

Effect of Iron Carboxylates on the Photodegradability of Polypropylene. II. Artificial Weathering Studies

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ABSTRACT: The various iron carboxylates such as ferric caprate, ferric laurate, ferric myristate, ferric palmitate, and ferric stearate were synthesized to enhance the photodegradability of polypropylene (PP). The prodegradants (0.2%) synthesized were blended with virgin PP and then blown into films. All the PP films mentioned were exposed to ultraviolet (UV) radiation of 365 nm at room temperature to study the photodegradation behavior of PP with and without the prodegradants under artificial weathering conditions. The photoirradiated films were found to degrade after certain hours of UV exposure, which could be found from the steep increase of hydroxyl, carbonyl, lactone, ester, carboxylic acid, and crystallinity index. At the same time, a sudden decrease of elongation at break percentages and tensile strength; development of surface cracks indicated the scission of the main chain of the PP. The results revealed that

PP containing prodegradants degraded at a faster rate than the virgin material. However, the effectiveness of the prodegradants for the photodegradation of PP was found to be in the order: ferric caprate > ferric laurate > ferric myristate > ferric palmitate > ferric stearate. The results showed that the number of carbon atoms present in the alkyl part of the various prodegradants played a vital role in the degradation phenomenon. Furthermore, it could be concluded that the mobility of the alkyl radicals formed from the decomposition of the incorporated prodegradants during artificial weathering played a prominent role in the photooxidative degradation behavior of PP films. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2968–2976, 2012

Key words: polypropylene; iron carboxylates; artificial weathering; FTIR; elongation at break; SEM

INTRODUCTION

The high interest in degradable polymers for packaging and disposals to minimize litter has resulted in the availability of several commercialized products. The most presently available commercial polymer such as polyolefins is not responsive to biodegradation by bacterial, fungi, yeasts, or enzymes; photodegradation, photooxidation, and autooxidation are the main pathways for their degradation.¹ Photooxidation leads to an increase in the low-molecular weight fractions by chain scission, thereby facilitating bio-degradation.²

Generally, natural and artificial weathering methods are used to study the photodegradation behavior of a material. Due to the complex weathering conditions, natural weathering test yield different

results. Therefore, artificial weathering is so important that the physical and chemical changes induced by the tests duplicate those resulting from natural weathering. It is therefore necessary to determine precision of the method to describe the accuracy of the measurements.

In the literature,^{3–10} several light sources have been used to ultraviolet (UV) irradiation and the test was performed at different temperatures, which are listed in Table I. However, in this work, UV irradiation has been performed using low pressure mercury lamps, which produce UV radiation ($\lambda_{\text{max}} = 365 \text{ nm}$) at room temperature. The UV radiation of 365 nm was used for irradiation in this investigation as large amounts of UV-A (400–315 nm) radiation reach the earth surface than UV-B (315–265 nm).

Today polypropylene (PP) is one of the most widely used among all the commodity polymers. The versatility of this material arises from the cheap petrochemical stocks as raw materials, the sophisticated and efficient catalytic polymerization processes, and the ease of processing the final polymer as a fabricated article by injection molding or as textile by spinning or as film by blown extrusion.¹¹ With increased production, PP film has been extensively used for food contact applications, due to its

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TABLE I
Light Sources and Temperatures Used for Photooxidation Experiments Cited in the Literature

Light source	Irradiation wavelength (nm)	Testing temperature (°C)
SEPAP 12-24 chamber	>300	60
Fluorescent tubes UVA-340	290–320	30
Fluorescent lamps (Philips TLK 05–40 W)	300–450 ($\lambda_{\text{max}} = 365$ nm)	40, 55, and 70
300 W High pressure mercury Lamp (Orc-OHD-320 M)	254, 290, and 365	Ambient
Xenon arc (weather-o-meter)	290–400, 290–80	Ambient
UV lamp (Philips TL 40W/05)	290–500 ($\lambda_{\text{max}} = 365$ nm)	60
40 W UV-B lamps	280–370 ($\lambda_{\text{max}} = 313$ nm)	Ambient
UV lamp	400	55

higher melting point, low water absorption tendency, and aroma retention capacity. Thus, its consumption increases and causes littering which leads to environmental pollution.

Eventhough there are lot of methods available to solve this pollution problem, many authors^{12–16} have made an investigation on the photodegradation behavior of PP without incorporation of any prodegradants. Hence, the author's previous work¹⁷ reported that the effect of iron carboxylates on the photodegradability of PP under natural weathering conditions was shown. The detailed reports on the photodegradation of PP under artificial weathering conditions were not found in the literature. However, several authors made an investigation on the photodegradation of polyethylene and few reports are mentioned below.

Havnden¹⁸ has extensively studied about photodegradability of low density polyethylene using cerium (III) and cerium (IV) stearate as the prodegradant. The author demonstrated that cerium (III) was effective in promoting both photo- and thermo-oxidation of low density polyethylene (LDPE), with effectiveness increasing with concentration. But, cerium (IV) was less effective in promoting photooxidation.

The effect of a series of transition metal (Ti, V, Mn, Fe, Co, Ni, Cu, and Zn) stearates on the photodegradation of a high density polyethylene was studied by Osawa et al.¹⁹ The authors reported that iron stearate was more effective at an early stage of photodegradation, vanadium and manganese stearates accelerated while copper stearate retarded it. Other stearates show no appreciable effect on the photodegradation.

Roy et al.⁹ have reported that the cobalt carboxylates namely laurate, palmitate, and stearate promoted photodegradation of low density polyethylene but the order of photodegradation was stearate > palmitate > laurate.

A detailed investigation of the effect of metal (Mg, Al, Ca, Ti, V, Fe, Cu, and Zr) 2,4-pentanedione complexes with PP film on UV aging (A 340 lamps at 45°C) was made by Eyenga et al.²⁰ The authors found that the ferric complex had the highest photo activity of all the aforementioned metal complexes. Moreover, the authors compared the photocatalytic

activity of 1, 2-dihydro-2, 2, 4-trimethyl quinolene (OTMQ) with commercially available ferric stearate, and the results indicated that ferric stearate was much more efficient than OTMQ. Thus, we made a detailed attempt to investigate the effect of iron carboxylates on the photo degradability of polypropylene under artificial weathering conditions.

EXPERIMENTAL

Materials

The polymeric material selected for this investigation is polypropylene (Repol grade H100EY) obtained from Reliance Industrial, Jamnagar, India. This material contains Irganox antioxidant (500–1000 ppm). The list of physical properties of this PP material found elsewhere.¹⁷ To synthesize prodegradants (iron salts of various fatty acids), potassium hydroxide pellets and ferric sulphate monohydrate purchased from Merck, Mumbai, India, and decanoic acid (capric acid), dodecanoic acid (lauric acid), tetradecanoic acid (myristic acid), palmitic acid, and stearic acid supplied by Alfa Aesar Johnson Matthey GMBH, Karlsruhe, Germany, were used as such without further purification.

Synthesis of iron salts of fatty acids

Iron salts of capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid were synthesized according to the procedure reported in the literature,²⁰ by reacting ferric sulphate monohydrate with corresponding potassium salt of fatty acid, and the resultant salts are represented as ferric caprate (MF03), ferric laurate (MF04), ferric myristate (MF05), ferric palmitate (MF06), and ferric stearate (MF07).

Blending and film extrusion

The virgin PP (4 kg batches) was blended with 0.2% of the synthesized prodegradants (MF03, MF04, MF05, MF06, and MF07) with a blender made by Modern Plastic Industries (Coimbatore, India). The virgin PP and the various prodegradants-blended

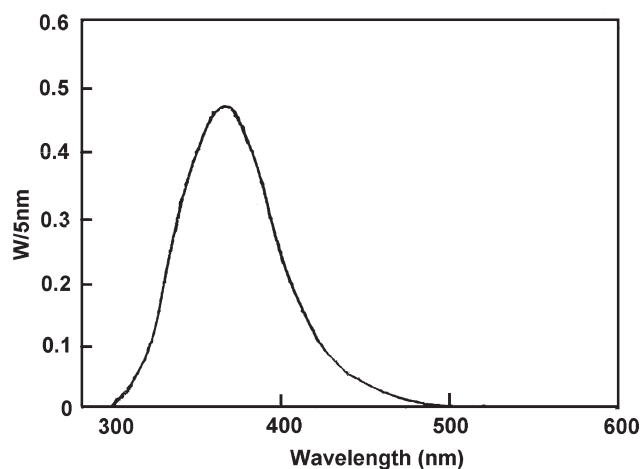


Figure 1 Spectral energy distributions of 30 W low pressure mercury vapor UV lamp.

PPs were extruded and blown into films using an extruder (model PP-750) made by Klockner Windsor India (Thane, Mumbai, India) with the blow-up ratio (6 : 1). During extrusion, the three barrel zones were kept at 200°C, the die was maintained at 175°C, and the screw revolution was maintained at 200 rpm. The films were obtained with the width of 36 cm and a thickness of 62 μm . We cleaned the extruder by running 4 kg of virgin PP material before the addition of every new material.

Artificial weathering procedure

The PP and PP containing various prodegradants (0.2%) such as MF03, MF04, MF05, MF06, and MF07) were exposed to UV radiation at room temperature using UV chamber (Heber Scientific, Chennai, India) with two 30 W low pressure mercury vapor UV lamps (Philips, Holland) emitting the radiation between 300 and 460 nm with a maxima of 365 nm. The absolute spectral energy distribution of the lamps is depicted in Figure 1. Samples were mounted on the racks and were positioned 14 cm from the lamps. Samples were collected at varying exposure time corresponding to maximum degradation of the PP film. The artificially weathered samples were analyzed by Fourier transform infrared (FTIR) spectroscopy, a universal testing machine, and scanning electron microscopy (SEM).

FTIR studies

The structural changes of the artificially weathered PP films were evaluated by recording the FTIR spectrum with an FTIR-8400S spectrophotometer, which was supplied by Shimadzu (Tokyo, Japan). The FTIR spectra for all samples were recorded with 20 scans with 4 cm^{-1} resolution. The various indices like hydroperoxide, hydroxyl, carbonyl, carboxylic acid, ester, and lactone were calculated as the ratio of absorbance corre-

sponding to peak maxima of the functional group concerned to the absorbance corresponding to peak maxima of the reference peak from the FTIR spectra of weathered samples. The maximum absorbance region for some groups which were related to degradation products are listed in Table II. In literature, the absorbance bands occur at 840, 974, 1166, 1455, and 2720 cm^{-1} were considered as reference peaks for polypropylene.^{21–25} In this work, the peak at 974 cm^{-1} ($-\text{CH}_3$ rocking band) was chosen as reference peak, which remains unchanged during degradation.

Mechanical properties measurements

The mechanical properties (elongation at break (%) and tensile strength) of the artificially weathered PP film samples were determined with a HOUNSFIELD Material Testing Machine (Model S-series, H5K-S), which comprises of a load cell (5 kN) and HT55 ultra light vice grips, supplied by Tinius Olsen (Salfords, Surrey, England). It was operated at a speed of 150 mm min^{-1} with the grip distance of 80 mm on the rectangular bar film samples which were cut in machine direction, with a length of 12 cm, a breadth of 2 cm, and a thickness of 62 μm . For each sample, three tests were conducted, and the average value has been chosen for further data analysis.

SEM studies

The morphological changes occurring in the artificially weathered PP films due to the UV irradiation were investigated with the help of SEM. Sample surfaces were sputtered with gold using usual techniques and then analyzed with a JEOL (JSM-840A) SEM supplied by JEOL (Tokyo, Japan), at a voltage of 10 kV. Photo-micrographs were captured at a uniform magnification of 500 \times .

RESULTS AND DISCUSSION

Photooxidative degradation mechanism

The chemical changes occurring in the material during photooxidative process are very complex, and it was generally assumed as a free radical chain

TABLE II
IR Absorbance Region for Different Groups Formed During Photooxidation of PP

Functional groups	Absorbance (cm^{-1})
Hydroxyl and hydroperoxide	3600–3200
Carbonyl	1800–1700
Lactone	1785–1760
Ester	1750–1735
Ketone	1725–1715
Carboxylic acid	1712–1705
Vinyl	909
Vinylidene	888

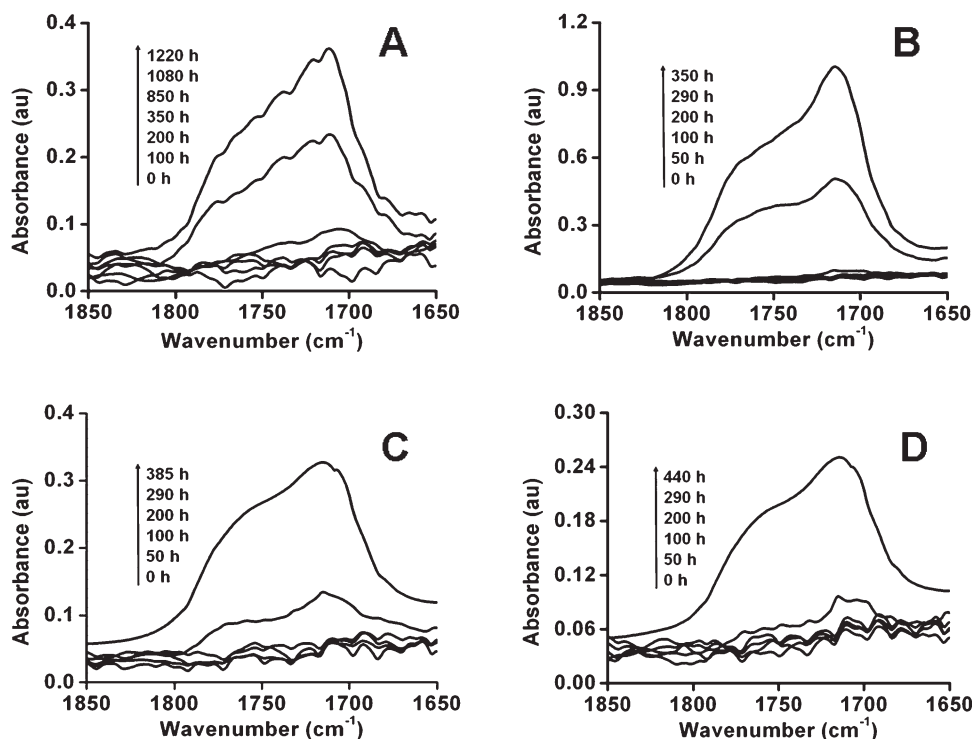


Figure 2 FTIR spectra (carbonyl region) of UV irradiated PP and PP containing 0.2% of ferric carboxylates at room temperature: (A) Virgin PP, (B) PP : MF03, (C) PP : MF05, and (D) PP : MF07.

mechanism.^{26–28} In general, in the absence of photoinitiators, the initiation of polypropylene photooxidation is by the abstraction of hydrogen atom preferably tertiary hydrogen by free radicals produced due to the decomposition of chromophoric impurities such as hydroperoxide formed during processing.²⁹ The most probable mechanism for the degradation of polypropylene in the presence of photoinitiators like iron carboxylates was presented in our previous article.¹⁷

Evaluation of structural changes: FTIR studies

The hydroperoxide, hydroxyl, lactone, ester, carbonyl, carboxylic acid, and crystallinity indices were calculated using FTIR spectra of weathered PP samples to investigate the structural changes occurring in the material due to UV irradiation.

Carbonyl index

The structural changes occurring in virgin PP and PP containing different prodegradants owing to increased UV exposure time was followed by monitoring the carbonyl group absorption region in the FTIR spectra recorded (Fig. 2). It was obvious that as the UV exposure time increased, the carbonyl group absorbance in the FTIR spectra also increased after certain hours of UV exposure.

The carbonyl index is the most used parameter to assess the degree of degradation³⁰ and was calculated using the following formula,

$$\text{Carbonyl Index} = \frac{\text{Absorbance } 1715 \text{ cm}^{-1}}{\text{Absorbance at } 974 \text{ cm}^{-1}}$$

The variations of the carbonyl index value due to the increase in UV exposure time for the different PP film materials under investigation are depicted in Figure 3. The virgin PP showed considerable changes in the carbonyl index only after irradiating UV rays for a period of 1080 h (Fig. 3). Incorporation of ferric carboxylates in PP reduces sufficiently this time to around 290 to 440 h, and this induction time being dictated by the number of carbon atoms present in the alkyl part of the prodegradants employed. As the number of carbon atoms in the alkyl part of the added prodegradants (ferric carboxylates) increased, carbonyl index showed a lower value and justifies the fact that longer the alkyl chain in the carboxylate unit, the slower is the degradation of PP. Thus, the mobility of the alkyl radicals formed from the decomposition of the incorporated prodegradants during UV irradiation played a prominent role in the photooxidative degradation behavior of PP films.

The effect of chain length of cobalt carboxylates (laurate, palmitate, and stearate) as prodegradants on the enhancement of photooxidative degradation of LDPE was recently studied by Roy et al.⁹ The authors found that the rate of photooxidative degradation increased as the length of the alkyl chain present in the cobalt carboxylate increased. This result

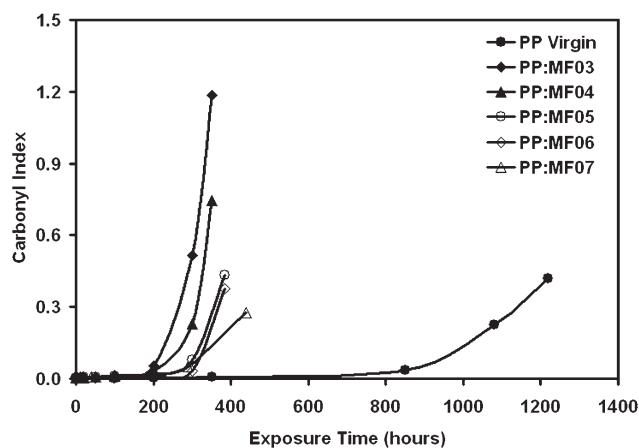


Figure 3 Variation in carbonyl index of UV irradiated virgin PP and PP containing 0.2% of ferric carboxylates.

was attributed to the fact that as the alkyl chain length increased, the carboxylate was capable of blending easily with the base polymer; this resulted in its increased capability to act as prooxidant.

The various indices of ketone, lactone, ester, and carboxylic acid were calculated using the ratio of cor-

responding peak absorbance maximum (Table II) to the maximum absorbance value of a reference peak (974 cm^{-1}) because of the observed broad peak for the carbonyl group in the region of $1800\text{--}1700\text{ cm}^{-1}$ in the FTIR spectrum of weathered PP. It may be due to the overlap of different degradation products like lactone, ester, ketone, carboxylic acid, etc.³¹ From Figure 4, one can be observed that a steep increase of all these indices for the artificially weathered virgin PP as well as PP incorporated with 0.2% of ferric carboxylates started at the same exposure day. The decreasing order of these indices for all the samples was found as follows: carboxylic acid > ketone > ester > lactone. This may be attributed to the fact that carboxylic acid is the final stable degradation product,³² whereas it is a precursor for the lactone formation.³³

Furthermore, Figure 4 showed that the trend of variation of these indices observed for the weathered virgin PP is similar to those of weathered PP containing various prodegradants. At the same time, the rate of increase of these indices differed depending on the prodegradants added. This observation revealed that the degradation mechanism was not

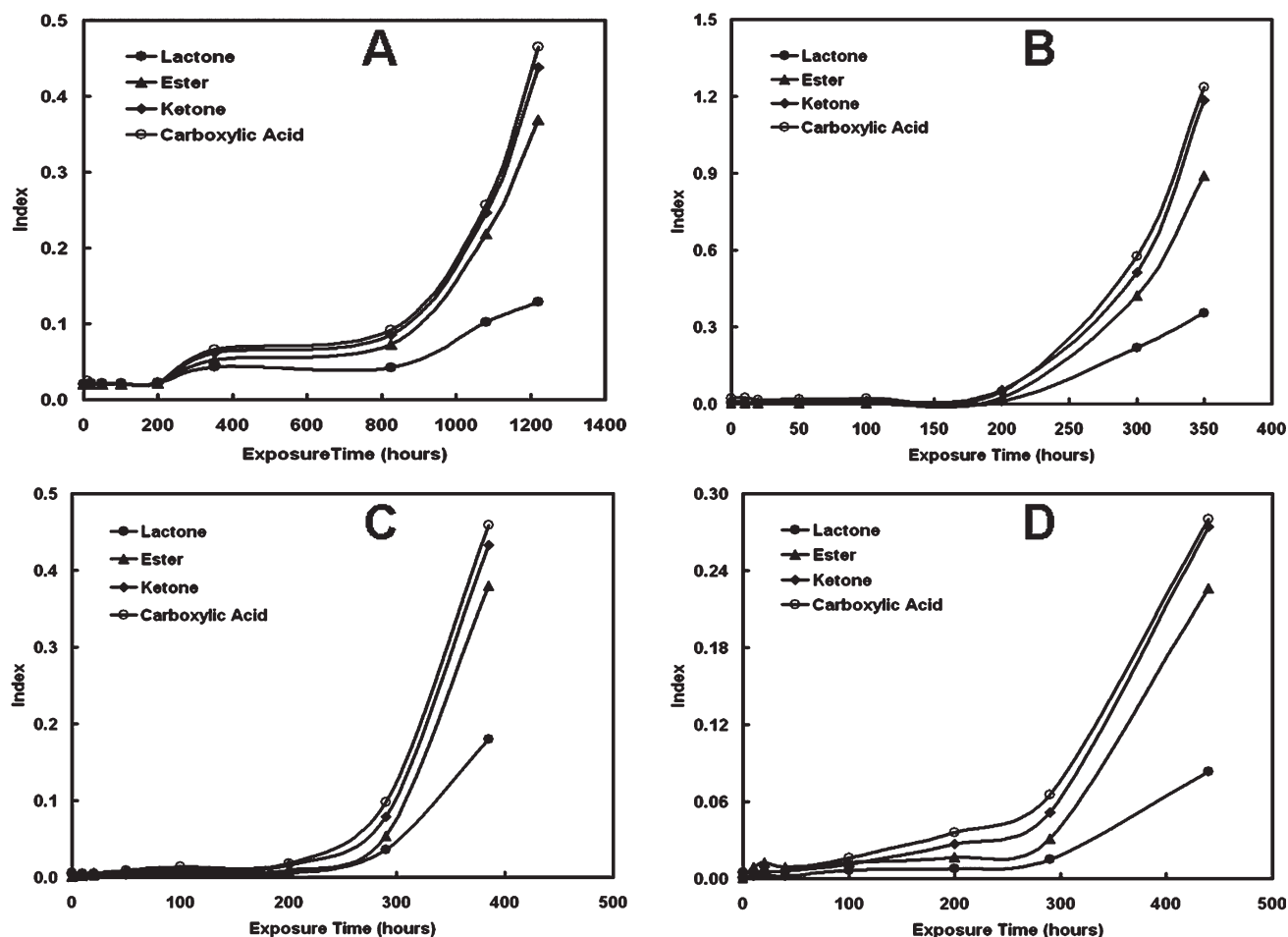


Figure 4 Variation in lactone, ester, ketone, and carboxylic acid indices of UV irradiated PP and PP containing 0.2% of ferric carboxylates: (A) Virgin PP, (B) PP : MF03, (C) PP : MF05, and (D) PP : MF07.

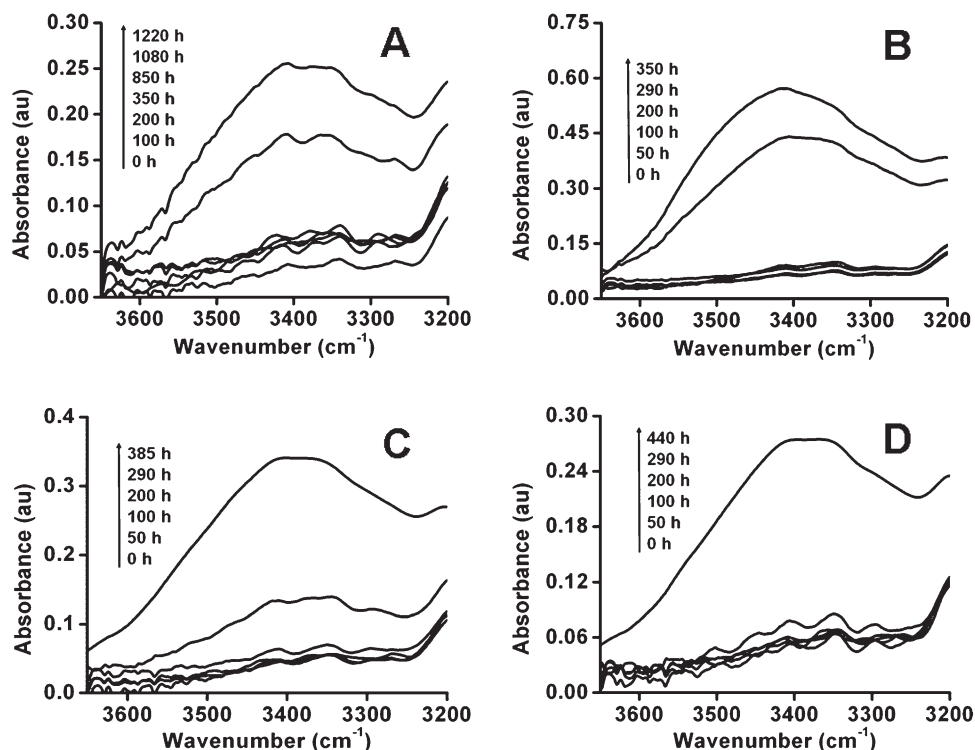


Figure 5 FTIR spectra (hydroxyl region) of UV irradiated PP and PP containing 0.2% of ferric carboxylates at room temperature: (A) Virgin PP, (B) PP : MF03, (C) PP : MF05, and (D) PP : MF07.

much altered by the addition of ferric carboxylates as prodegradants during weathering, but the rate of degradation was altered. A similar trend was observed in the study of polypropylene natural weathering at Messina, Italy by Gallo et al.³⁴

Hydroxyl index

The spectral range 3650–3200 cm^{-1} which corresponds to hydroxyl group absorbance region in FTIR spectrum for UV irradiated virgin PP and PP containing prodegradants such as MF03, MF04, MF05, MF06, and MF07 are presented in Figure 5.

The ratio of absorbance at 3600 cm^{-1} to absorbance at 974 cm^{-1} was evaluated as the hydroxyl index, and its variation with respect to UV exposure time is depicted in Figure 6. A comparison of the Figures 3 and 6 indicated that the time necessary to show a step increase in the hydroxyl index value is in phase with the time needed for the increase of carbonyl index. The results revealed that the formed unstable hydroperoxide decomposed to yield carbonyl and hydroxyl group compounds. The aforementioned processes occur simultaneously during the photodegradation of virgin PP and PP containing iron carboxylates as prodegradants.

Crystallinity index

Crystallinity index was calculated as the ratio of absorbance of band at 998 cm^{-1} to the absorbance of band

at 974 cm^{-1} to gather information on the variation of crystallinity as the function of UV exposure time which is presented in Figure 7. The first band is regularity band characteristic of the crystalline PP, whereas the second band corresponds to both crystalline and amorphous PP phases.^{35,36,37} From Figure 7, it was clear that as the photodegradation of PP progressed, the crystallinity value increased after certain hours of exposure. This time may be considered as the induction period where the structural reorganization occurred due to UV radiation. Moreover, the enhancement of

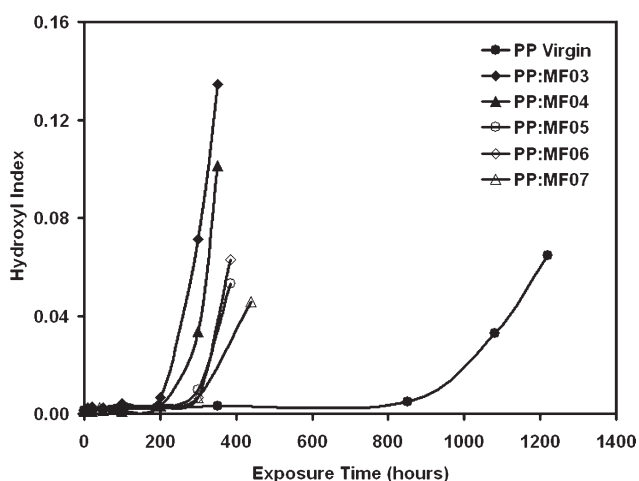


Figure 6 Variation in hydroxyl index of UV irradiated virgin PP and PP containing 0.2% of ferric carboxylates.

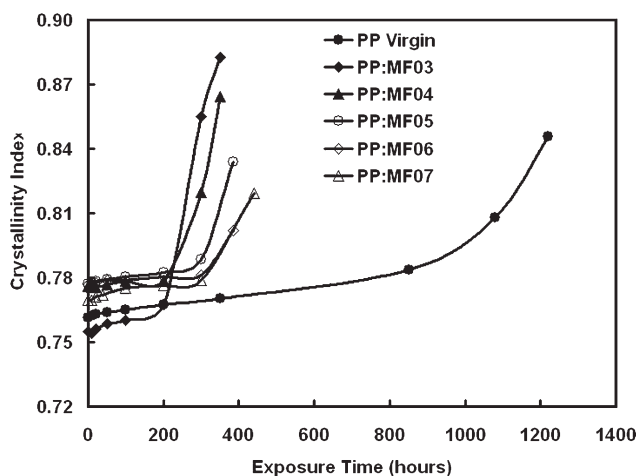


Figure 7 Variation in crystallinity index of UV irradiated virgin PP and PP containing 0.2% of ferric carboxylates.

crystallinity index value could be explained by (a) degradation and disappearances of amorphous phase preferentially by the attack of oxygen, (b) formation of new low molecular weight photooxidation products, which were capable of forming new crystalline domains.³⁸ The crystallinity index thus increased when the indices of hydroxyl, carbonyl, lactone, ester, and carboxylic acid increased.

Measurements of mechanical properties

The mechanical properties like elongation at break and tensile strength depend on the nature of the orientation and strength of the polymer chain. The polymer chains might have been broken and reorganized themselves due to the energy of UV radiation, and hence, these parameters are important to evaluate the degradation of the materials.

Elongation at break (%)

The most used degradation parameter, elongation at break (%) were calculated using force versus elongation curves. The force versus elongation curve for the nonirradiated (0 h), 350 h, and 440 h UV irradiated PP : MF07 are depicted in Figure 8.

The variations of elongation at break (%) with respect to UV exposure time are depicted in Figure 9. In the case of virgin PP, a sudden decrease of elongation at break percentage is noted when the material was exposed to UV radiation for nearly 900 h. Hence, this period may be safely taken as the induction period for the photooxidative degradation for PP during artificial weathering conditions used in this investigation. After this induction period, main chain scissions were occurring in the material, which is reflected in the steep drop in the elongation at break percentage value. This behavior may be attributed to the presence of incorporated stabilizers

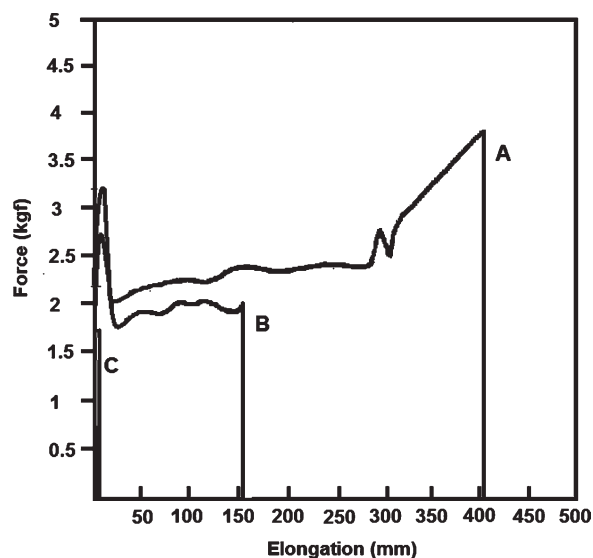


Figure 8 A plot of force versus elongation for UV irradiated PP containing 0.2% of ferric stearate: (A) 0 h irradiated, (B) 350 h irradiated, and (C) 440 h irradiated,

in the commercial grades of PP, which have a role to protect polymer against degradation due to UV radiation. But, in the case of PP containing prodegradants, the drop in the elongation at break percentages value was observed even at 500 h of exposure to UV irradiation. The time (h) of exposure to UV irradiation to reach near zero value for the elongation at break (%) for the different materials investigated are in the order MF03 > MF04 > MF05 > MF06 > MF07. This result indicated that as the number of carbon atoms in the alkyl part of the prodegradants increased, the time necessary for the main chain scission increased. So, the mobility of the alkyl radical in the polypropylene matrix during

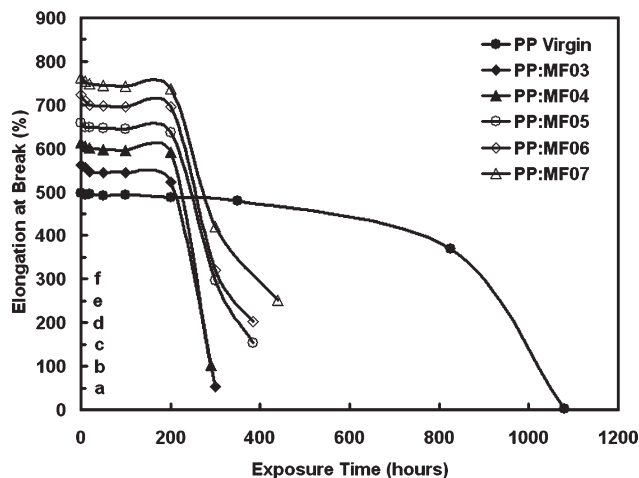


Figure 9 Variation in elongation at break (%) of UV irradiated virgin PP and PP containing 0.2% of ferric carboxylates. Except the curve for virgin PP, the curves of PP : MF03, PP : MF04, PP : MF05, PP : MF06, and PP : MF07 are shifted on the ordinate by the distance ab, ac, ad, ae, and af, respectively.

TABLE III
Tensile Strength of UV Irradiated Virgin PP and PP Containing 0.2% of Ferric Carboxylates

Exposure time (h)	Tensile strength (MPa)					
	PP Virgin	PP : MF03	PP : MF04	PP : MF05	PP : MF06	PP : MF07
0	27.6	27.6	28.4	30.4	30.3	30.72
10	26.2	27.6	26.8	27.7	28.6	28.7
20	25.5	26.5	25.9	27.4	28.9	27.6
50	25.4	26.2	25.7	26.9	27.6	27.0
100	25.3	25.5	25.0	26.6	26.2	25.3
200	24.6	22.9	24.1	25.1	25.9	24.9
300	23.9	9.5	6.9	17.8	19.5	20.8
350	23.6	–	–	13.5	12.6	16.7
385	23.1	–	–	9.3	9.5	13.7
440	22.3	–	–	–	–	9.0
850	16.7	–	–	–	–	–
1080	9.1	–	–	–	–	–

MF03, ferric caprate; MF04, ferric laurate; MF05, ferric myristate; MF06, ferric palmitate; MF07, ferric stearate.

photooxidation is an important factor which governs the rate of UV-induced photooxidative degradation.

Tensile strength

The tensile strength of artificially weathered PP materials was also calculated using force versus elongation curves. It was also used frequently to

judge the degradation phenomena because it dictates the product quality. The values of tensile strength for weathered PP materials are presented in Table III. In almost all cases of PP films and PP containing prodegradants, tensile strength decreased gradually at the initial stages of photooxidation, and then it decreased rapidly. The decrease in tensile strength could just be the result of voids which came from

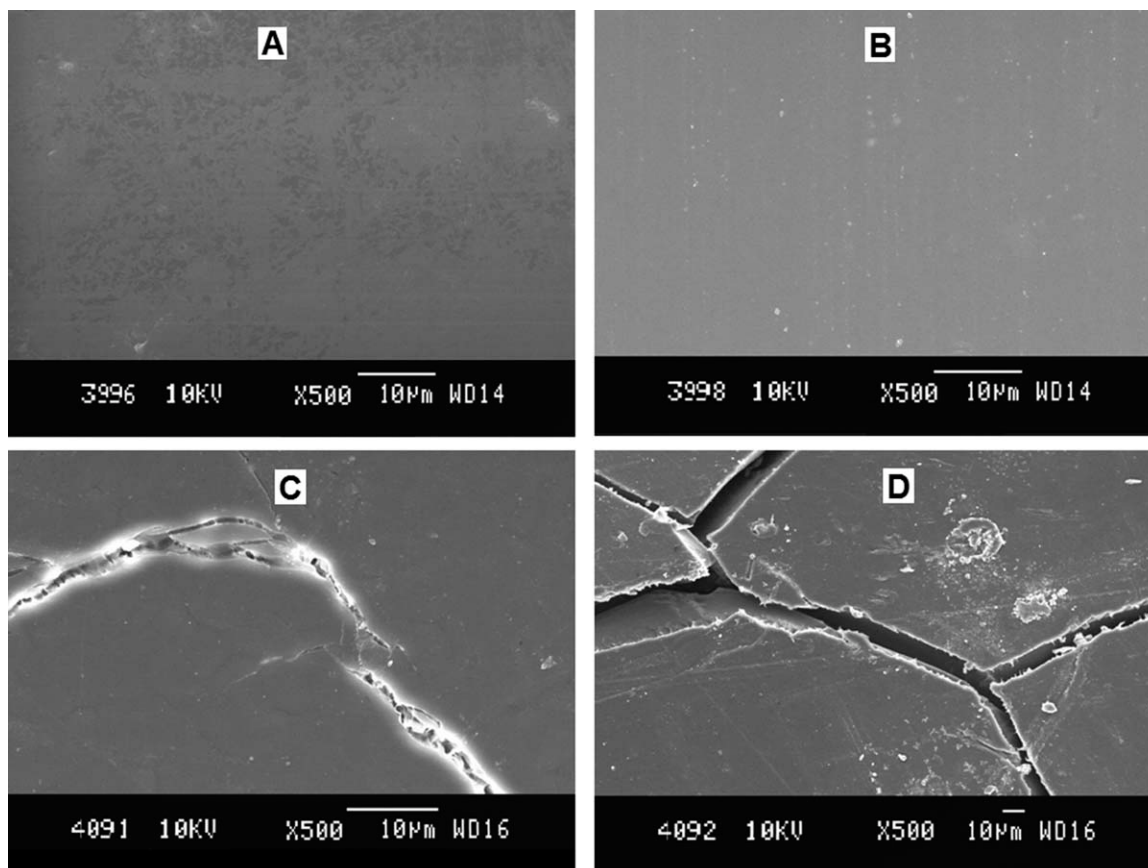


Figure 10 SEM images: (A) Virgin PP, (B) nonirradiated PP : MF04, (C) 290 h irradiated PP : MF04, and (D) 350 h irradiated PP : MF04.

the degradation. All the materials investigated (virgin PP and PP containing 0.2% of ferric carboxylates) retained 25–30% of their tensile strength.

Changes in morphology: SEM studies

The surface morphology of PP material during the course of photodegradation was altered due to UV irradiation, which could be studied using SEM. The SEM image of PP virgin [Fig. 10(A)] indicated the smooth surface without any cracks while Figure 10(B) which corresponds to nonirradiated PP : MF04, showed a few numbers of white spot. It may be due to the dispersion of added iron carboxylates in PP matrix. The slow development of cracks could be seen in Figure 10(C) which corresponds to SEM image of 290 h UV irradiated PP : MF04, while severe cracks and grooves appeared in the 350 h UV irradiated PP : MF04 [Fig. 10(D)] sample due to the stronger main chain scission.

CONCLUSIONS

In the case of artificial weathering studies of PP and PP containing 0.2% of ferric carboxylates, a steep increase of hydroxyl, carbonyl, lactone, ester, carboxylic acid, and crystallinity indices; a sudden decrease of elongation at break percentages and tensile strength; and development of surface cracks indicated the scission of the main chain of the polypropylene. Eventhough all the ferric carboxylates used as prodegradants have a strong influence on the photodegradation behavior of PP, the effectiveness of the prodegradants for the photodegradation is found to be in the order: ferric caprate > ferric laurate > ferric myristate > ferric palmitate > ferric stearate. The above results revealed that the number of carbon atoms present in the alkyl part of the various prodegradants played a vital role in the degradation phenomenon. Thus, it can be concluded that the interplay of the ease of formation of the alkyl radical from the ferric carboxylate, the stability of the produced alkyl radical and its mobility in the weathering polypropylene matrix are the parameters which determine the rate of the photodegradation of polypropylene.

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