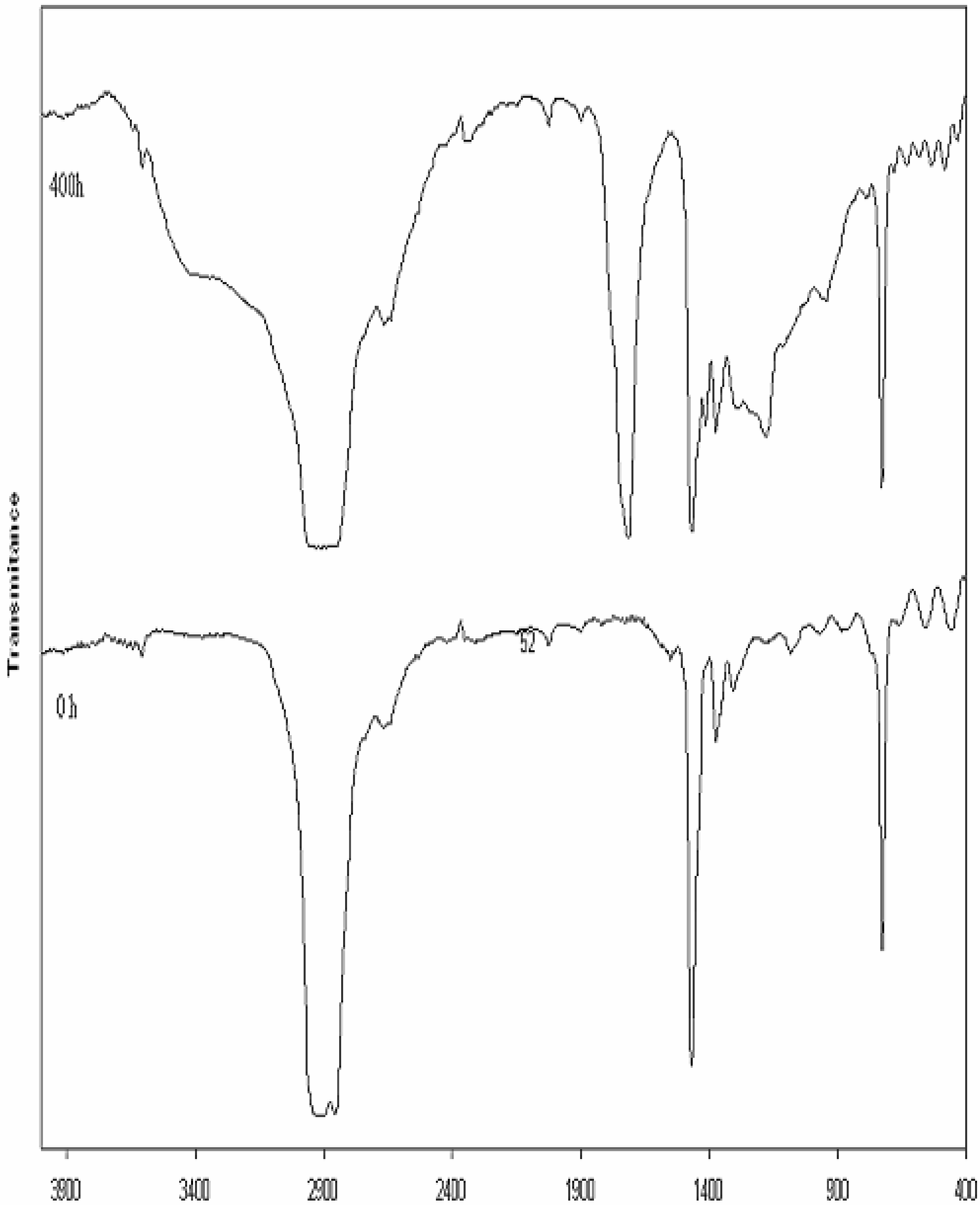


Figure 4.25 FTIR spectra of FMS4 film before and after thermal exposure

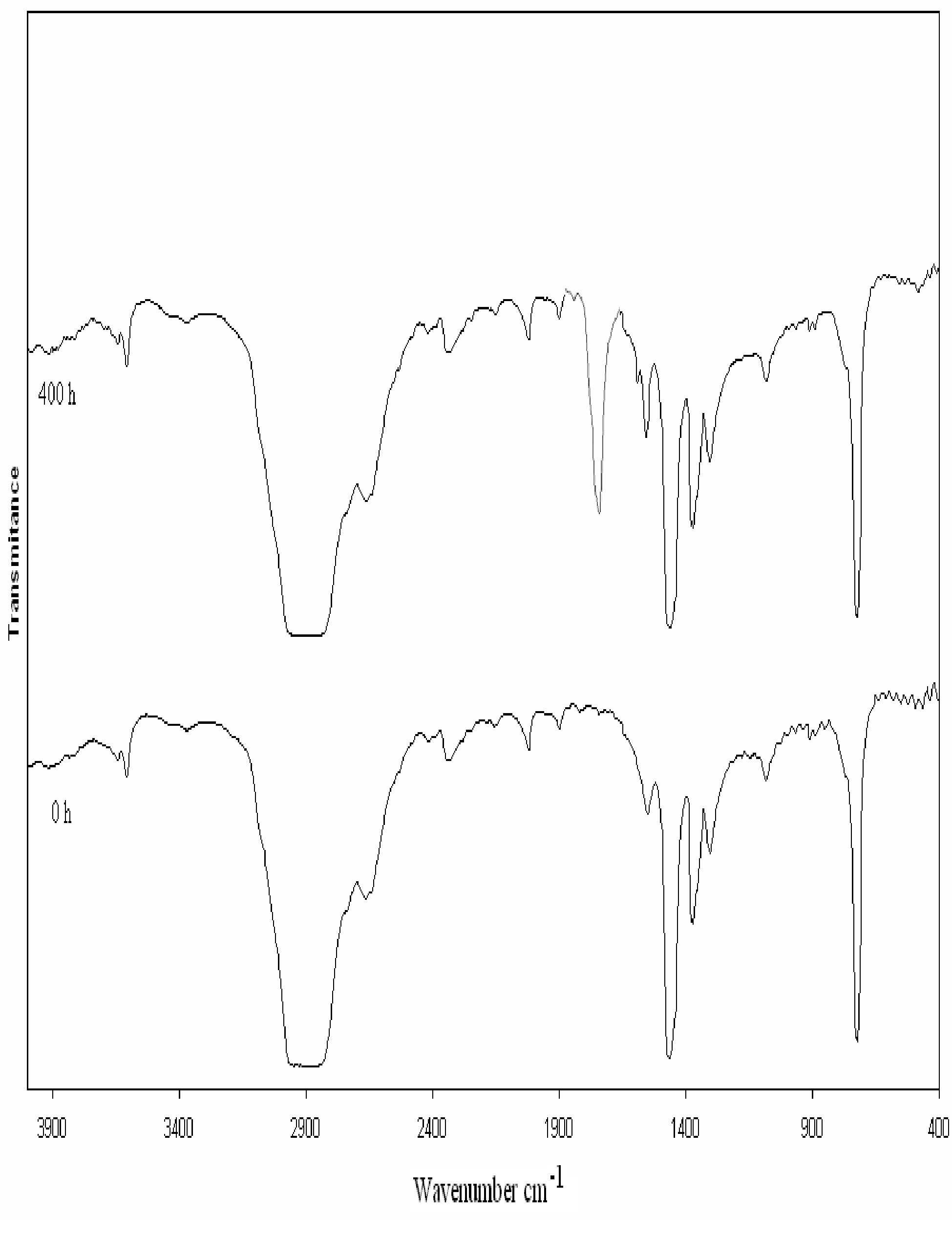


Figure 4.26 FTIR spectra of FMS5 film before and after thermal exposure

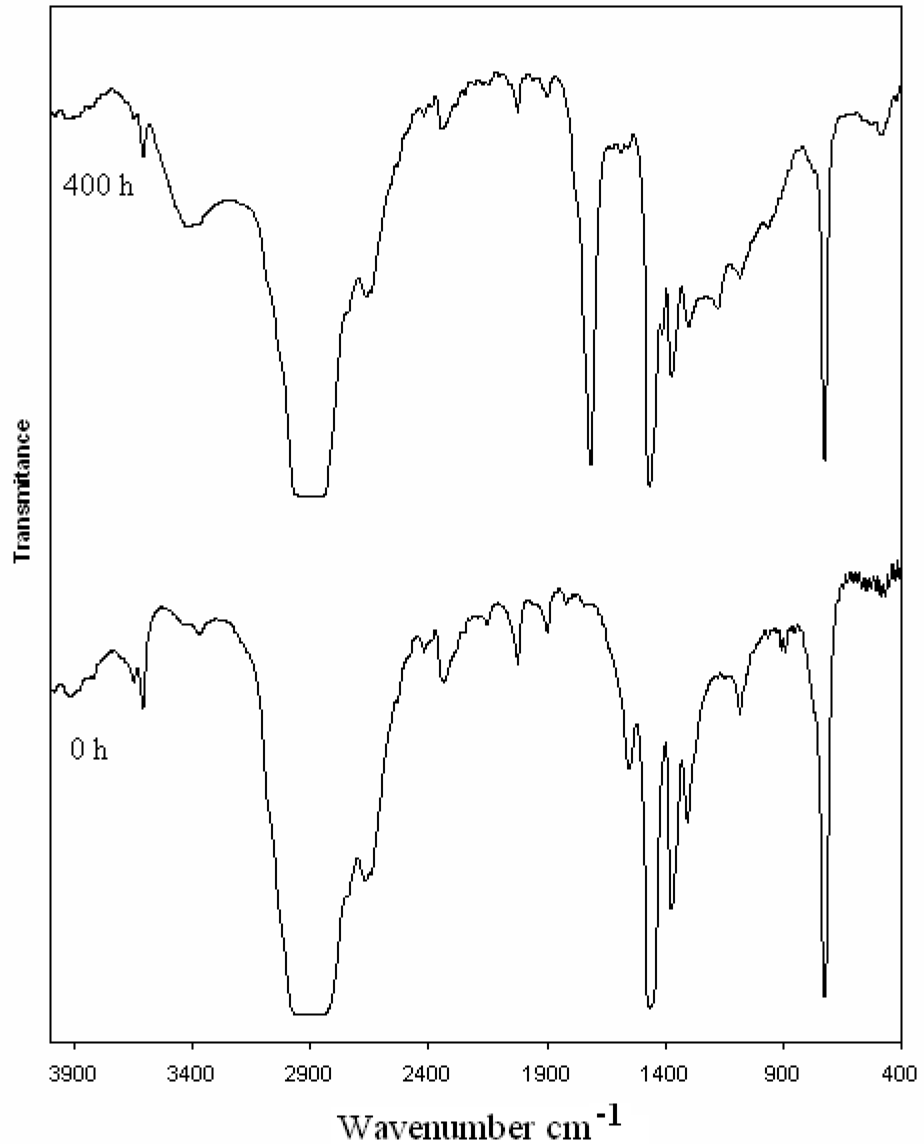


Figure 4.27 FTIR spectra of FMS6 film before and after thermal exposure

Table 4.16 Effect of photo-exposure on carbonyl index (CI) of different formulations with or without manganese stearate

Sample Designation	Carbonyl index after thermal exposure	
	0 h	200 h
F1	0.87	1.44
F2	0.16	0.76
FMS4	0.72	8.6
FMS5	0.7	6.7
FMS6	0.69	4.4

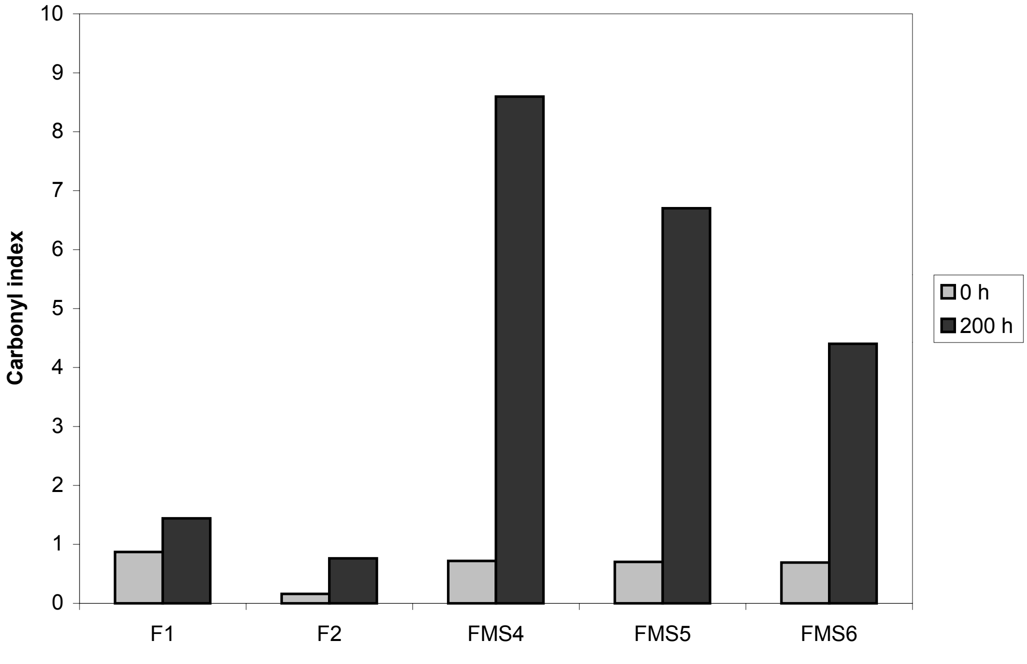


Figure 4.28 Effect of photo-exposure on carbonyl index (CI) of different formulations with or without manganese stearate

Conclusions

Main objective of this work was to enhance the susceptibility of LDPE and its blends towards environmental degradation. For this purpose, manganese and iron stearate were synthesized and studied for their pro-oxidative ability to initiate thermo/photo–degradation in the base polymers.

1. Both metal stearates were found to be effective photo and thermo-oxidative initiator.
2. Changes in mechanical properties, structure and MFI behaviour indicate that the extent of degradation in presence of manganese stearate was more significant under thermo-oxidative environment.
3. Manganese stearate was found to be more effective initiator as compared to iron stearate as indicated by structural and mechanical properties.
4. LLDPE is less sensitive to degradation as compared to LDPE. Degradation of LLDPE can be enhanced by blending it with LDPE and additive manganese stearate.
5. Lifetime of films was found to decrease by the incorporation of these additives. The lifetime of the neat LDPE was 8.2E+26 in nitrogen atmosphere, which reduces to 1.8E+7 when blended with 0.5%w/w manganese stearate and to 2.1E+10 when blended with 0.5%w/w iron stearate.

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