Effect of Iron Carboxylates on the Photodegradability of Polypropylene. I. Natural Weathering Studies

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ABSTRACT: To enhance the photodegradability of polypropylene (PP), various carboxylates of iron, including ferric caprate (MF03), ferric laurate (MF04), ferric myristate (MF05), ferric palmitate (MF06), and ferric stearate (MF07), were synthesized. Virgin PP was blended with the synthesized prodegradants (0.2%) and blown into films. To study the photodegradation behavior of PP with and without the prodegradants under natural weathering conditions, all of the films were exposed to sunlight according to the procedure of ASTM 1435. All of the weathered films were found to degrade after a certain number of days of exposure; this was found from the steep increases in the carbonyl, hydroperoxide, hydroxyl, lactone, ester, carboxylic acid, and crystallinity indices. At the same time, a sudden decrease in the elongation at break percentages and tensile strength and surface cracks were also observed. PP containing the prodegradants degraded at a faster rate than the virgin material. The time taken for the material to lose half of the elongation at break value was taken as the halftime, and this was used to determine the effectiveness of the prodegradants. The effectiveness of the prodegradants for the photodegradation of PP was found to be in the following order: MF03 > MF04 > MF05 > MF06 > MF07. With increasing alkyl chain length of the prodegradants, the stability of the alkyl radical increased, whereas the mobility of the radical in the PP matrix decreased. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2601–2612, 2010

Key words: degradation; FT-IR; mechanical properties; photochemistry; poly(propylene) (PP)

INTRODUCTION

Polyolefins have achieved a central position in the distribution of consumer goods because of their combination of flexibility, toughness, excellent barrier properties, and also inertness toward outside factors such as heat, radiation, chemicals, and microorganisms; this has made them the material of choice for packaging applications. Nowadays, plastic shopping bags have become an integral part of our daily life,[1,2] and so their consumption has increased because of their low cost and lower weight. Frequently, they are discarded by uncaring persons; this leads to environmental pollution.

The growing amount of plastic waste is generating more and more environmental problems worldwide through a decrease in the landfill capacity for plastic disposal and the slow degradation of plastic litter in the environment. To minimize this problem, there are three ways to use plastic waste: landfilling, incineration with or without energy recovery, and recycling. The largest amount of plastic waste goes to landfilling (65–70%), incineration consumes 20–25%, and recycling uses only about 10%.[3,4] Therefore, it is obvious that the environmental problem from this waste still exists. So, research has focused on the development of degradable polymers that are environmentally friendly, and several research articles[5–12] have included such investigations.

Polypropylene (PP) is an attractive material for packaging because of its low cost of production, higher tensile strength, gloss, and versatility.[13] Therefore, an increase in the use of PP leads to an increase in litter. PP is one among the important polluters because of its nonpolar nature[14] and because it does not degrade for a long period after disposal.

PP does not respond to biodegradation by bacteria, fungi, yeasts, or enzymes, but photodegradation, photooxidation, and auto-oxidation are the main pathways for its degradation.[15] Consequently, numerous attempts have been made to develop photodegradable plastics. Prior methods have synthesized a polymer composed of carbonyl groups in its chain or pendent side chain, blended a degradable polymer with a nondegradable polymer, or incorporated a photodegradation-promoting agent (*prodegradant*)

TABLE I
Physical properties of Repol H100EY (PP)

Property	ASTM test method	Unit	Typical value
Melt flow index (230°C/2.16 kg)	D 1238	g/10 min	11.0
Tensile strength at yield (50 mm/min)	D 638[a]	MPa	35
Elongation at yield (50 mm/min)	D 638[a]	%	10
Flexural modulus (1% secant)	D 790A[a]	MPa	1600
Notched Izod impact strength (23°C)	D 256[a]	J/m	26
Heat deflection temperature (455 kPa)	D 648	°C	104

[a] ASTM D 638 type I specimen injection-molded and tested in accordance with ASTM D 4101 04–05.

into a polymer.[16] Among these, the more convenient and simplest method of blending prodegradants with a polymer was involved in this study.

Osawa et al.[17] studied extensively the photodegradation behavior of polyethylene (PE) and PP using various transition-metal stearates as prodegradants. The results indicate that iron stearate was the most effective in the early stage of photodegradation, vanadium and manganese stearates accelerated it, and copper stearate retarded it. Other stearates showed no appreciable effect on the photodegradation.

The effect of the chain length of cobalt carboxylates, namely, laurate, palmitate, and stearate, on the photodegradation behavior of PE was reported by Roy et al.[18] The authors concluded that all of these cobalt carboxylates promoted photodegradation, but the effectiveness in promoting photodegradation was in the order: Stearate > Palmitate > Laurate.

Environmental weathering is the result of combined physical and chemical reactions, that is, photochemical reactions associated with photons of different energies; mechanical actions of wind, rain, and pollutants; and thermal cycles associated with day and night alteration. These effects can induce nonnegligible changes in the polymer.[19] Only a few authors[20,21] have investigated the degradation behavior of PE with various photoiniators under natural weathering conditions.

The degradation of injection-molded PP bars stabilized by carbon black or by a hindered amine was compared to that of an unstabilized polymer by Qayyum and White.[22] Samples were weathered in Jeddah, Saudi Arabia, where the climate is very hot and humid with very little rainfall, for periods of up to 8 years. The authors stated that the unstabilized grade became brittle within a few weeks of outdoor exposure, whereas the stabilized materials retained significant ductility for extended periods of weathering.

Leong et al.[23] investigated the characteristics of single-filler PP composites (containing either talc or calcium carbonate) and hybrid–filler PP composites (consisting of a mixture of talc and calcium carbon-

ate) weathered in the natural tropical environment in Penang, Malaysia, for 6 months. After 6 months of exposure, the authors showed that the mechanical properties of the single-filler PP composites deteriorated because of severe physical and chemical degradation. However, the hybrid–filler PP composites showed better retention of mechanical properties, although they underwent some degree of surface degradation as well. However, there is no report on the effect of the addition of transition-metal carboxylate as a prodegradant on the photodegradation behavior of PP under natural weathering conditions. Hence, in this investigation, we made a detailed attempt to investigate the effect of added iron carboxylates on the photodegradation behavior of PP films.

EXPERIMENTAL

Materials

The polymeric material selected for this investigation was PP (Repol-grade H100EY) obtained from Reliance Industrial, Ltd. (Jamnagar, India). This material contained Irganox antioxidant (500–1000 ppm). The physical properties of the PP material are listed in Table I. To synthesize the iron salts of various fatty acids, potassium hydroxide pellets manufactured by S. D. Fine-Chem, Ltd. (Mumbai, India), ferric sulfate monohydrate manufactured by Reachem Laboratory Chemicals Private, Ltd. (Chennai, India), 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 without further purification.

Synthesis of iron salts of fatty acids

According to a procedure reported in the literature,[2] iron salts of capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid were synthesized by the reaction of ferric sulfate monohydrate with the

Figure 1 Outdoor exposure racks used for natural weathering studies.

corresponding potassium salt of fatty acid, and the resulting 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 was taken in 4-kg batches and blended with 0.2% of the prepared prodegradants (MF03, MF04, MF05, MF06, and MF07) with a blender made by Modern Plastic Industries (Coimbatore, India). The virgin PP and the various prodegradant-blended PPs were extruded blown into films with an extruder (model PP-750) made by Klockner Windsor India, Ltd. (Mumbai, India). 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 2000 rpm. The films were obtained with a 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.

Natural weathering procedure

The extruded films (virgin PP and virgin PP blended with MF03, MF04, MF05, MF06, and MF07) were exposed to natural weathering on suitably designed and fabricated outdoor exposure racks (Fig. 1) made by Star Engineering Works (Thiruthangal, India) according to the specification of ASTM 1435, which included an angle of 45° to the ground and placement toward the south. Each rack had 12 segments, in which each segment has four subdivisions for each sampling. In these racks, each segment had dimensions of 58.5×41.5 cm², and each subdivision had dimension of 26×17.5 cm².

The outdoor exposure racks were located at Kamaraj College of Engineering and Technology,

S. P. G. C. Nagar, K. Vellakulam Post 625 701 (Virudhunagar, India), which is located at a latitude of 9.36° N and a longitude 77.58° E and situated near Madurai in the southern part of Tamil Nadu, India. The average annual rainfall is about 60–80 cm, and the annual average temperature is above 27.5°C.

In this investigation, the natural weathering of all PP film materials mentioned previously were carried out from December 1, 2006 to the end of March 2007. During the course of natural weathering, the average temperature, pressure, and relative humidity were about 34°C, 748 mmHg, and 40%, respectively. The average visible and UV light intensity recorded were 937×10^2 LUX and 998 uW/cm², respectively. The sampling was done once every 3 days. The naturally weathered samples were analyzed by Fourier transform infrared (FTIR) spectroscopy and a universal testing machine.

Weathering parameter measurements

To measure the outdoor temperature, we used a Jennson Research GRD glass thermometer, Heber Scientific, Chennai, India. The pressure was measured with a Besto barometer (640–810 mmHg), Heber Scientific, Chennai, India. A Huger hygrometer (85 mm, model 3123), Heber Scientific, Chennai, India was used to measure the humidity. The UV light intensity was measured by a Lutron UV-340 UV light meter, Heber Scientific, Chennai, India 0-1999 (x1 uW/cm², model D 44197). Visible light intensity was measured with a Lutron LX-101 model (CE 35187), Heber Scientific, Chennai, India. 20,000–50,000 (×100 LUX). All of the weather parameters were measured between 12 : 00 and 13 : 00 h of the day.

FTIR studies

We evaluated the structural changes of the naturally weathered PP films 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 a 4-cm^{-1} resolution. From the FTIR spectrum of the weathered PP samples, significant changes were observed in the hydroxyl (3600–3200 cm^{-1}), carbonyl (1800–1700 cm^{-1}), and unsaturated (1000–800 cm^{-1}) groups as a function of exposure time under the natural weathering conditions. On the basis of these changes, indices of hydroperoxide, hydroxyl, carbonyl, carboxylic acid, ester, lactone, and vinylidene were calculated as the ratio of the corresponding peak absorbance maximum to the maximum absorbance value of a reference peak. The maximum absorbance regions for some groups, which were related to degradation products, are

TABLE II
IR Maximum Absorbance Region for Groups Formed During Weathering

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

listed in Table II. Several peaks at 840, 974, 1166, 1455, and 2720 cm^{-1} were found in the literature[24–28] as reference peaks for PP. In this study, the band at 974 cm^{-1} (CH_3— rocking band) was chosen as a reference peak because it remained unchanged during the degradation process. The crystallinity index[25] was also evaluated as the ratio of maximum absorbance at 998 cm^{-1} to the maximum absorbance at 974 cm^{-1}.

Mechanical properties measurements

The mechanical properties, including elongation at break (%) and tensile strength, of the naturally weathered PP film samples were determined with a Hounsfield material testing machine (model S series, H5K-S) with a load cell (5 kN) and grips (HT55 Ultra Light vice grips), supplied by Tinius Olsen, Ltd. (Surrey, England). It was operated at a speed of 150 mm/min with a grip distance of 80 mm on the rectangular bar film samples with a length of 12 cm, a breadth of 2 cm, and a thickness of 62 μm. For each sample, four tests were conducted, and the average value was chosen for further data analysis.

Scanning electron microscopy (SEM) studies

The morphological changes occurring during the course of natural weathering of the PP films were investigated with a scanning electron microscope. Sample surfaces were sputtered with gold with the usual techniques and then analyzed with a JEOL (JSM-840A) scanning electron microscope, JEOL Ltd., (Tokyo, Japan) at a voltage of 10 kV. Photomicrographs were taken at a uniform magnification of 500×.

RESULTS AND DISCUSSION

### Photooxidative aging mechanism

The chemical changes that occur during the photooxidative process are very complex, and it is generally assumed to be a free-radical chain mech-

anism.[29–31] In general, in the absence of photoinitiators, the initiation of PP photooxidation is done by the abstraction of the hydrogen atom, preferably tertiary hydrogen, by free radicals produced because of the decomposition of chromophoric impurities, such as hydroperoxide formed during processing.[32]

The most probable mechanism for the degradation of PP in the presence of photoinitiators such as iron carboxylates[20] is presented in Schemes 1–3. Iron carboxylates absorb energy in the form of light and heat and undergo decarboxylation to liberate alkyl free radicals. These alkyl-free radicals abstract tertiary hydrogen from PP and form propyl macroradicals. These propyl macroradicals react with oxygen and generate peroxy macroradicals, which are converted to hydroperoxide. Alkoxy radical formation from the decomposition of hydroperoxide is an important step because the resulting alkoxy macroradical leads to main-chain scission, which results in the formation of ketone. The generated ketones finally undergo Norrish type I and type II reactions and liberate different kinds of photooxidation products, such as aldehydes, carboxylic acids, esters, lactones, peracids, and peresters.[19,33,34]
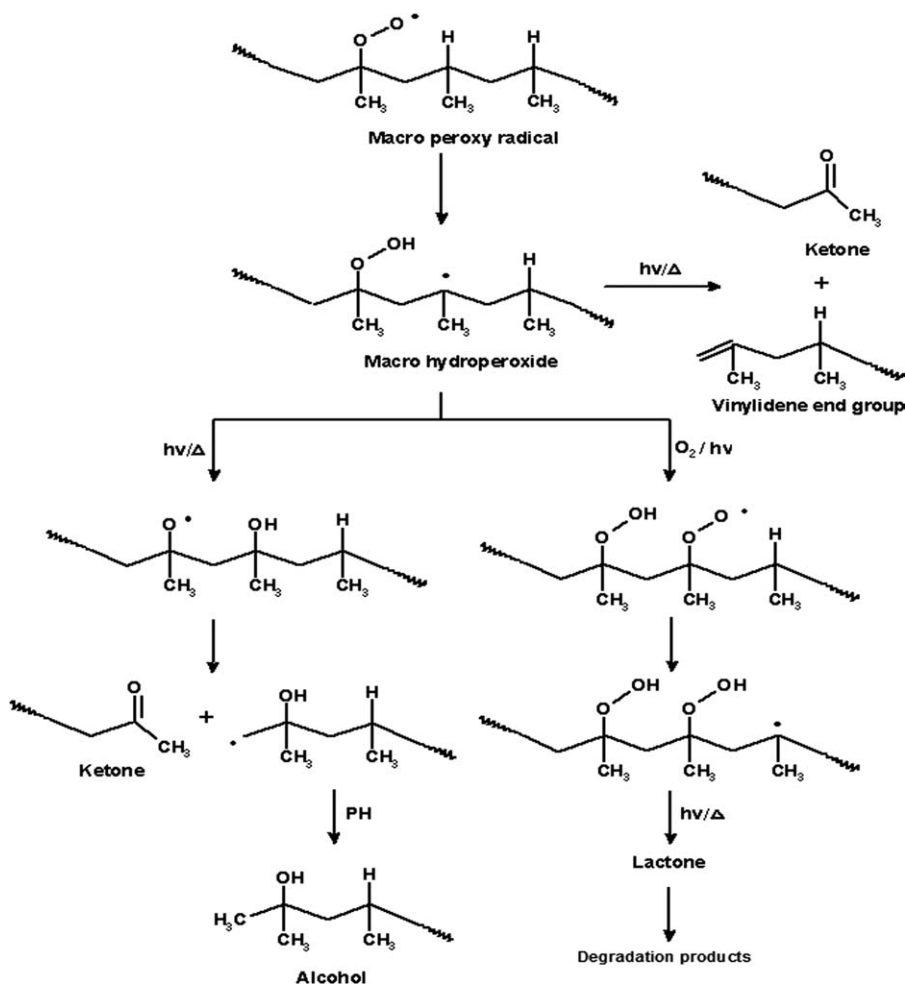
FTIR studies

To investigate the chemical changes taking place in the material during natural weathering, the FTIR
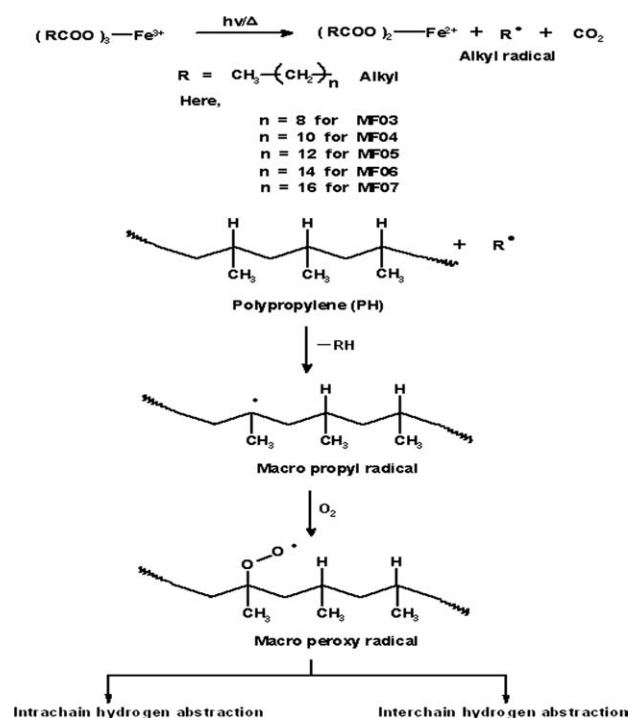
Scheme 1 Initiation reaction of iron carboxylates toward polymer degradation.

Scheme 2 Intrachain hydrogen abstraction during the course of degradation.

spectrum of the sample was recorded. The hydroperoxide, hydroxyl, lactone, ester, carbonyl, carboxylic acid, vinylidene, and crystallinity indices were calculated and are discussed.

Carbonyl index

The carbonyl index is the most used parameter for monitoring the degree of degradation.[35] The carbonyl index was calculated as the ratio of the maximum absorbance at 1715 cm^{-1} to the absorbance at 974 cm^{-1}.

For naturally weathered PP samples, the carbonyl index value increased with increasing exposure period after a certain number of days, and this period was considered the induction period for the photodegradation behavior. For the virgin PP films, the carbonyl index value started to steadily increase after an exposure period of 50 days, whereas all of the prodegradant-blended PP samples showed prominent increases in the carbonyl index values

within 20 days of exposure. From Figure 2, it is clear that the total number of carbons present in the alkyl chain of the iron carboxylate played an important role in the degradation rate of PP under natural environmental conditions. As the number of carbons in the alkyl group increased, the induction period for the initiation of the photodegradation of PP increased; this indicated that the mobility of the alkyl radical produced by the decomposition of the iron carboxylate played a substantial role in the photodegradation of PP.

Recently, Roy et al.[18] investigated the photooxidative degradation of low-density PE with cobalt carboxylates as prodegradants. The photooxidation was conducted in an artificial weathering chamber. The authors concluded that the rate of photodegradation increased as the length of the alkyl chain present in the cobalt carboxylate increased. This result was attributed to the fact that as the alkyl chain length increased, the carboxylate was capable of blending easily with the base polymer; this
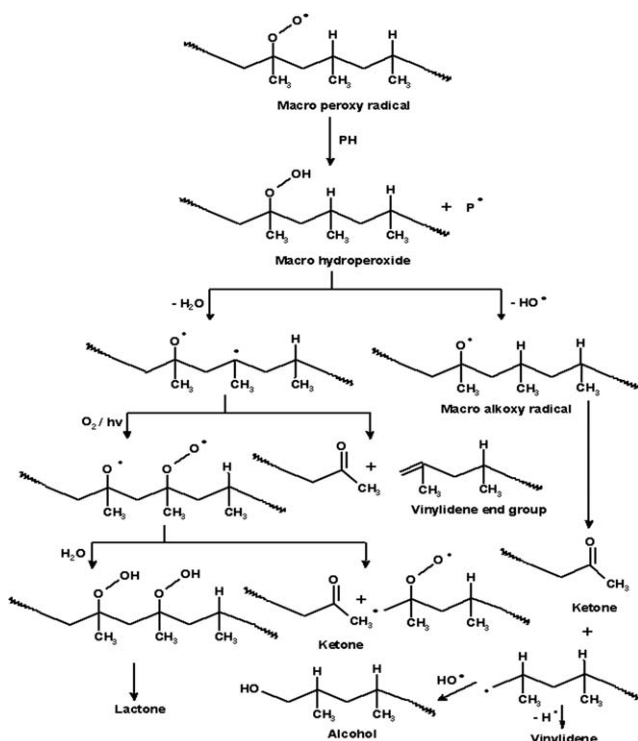
Scheme 3 Interchain hydrogen abstraction during the course of degradation.

resulted in its increased capability to act as a prooxidant.

In general, carbonyls groups were observed as a broad peak in the region of 1800–1700 cm^{-1} in the FTIR spectrum of weathered PP because of the overlap of different degradation products, such as lactone, ester, ketone, and carboxylic acid.[36] Figure 3 shows that the carboxylic acid group concentration was higher, whereas the lactone concentration was low because the carboxylic acid was the final stable product of degradation,[37] whereas it is a precursor for lactone formation[38] in almost all cases. A similar trend was observed in the study of PP natural weathering at Messina, Italy, by Gallo et al.[39] and also in our previous study.[40]

Hydroperoxide index

Hydroperoxide is the first product formed during the degradation of PP, and hence, it is important to measure. However, hydroperoxides are rather unstable, and hence, they usually decompose and form carbonyl compounds, which accumulate as the oxidation process continues. Hydroperoxide concentration was used as one of the indicators for the extent of degradation with respect to the exposure time. Hydroperoxide group formation and its decomposition in the course of natural weathering is an impor-

tant aspect, which may justify the faster degradation of materials.[41]

The hydroperoxide index was calculated with the following formula:

Hydroperoxide index =

Absorbance at 3445 cm^{-1}/Absorbance at 974 cm^{-1}

Broska and Rychly[42] followed the buildup of hydroperoxide by direct FTIR measurement of the absorbance at 3420 cm^{-1}, attributed to adjacent hydroperoxides. The authors revealed that there was a maximum and a subsequent decrease in the concentration of hydroperoxide with aging time.

In contrast, Luzuriaga et al.[41] and Valadez-Gonzalez and Veleva[43] showed a gradual increase in the hydroperoxide concentration on thermal aging. The higher hydroperoxide concentration in PP was expected because of structural factors that favor chain scission.

From Figure 4, the time taken to reach a hydroperoxide index value of 0.2–0.3 was calculated. For the prodegradants MF03, MF04, MF05, MF06, and MF07 blended with PP, this value was reached in 6, 9, 12, 15, and 17 outdoor exposure days, respectively. Thus, a nearly linear trend was seen. The results showed that the induction time needed for the degradation increased as the number of carbon atoms in the alkyl part of the iron carboxylates used as prodegradants for PP increased. The probable explanation for this observation was that as the length of the alkyl radical formed from the prodegradants increased, the mobility of the radical in the PP matrix was reduced, and hence, the rate of the degradation reaction decreased.
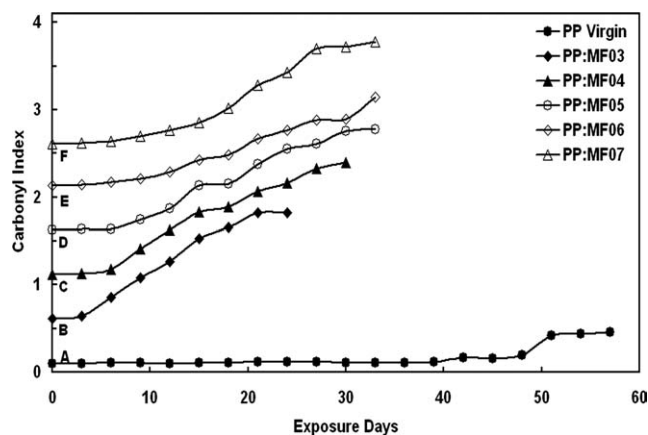
Figure 2 Carbonyl index value changes as a function of exposure days for virgin PP and PP blends with various prodegradants during natural weathering. The curves of the samples PP–MF03, PP–MF04, PP–MF05, PP–MF06, and PP–MF07 were shifted on the ordinate by the distances AB, AC, AD, AE, and AF, respectively.
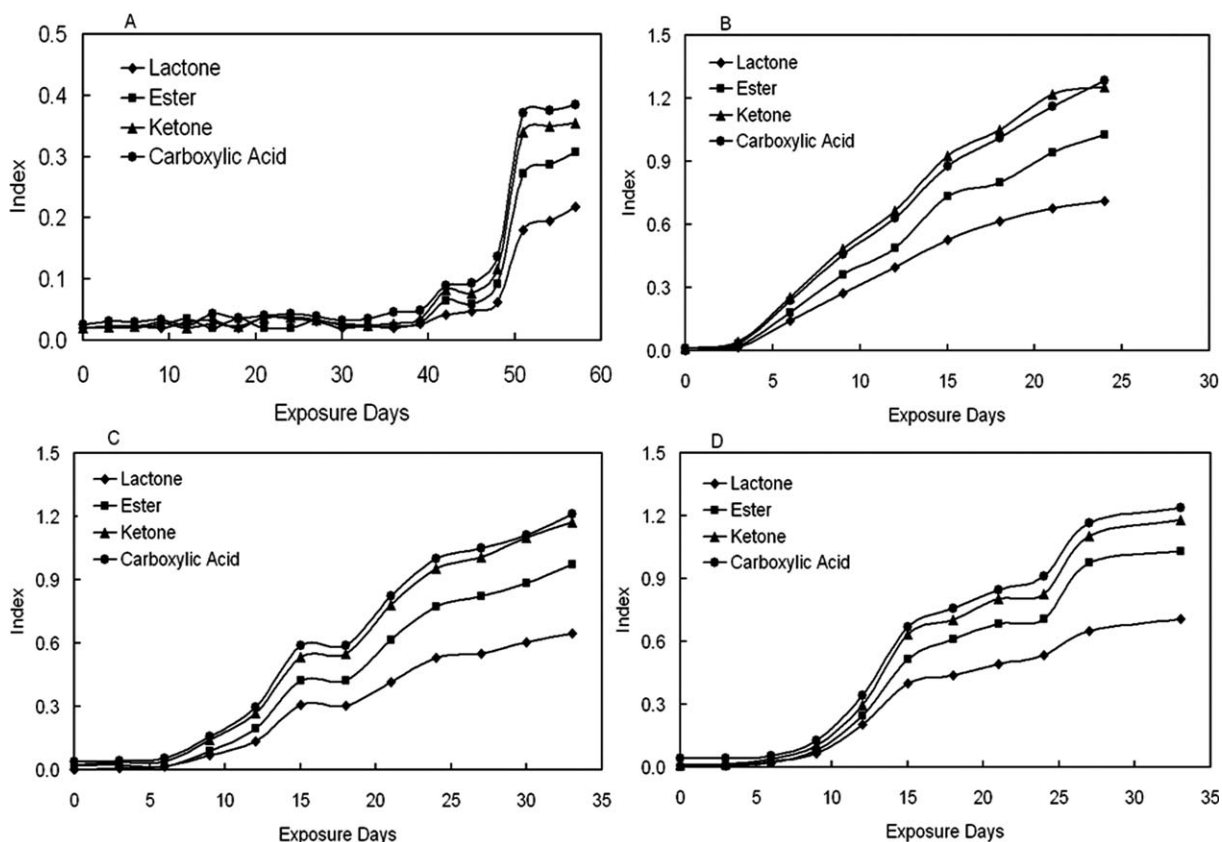
Figure 3 Variations in the indices of lactone, ester, ketone, and carboxylic acid of the (A) virgin PP and PP blends with prodegradants (B) MF03, (C) MF05, and (D) MF07 during natural weathering.

As shown in Figure 5, it was clear that the steep increase of hydroperoxide groups and carbonyl groups occur in the same time span. So, the unstable hydroperoxide formation and its decomposition occurred simultaneously during the photodegradation of PP containing iron carboxylate prodegradants.

Hydroxyl index

Hydroxyl-group-containing compounds, such as alcohol, carboxylic acid, and peracid, were formed during the course of degradation (Schemes 1–3). The ratio of the absorbance at 3600 cm^{-1} to that at 974 cm^{-1} was evaluated as the hydroxyl index. The variation of the hydroxyl index values with respect to the number days of exposure to the natural weathering conditions is depicted in Figure 6. It was obvious that the time necessary to show a steep increase in the hydroxyl index value was in phase with the time needed for the increase in both the hydroperoxide and carbonyl indices. The results reveal that carbonyl and hydroxyl group compounds occurred simultaneously during the photodegradation of PP (Fig. 5).

Crystallinity index

In general, degradation can be easily effected in the amorphous region, and therefore, the amorphous region disappeared as the degradation progressed.
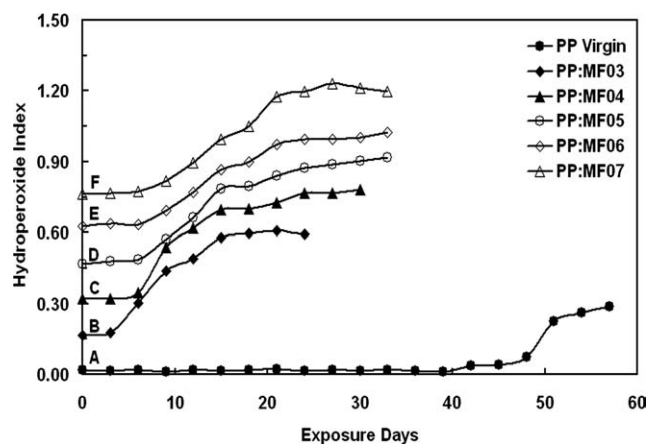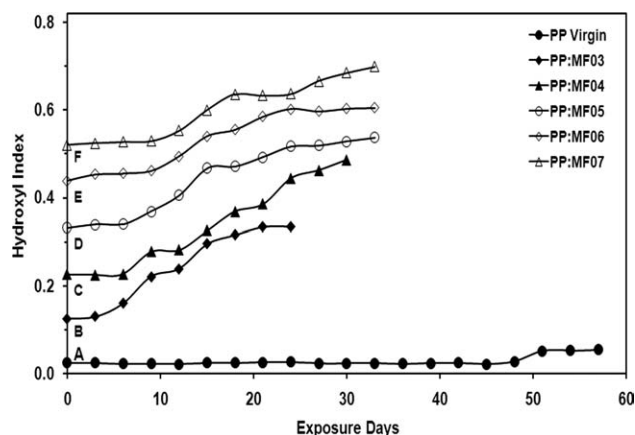

Figure 4 Hydroperoxide index value changes as a function of exposure days for the virgin PP and PP blends with various prodegradants during natural weathering. The curves of the samples PP–MF03, PP–MF04, PP–MF05, PP–MF06, and PP–MF07 were shifted on the ordinate by the distances AB, AC, AD, AE, and AF, respectively.
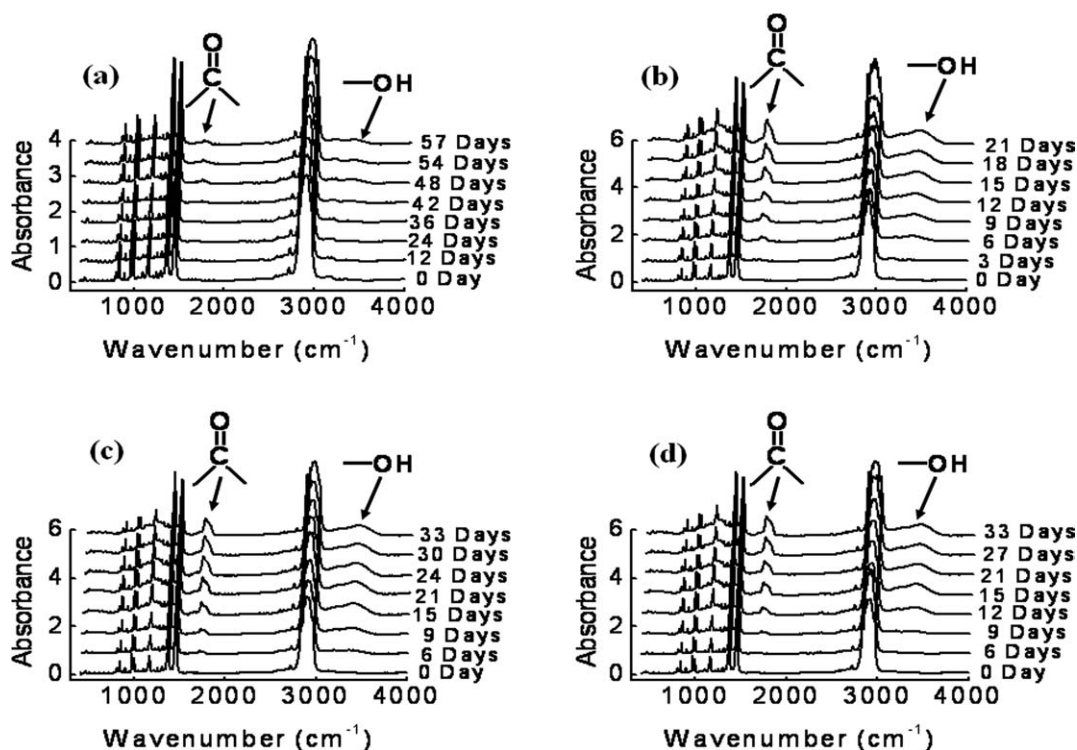
Figure 5 FTIR spectrum of the (a) weathered virgin PP and PP blends with prodegradants (b) MF03, (c) MF05, and (d) MF07 during natural weathering.

To gather information on the variation of crystallinity as a function of outdoor exposure days, the ratio of absorbance of the 998-cm^{-1} band to the absorbance of the 974-cm^{-1} band was calculated as the crystallinity index. The first band was a regularity band characteristic of the crystalline PP, whereas the second band corresponded to both the crystalline and amorphous PP phases.[44,45]

The crystallinity index calculated for the PP samples undergoing photodegradation are presented in Figure 7. As the photodegradation of PP progressed, the crystallinity value increased. This enhancement in the crystallinity index value could be explained by (1) the degradation and disappearance of the amorphous phase by preferential attack by oxygen and (2) the formation of new,


Figure 6 Hydroxyl index value changes as a function of exposure days for the virgin PP and PP blends with various prodegradants during natural weathering. The curves of the samples PP–MF03, PP–MF04, PP–MF05, PP–MF06, and PP–MF07 were shifted on the ordinate by the distances AB, AC, AD, AE, and AF, respectively.
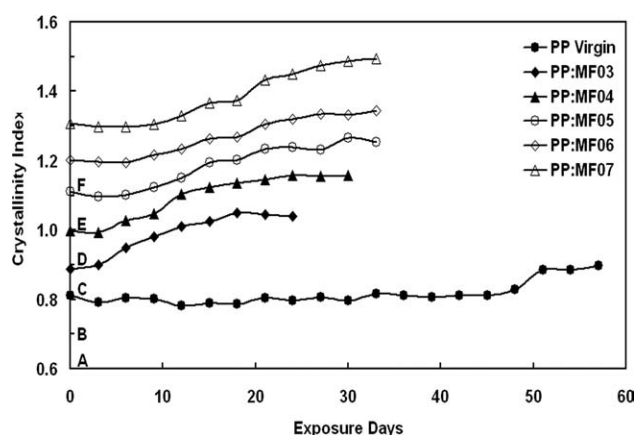
Figure 7 Crystallinity index value changes as a function of exposure days for the virgin PP and PP blends with various prodegradants during natural weathering. The curves of the samples PP–MF03, PP–MF04, PP–MF05, PP–MF06, and PP–MF07 were shifted on the ordinate by the distances AB, AC, AD, AE, and AF, respectively.
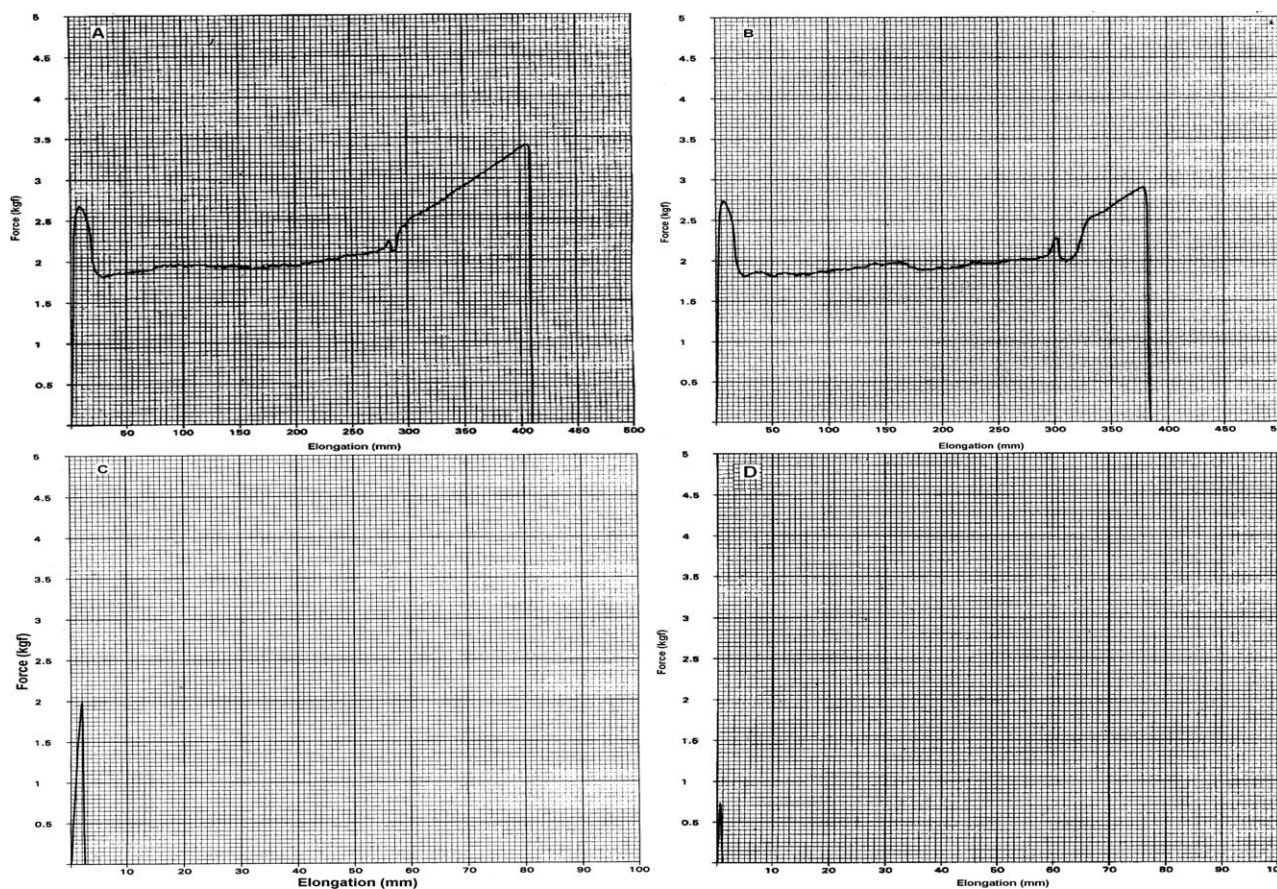
Figure 8 Force versus elongation curve for PP–MF03: (A) nonweathered and weathered for (B) 6, (C) 9, and (D) 12 days.

low-molecular-weight photooxidation products, which were capable of forming new crystalline domains.[19] Thus, the crystallinity index increased when the indices of hydroperoxide, hydroxyl, carbonyl, lactone, ester, and carboxylic acid increased.

Measurements of the tensile properties

Elongation at break (%)

Several authors[46–48] have shown that the elongation at break (%) can frequently be used to monitor the degradation of polymers, which show a drop of 50% at the initial stage of exposure to sunlight or artificial irradiation with UV light followed by a continuous drop until the elongation at break reaches a value near zero; this is attributed mainly to the occurrence of main-chain scissions. The force versus elongation curve for the nonweathered (0 day) sample and PP–MF03 samples weathered for 6, 9, and 12 days are depicted in Figure 8(A–D).

In the case of virgin PP for up to 45 days of exposure to sunlight, the elongation at break percentages showed no conspicuous changes (Fig. 9), and then, a sudden decrease to a value near zero was noted; this indicated the occurrence of main-chain
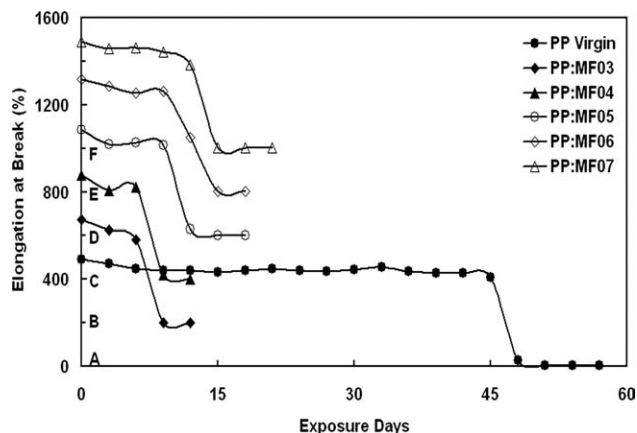
Figure 9 Elongation at break (%) value changes as a function of exposure days for the virgin PP and PP blends with various prodegradants during natural weathering. The curves of the samples PP–MF03, PP–MF04, PP–MF05, PP–MF06, and PP–MF07 were shifted on the ordinate by the distances AB, AC, AD, AE, and AF, respectively.
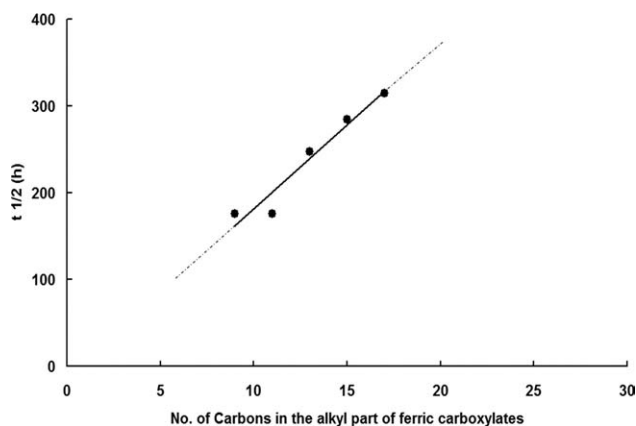
Figure 10 Plot of $t^{1/2}$ (h) versus the number of carbons present in the alkyl part of the ferric carboxylates for PP blends with various prodegradants during natural weathering.

scissions. An induction period of 45 days of exposure was observed before the elongation at break percentages decreased rapidly. This behavior may have been due to the presence of incorporated stabilizers in the commercial grades of PP, which have a role in protecting the polymer against degradation during outdoor weathering and to the exclusive morphological changes occurring for oxidation, not any chemical changes. However, in the case of the prodegradant-added PP materials, the loss of the elongation properties happened after around 15 days of exposure and, thereby, rendered the films useless for practical applications. The order of this loss of elongation at break (%) was observed as follows: MF03 > MF04 > MF05 > MF06 > MF07. This result indicates that as the number of carbons 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 PP matrix undergoing natural weathering is an important factor, which governs the rate of UV-induced photooxidative degradation. The time needed for the material to lose 50% of the elongation at break from its initial value was taken as the half-time ($t^{1/2}$). A plot of $t^{1/2}$ versus the number of carbon atoms present in the alkyl part of the added prodegradants gave a straight line (Fig. 10). Hence, the rate of UV-induced photooxidative degradation of PP was linearly related to the number of carbon atoms present in the alkyl part of the added prodegradant, ferric carboxylate.

Tensile strength

Tensile strength is an important measure of product quality in certifying product, and therefore, its

variation during weathering is to be followed to judge the degradation. The variation of tensile strength of virgin PP and PP blended with different prodegradants during natural weathering are shown in Figure 11. In almost all cases, for the PP films and PP containing prodegradants, the tensile strength decreased gradually at the initial stages of weathering, and then, the tensile strength decreased rapidly. The behavior was explained by the chain reorganization phenomenon and lower degree of orientation[49] that was present in PP. All of the materials investigated (virgin PP and PP blended with prodegradants) retained 20–40% of their tensile strength.

SEM studies

The dispersability of the iron carboxylates in PP and the surface morphology changes of the PP material during weathering were characterized with SEM. Figure 12(A) shows the SEM images of the virgin PP; the figure shows a smooth surface without any cracks, whereas in Figure 12(B), a few white spot are present, which may be attributed to the added iron carboxylate particles. The SEM images of PP–MF03 weathered for 7 days [Fig. 12(C)] showed a slow development of cracks, but cracks and grooves appeared in the PP–MF03 weathered for 9 days [Fig. 12(D)] because of stronger main-chain scission.

CONCLUSIONS

In the weathering studies of PP and prodegradant-blended PP, a steep increase in the carbonyl,
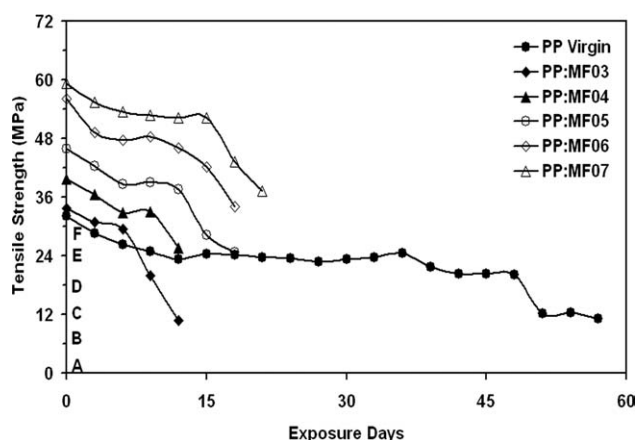
Figure 11 Tensile strength changes as a function of exposure days for the virgin PP and PP blends with various prodegradants during natural weathering. The curves of the samples PP–MF03, PP–MF04, PP–MF05, PP–MF06, and PP–MF07 were shifted on the ordinate by the distances AB, AC, AD, AE, and AF, respectively.
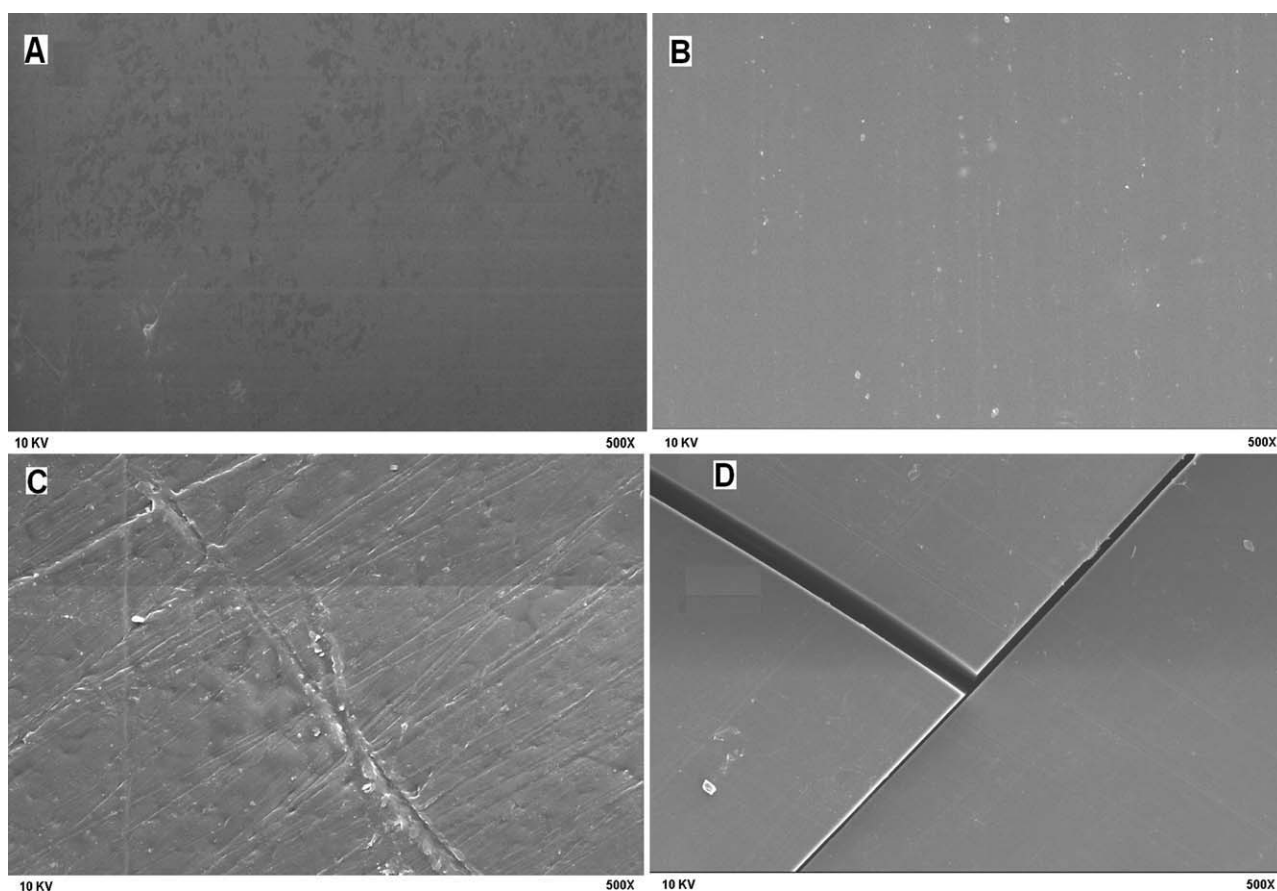
Figure 12 SEM pictures of (A) virgin PP, (B) nonweathered PP–MF03, (C) PP–MF03 weathered for 7 days, and (D) PP–MF03 weathered for 9 days.

hydroperoxide, hydroxyl, lactone, ester, carboxylic acid, and crystallinity indices, a sudden decrease in the elongation at break percentage and tensile strength, and the development of surface cracks indicated the scission of the main chain of the polyolefin. All of the ferric carboxylates used as prodegradants had a strong influence on the photodegradation behavior of PP and facilitated UV-induced photooxidative degradation. The effectiveness of the prodegradants was in the following order: MF03 > MF04 > MF05 > MF06 > MF07. The $t^{1/2}$ parameter obtained from the elongation at break percentages versus the number of carbon atoms present in the alkyl part of the added prodegradants plot indicated that the rate of UV-induced photooxidative degradation of PP was linearly related to the number of carbon atoms present in the alkyl part of the added prodegradant, ferric carboxylate. Thus, the results show that the chain length of the various prodegradants played a vital role in the degradation phenomenon. 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 of the PP matrix were parameters that determined the rate of the photodegradation of PP.

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