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A COMPARATIVE STUDY OF THE DEGRADABILITY AND RECYCLABILITY OF DIFFERENT CLASSES OF DEGRADABLE POLYETHYLENE

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ABSTRACT

Abiotic degradation of representative samples from available commercial photo(bio)degradable polyethylene films was examined with respect to the rate and extent of degradation, oxidation products, and changes in molecular weight both during outdoor exposure and in laboratory photoaging devices with different accelerating factors. Although the rate of photoxidation was found to depend on the type of degradation system used, all the samples showed rapid rate of carbonyl formation with concomitant reduction in molecular weight and mechanical properties on exposure to UV light. The photofragmented polymers were shown to be much more hydrophilic in nature compared to the unoxidized analogues, and photofragments of all samples were found to contain high levels of low molecular weight (bioassimilable) carboxylic acids and esters. Recycling behavior of virgin polyolefins, both as homopolymers and heterogenous polymer blends, which contained 10% of nonoxidized and photooxidized photo(bio)degradable plastics was examined. It was found that the initial mechanical performance of homogeneous blends was not greatly affected by the presence of nonoxidized degradable materials. However, blends containing degradable films which were initially partially photooxidized had a much more detrimental effect on the recycled blends properties during processing and weathering; the effect was minimal for degradable polymers containing the iron–nickel dithiocarbamate system.

INTRODUCTION

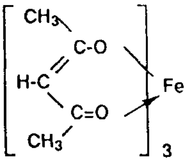
All commercial polyolefins will degrade eventually as they are not chemically "pure" materials: they contain several chemical impurities which are introduced at different stages of their life cycle (polymerization, processing, manufacturing, storage, and upon environmental exposure in-service) [1]. Impurities such as metal ions, peroxides, unsaturation, and carbonyl compounds initiate oxidation of the polymer, and even stabilized polymers undergo eventual oxidation with the introduction of a variety of carbonyl species, in particular carboxylic acids and esters [2]. Antioxidants contribute to prolonging the product outdoor lifetime; this aspect raises many environmental problems in the form of plastics litter and as hazards to animals. Plastics products in many applications, e.g., high volume packaging and agricultural, are often made to be too stable for their intended purpose. In response to these problems, manufacturers produced a number of polyolefin-based materials with enhanced degradability, and products based on these materials have been claimed to be photodegradable, biodegradable, or both, often without defining the conditions or the way in which the polymer product degrades. The lack of sufficient scientific evidence and objective criterion to test the manufacturer's claims on the performance and degradability attributes of their products has raised public concern [3]. We report here some of the work carried out under the Brite-Euram collaborative research program [4] which was set up to examine how chemical, physical, and biological factors affect the degradability of commercially available photo(bio)degradable polyethylenes. Some of the issues addressed in this research program have already been reported [5]. Three classes of commercial degradable polyethylene-based materials were used throughout this work:

A. Photolytic polymers (A samples): In this class the photosensitizing group forms an integral part of the polymer chain. Two different types of polyethylene (PE) containing carbonyl groups are available commercially:

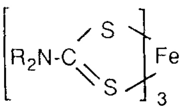
- (i) The carbonyl is built in the polymer chain by copolymerizing carbon monoxide with ethylene, ECO system [6]; this is now used for specialized applications such as "six-collar packs" for beverage cans.
- (ii) Polyethylene containing copolymerized vinyl ketone in the side chain, Ecolyte (Guillet process) [7].

B. Polyethylene containing metal compounds as photoactivators (B samples):
  - (i) Polymer containing organo-soluble transition metal ion (generally iron in the form of carboxylate [8], e.g., acetyl acetonate, FeAcAc) [8a], and
  - (ii) Polyethylene containing metal chelates (with sulfur ligands) which act as antioxidants and photoactivators (AOPA); e.g., Fe^{III} dithiocarbamate, FeDRC (Scott-Gilead process) [9].

C. Starch-filled polyethylene (C samples): PE-starch formulation (Griffin process) [10, 11] may be subdivided into two categories:
  - (i) Polymer containing starch, normally at 6-8%, and
  - (ii) Polymer containing starch and iron carboxylate (generally stearate, FeSt).



FeAcAc



FeDRC

$(C_{17}H_{35}COO)_3Fe$

FeSt

This paper reports on some aspects of abiotic degradation and recycling potential of representative samples of each of the above materials, together with degradable systems, "similar" to the commercial Scott-Gilead polymers, prepared in the laboratory under controlled and known thermal history. The key role of the prior oxidation on the subsequent biodegradation of these polymers will be highlighted but their biodegradative behavior, which has also been examined [4], will not be discussed.

EXPERIMENTAL

Materials and Recycling Operation

Tables 1a and 1b show the origin and composition of representative samples of commercially available photo(bio)degradable polyethylene films (thickness: 12–40 μm except **A3** which was 508 μm). All the samples were low density polyethylene (LDPE)-based except for **B7** and **B8** which were high density polyethylene (HDPE). Virgin unstabilized polymers, LDPE (Novex L-61, from B.P), PP (propathene HF23, from ICI) and EPDM (Vistalon 250, from Exxon) were used for recycling experiments. All solvents used were either HPLC or spectroscopic grades.

LDPE samples containing different concentrations of FeDRC (similar to the Scott-Gilead commercial degradable polymer) were extruded into thin films (75 μm) under controlled laboratory conditions using a single screw extruder, SSE (Humboldt HE 45-25DE, L/D ratio 25:1) at 45 rpm with the three barrel zones set

TABLE 1a. Commercial Degradable Low Density Polyethylene Samples (except B7 and B8 which are high density polyethylene). All Samples Are Thin Films Except A3 Which is a Thicker Sample from a "6-Collar Pack"

Type	Code	Origin	Apperance	Composition
Photolytic copolymer	A1	Ecolyte	Transparent	Ethylene-vinyl ketone copolymer
	A2	Dupont	Transparent	Ethylene-CO copolymer
	A3	ITW Hi-Cone PE	6-Collar pack	Ethylene-CO copolymer
Metal compounds	B1	Atochem degralence	Transparent	Fe stearate
	B01	Plastopil	Transparent, light gray	FeDRC
	B5	Plastopil	Transparent, light green	FeDRC/NiDRC
	B7	Enichem 221 HT	Transparent	FeAcAc/HDPE
	B8	Enichem 2HT	Transparent	FeDRC/HDPE
Starch-filled PE	C2	Ampacet	White	Starch + FeSt + TiO_2
	C3	Ampacet	White	Starch + FeSt + 3% TiO_2
	C4	Ampacet	Green	Starch + organic dye
	C5	Ampacet	Black	FeSte + carbon black

at 160°C and the die head temperature set at 180°C. Multiple processing (recycling) was carried out either in a closed chamber of an internal mixer (Rapra-Hampden torquerheometer, TR) for 10 minutes at 180°C and 60 rpm (thin films for subsequent analysis were compression molded at 180°C), or extruded in the SSE as above. Polymer blends containing 10% of either a nonoxidized or photooxidized degradable polymer were processed (as above) and a portion of the processed polymer was removed for testing (melt flow index, MFI, carbonyl index, molecular weight, and weathering) before reprocessing the remainder (second pass). This

TABLE 1b. LDPE Degradable Films (75μm) Extruded (SSE) in the Laboratory (at Aston Univ)

Code	Origin	Appearance	Composition
Bs0	Laboratory prepared	Transparent	LDPE, unstabilized
Bs01	Laboratory prepared	Transparent, light gray	FeDNC, 0.01%
Bs02	Laboratory prepared	Transparent, light gray	FeDNC, 0.02%
Bs03	Laboratory prepared	Transparent, light gray	FeDNC, 0.03%
Bs04	Laboratory prepared	Transparent, light gray	FeDNC, 0.05%
Bs3	Laboratory prepared	Transparent, light green	FeDNC/NiDNC, 0.03%/0.01%

process was repeated twice more with further sampling and testing after each pass. Five polymer blend series, each containing 10% degradable polymers, were examined; LDPE (series I and II, with nonoxidized and photooxidized degradables, respectively); PE:PP at a ratio of 1:1 (series III and IV with nonoxidized and photooxidized degradables, respectively); and PE:PP:EPDM at a ratio of 1:1:0.2 (series V with nonoxidized degradables).

UV Exposure and Monitoring of Change in Properties and Degradation Products

Exposure of polymer samples was carried out under natural conditions (outdoor exposure in Birmingham facing south at 45°) and laboratory conditions using two different accelerated photoaging devices. Photoaging was performed in the mildly accelerated environment of a sunlamp-blacklamp (S/B) cabinet, comprising 7 sunlamps and 21 actinic blue lamps with a maximum relative intensity within the 280–370 nm range (radiation output of about 4.5 $W \cdot h \cdot m^{-2}$) and an average temperature of 39°C, and under a highly accelerated photoaging environment of a Sepap 12/24 unit (at 60°C) fitted with four 400 W medium pressure mercury lamps with the radiation filtered at $\lambda > 300$ nm. The rate of photooxidation of thin films was determined by monitoring changes in the carbonyl and, in some cases, the double bond area index using Fourier transform infrared analysis (FT-IR) which was run on a Perkin-Elmer PE-1710 FTIR and PE-data manager program (area index calculated by the PE-data manager program using predefined baseline for the functional group absorption peak over that of a reference peak due to absorption of a $-CH_2-$ in the backbone of the polymer which does not change during oxidation). For the laboratory-extruded PE samples containing a different initial [FeDRC], the concentration of photooxidation products (acid, ester, and ketone) was calculated after derivatization with SF_4 according to a literature method [12, 13]. Melt flow index (MFI) was measured on a Davenport polyethylene grader at 190°C (0.118 cm die, 2.16 kg). Molecular weight was determined by gel permeation chromatography using a Waters 150C/A LC chromatograph and results are expressed in equivalent weight of polystyrene. Mechanical properties were determined from tensometric measurements (using a micro 500 Testometric tensometer according to ASTM standard, D882. Extraction of photofragmented degradable polymers (degraded beyond embrittlement) was carried out with either an aqueous alkaline solution of different strengths (0.001 to 1.0 M NaOH) or with water. The extracted polymer fragments and the alkaline aqueous extracts, after neutralization and extraction with ether (in the case of water extracts, no further treatment was carried out except for concentrating the solution), were characterized by spectroscopic methods (FT-IR, using KBr disk and FT-NMR).

RESULTS AND DISCUSSION

Photooxidation

The rate and extent of photooxidation of representative samples of degradable polymers were studied by following the reduction in molecular weight and intrinsic viscosity (by GPC) and the build-up of carbonyl groups and, in some cases, unsaturation (by FT-IR). All the commercial degradable samples exhibited a rapid rate of carbonyl formation and molecular weight reduction on exposure to UV light. Figure 1 shows typical changes in functional groups (carbonyl and unsaturation) concentration during UV exposure (in S/B cabinet) of degradable films, e.g., for BsO3. The formation of the different carbonyl groups in LDPE, viz., carboxylic acid (1715 cm^{-1}), ketones (1720 cm^{-1}) and esters, both acyclic (1739 cm^{-1}) and cyclic (1785 cm^{-1}), and the vinyl (909 cm^{-1}) group occur by known mechanisms of photooxidation (Ref. 14 and references therein), see Scheme 1.

Transition metal ions, e.g., iron and cobalt, are known to be effective initiators for photooxidation since they catalyze the rate of hydroperoxide formation via the redox reactions 1 and 2, hence a number of commercial polymers designed for degradability contain iron ions as effective photoactivators. Figure 2 compares the rate of photooxidation (exposure in S/B cabinet) of representative samples of commercial PE-based degradable films containing transition metal ions.

$$Fe^{2+} + ROOH \longrightarrow Fe^{3+} + RO\cdot + OH^- \qquad (1)$$

$$Fe^{3+} + ROOH \longrightarrow Fe^{2+} + ROO\cdot + H^+ \qquad (2)$$

All polymer samples containing iron compounds (FeAcAc, B7, FeDRC, B8, B01, and the starch-filled FeSt containing polymer, C2) photooxidize without an induction period whereas the nickel-iron dithiocarbamate, Ni/Fe, containing polymer B5, shows a well-defined induction period followed by rapid photooxidation. The rapid increase in carbonyl concentration during UV irradiation, which is paralleled by reduction in molecular weight and intrinsic viscosity of the polymer (see inset Fig. 2b), is due to photoreduction of the trivalent iron complex, e.g., iron carboxylate, with the formation of initiating radicals leading to oxidative breakdown of the polymer, Reaction (3) [8]:

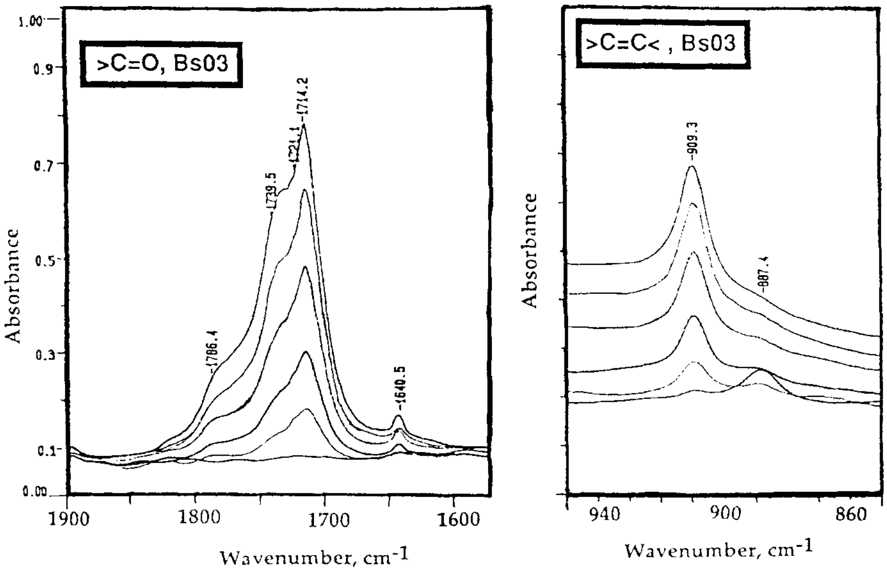
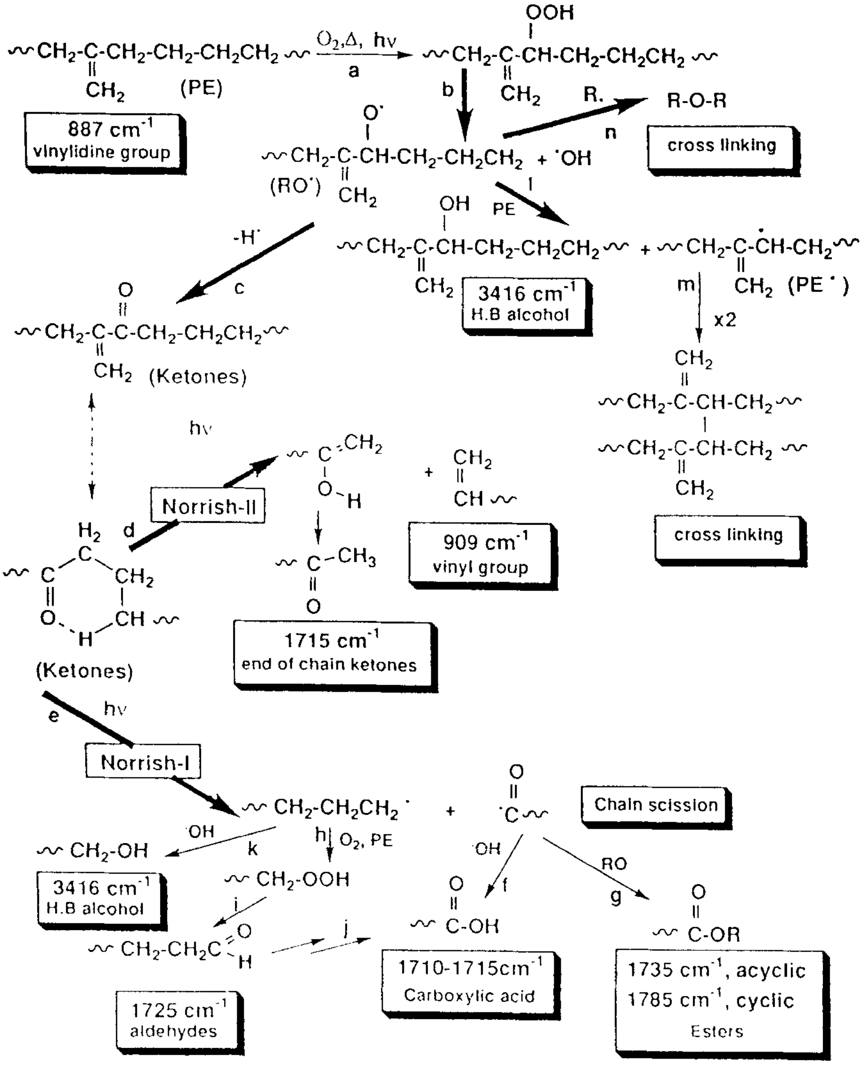


FIG. 1. Development of carbonyl and unsaturation groups (from IR) during photooxidation of laboratory-prepared FeDRC (0.03%) containing PE film.



SCHEME 1. Oxidation of LDPE during processing and exposure to UV light. Observed IR frequencies are shown; see Figs. 6 and 7.

$$(RCOO)_3Fe \xrightarrow{h\nu} (RCOO)_2Fe + RCOO^{\cdot}$$

$$RCOO^{\cdot} \longrightarrow CO_2 + R \qquad (3)$$

FeDRC-containing polymer (B8), inset Fig. 2(a). While FeSt, FeAcAc, and FeDRC are effective photosensitizers, the first two, unlike FeDRC [8a, 15], are not thermal (processing) antioxidants. Peroxidolytic metal dithiolates (e.g., dithiocarbamates, dithiophosphates, xanthates) are good processing antioxidants and many, particularly Ni and Co complexes, are also very effective photoantioxidants [16]. Iron complexes, e.g., FeDRC, however, are less photolytically stable than their Ni ana-

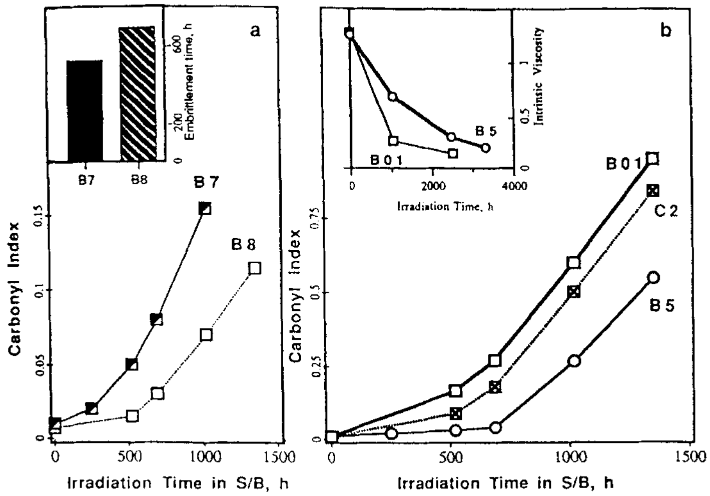


FIG. 2. Rate of photooxidation (S/B cabinet) of Fe-containing commercial PE degradables. Inset (a) shows embrittlement time for B7 and B8, and inset (b) shows changes in the intrinsic viscosity (from GPC) of Samples B01 and B5 during UV exposure.

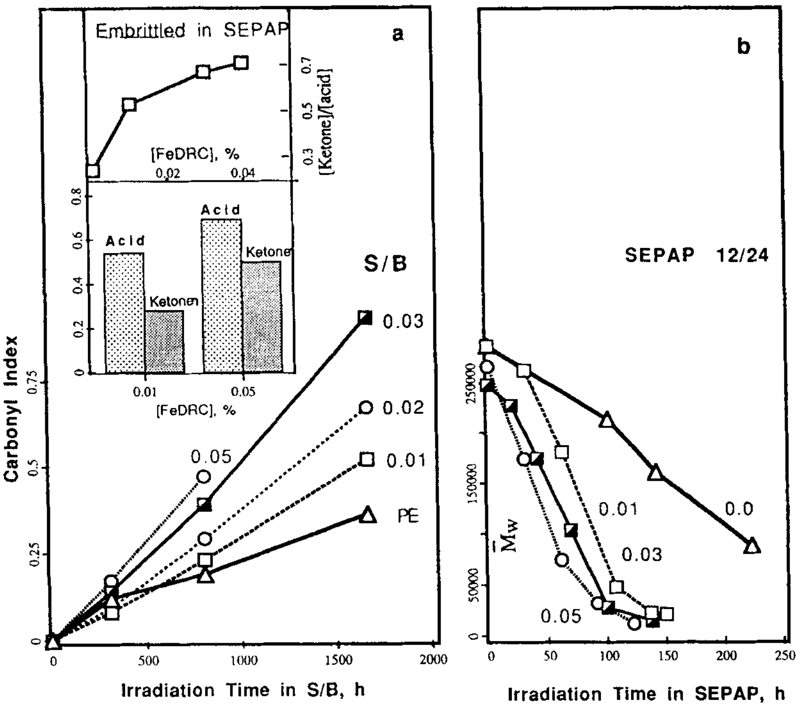
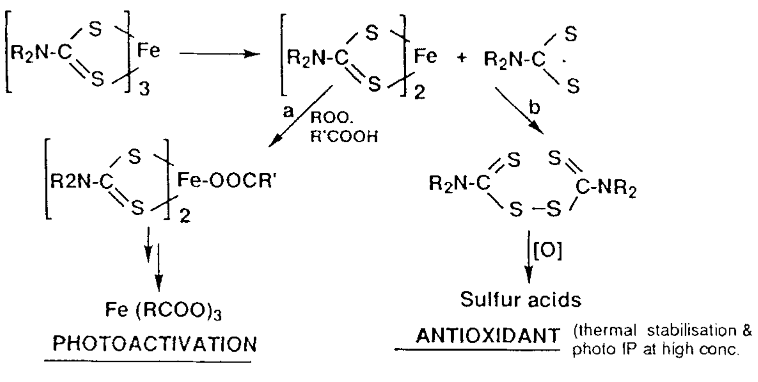


FIG. 3. (a) Rate of photooxidation (S/B cabinet) of laboratory-extruded PE films containing FeDRC at concentrations shown on curves. Inset shows concentration of carboxylic acids and ketones formed in these samples on embrittlement (exposed in SEPAP 12-24 device) after SF_4 derivatization. (b) Rate of reduction in $\overline{M}_w$ of these samples during UV exposure.

logues; FeDRC photolyzes by Reaction (4) in the absence (or presence, if used at high concentration) of an induction period, IP [15]. It was shown previously [15] that the embrittlement time for FeDRC-containing PE films is concentration-dependent. Laboratory-extruded LDPE films containing different low concentrations of FeDRC (in the range of concentration used in the Scott–Gilead process) showed higher rates of photooxidation and reduction in molecular weight at higher [FeDRC], see Fig. 3. This finding is further supported by the formation of higher concentrations of carboxylic acids and ketones in the photoembrittled samples containing higher initial [FeDRC], see inset Fig. 3(a) (calculated following SF_4 derivatization [13]). While the concentration of carboxylic acids formed at all FeDRC concentrations was higher than that of esters and ketones, the ratio of ketone to acid increased with higher FeDRC concentration, see inset Fig. 3(a). It is clear from these results that the major final photooxidation product in FeDRC-containing polymers is carboxylic acids and, to a lesser extent, esters, formed via Norrish I photolysis of intermediate ketones that are, in turn, formed from thermolysis (during processing) and photolysis of polymer hydroperoxide, see Scheme 1. Norrish II photolysis, which gives rise to end-chain ketones and vinyl groups (see formation of vinyl absorption peak at 909 cm^{-1} in Fig. 1), appears to play a more important role when higher FeDRC concentrations are initially added to the polymer. Both Norrish I and II processes lead to chain scission, which is reflected in the observed reduction in molecular weight at all [FeDRC], see Fig. 3(b), but only Norrish I leads to the formation of free radicals [17].

At much higher FeDRC concentration an IP becomes apparent [15, 18]. The length of this IP, however, can be controlled more effectively, while maintaining the subsequent fast rate of photooxidation, by using low concentrations of FeDRC in combination with very small concentration of the more photolytically stable nickel dithiocarbamate, NiDRC [9, 18]. The commercial sample B5, which is based on a Ni/Fe dithiocarbamate system, illustrates this clearly (Fig. 2b). Like other peroxide decomposers, the antioxidant effect of the dithiocarbamates is due to oxidation products of the thiocarbomoyl moiety, Reaction 4b, giving low molecular weight sulfur acids which are responsible for the nonradical decomposition of hydroperoxides [19]. Once the iron complex is destroyed by light, however, the free iron ion released (in the form of macromolecular carboxylate, Reaction 4a) undergoes the normal redox reaction with hydroperoxides (see Reactions 1 and 2), leading to the rapid photooxidation and reduction in molecular weight of the polymer, see inset Fig. 2(b). It is this dual activity of the FeDRC, as an antioxidant and photoactivator, which has led to the development of the Scott–Gilead process for degradables [9].



(4)

Exposure of the different photo(bio)degradable polymers outdoor and in the accelerated photoaging cabinets (S/B and SEPAP) gave good agreement in terms of the relative rates of photooxidation of the different commercial samples; see, for example, Fig. 4(a). Samples of starch-filled polyethylene containing ferric stearate (C2 and C3, Fig. 4a and b) showed the highest rate of photooxidation (C2 photooxidizes at a rate similar to films containing FeDRC, B01) due to the photoactivation role of the iron ion. On the other hand, films containing starch and an organic dye (C4) only showed a much reduced rate of photooxidation, not too dissimilar from a control LDPE film. This observation suggests clearly that starch does not mediate in the photooxidation of the polymeric matrix. Further, starch was shown [4] to exert no influence on the subsequent bioassimilation process unless the polymer substrate has been extensively photooxidized (with much reduced molecular weight, e.g., M_w 2000) and the starch has been released from the polymer. On the other hand, an LDPE film containing iron stearate and carbon black, C5, showed a fast rate of photooxidation, Fig. 4. This behavior is unexpected since carbon black (a highly UV-absorbing additive) is expected to prevent the photoexcitation of iron stearate. The possibility of a synergistic effect involving both the oxidation of carbon black and polymer surfaces may explain this observation.

The photoxidation rates of the photolytic polymers, the "Guillet" Ecolyte and the ECO copolymers (A1 and A2, respectively), and the "Scott-Gilead" Ni/Fe dithiocarbamate polymer, B5, are compared in Fig. 5 (inset). In contrast to B5, the photolytic polymers are immediately photooxidized on exposure to light without an

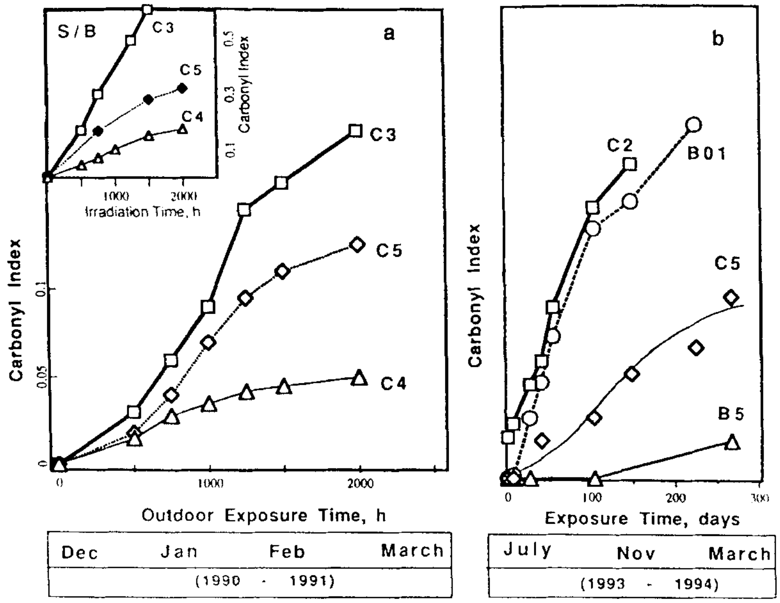


FIG. 4. Rate of photooxidation of starch-containing polymers (C samples), FeSt-carbon black (C5) and Ni/FeDRC (B5) polymers during outdoor exposure (in Birmingham). Inset compares rates of photooxidation of starch-containing films exposed in S/B cabinet.

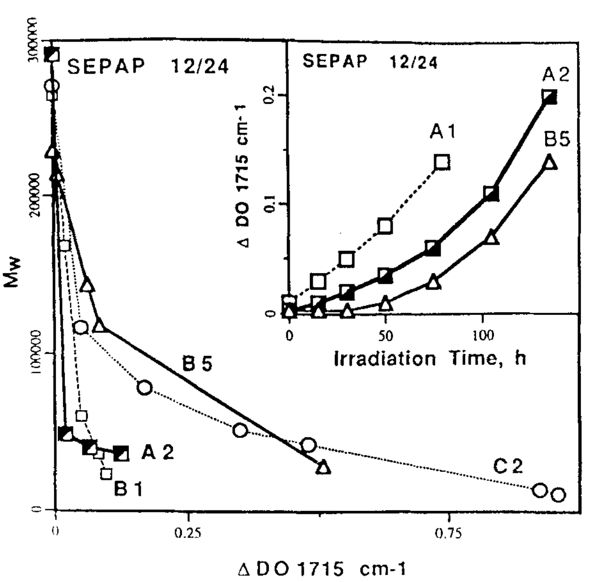


FIG. 5. Rate of reduction in $\overline{M}_w$ of ECO (A2) and Fe-containing polymers (B1, B5, C2) during UV exposure (in SEPAP 12-24) as a function of change in carbonyl absorption.

IP. A comparison of the rate of reduction in molecular weight of the ECO polymer (A2) with iron-containing polymers (see Fig. 5) reveals that, in all cases, the rate of reduction in molecular weight is fast at the early part of the photooxidation and is particularly rapid in A2 (M_w generally decreased from about 300,000 to 50,000–20,000, with a further decrease to 6000 to 2000 on prolonged UV-exposure well beyond the embrittlement time of the polymer).

While the molecular weight of all other commercial systems examined continued to decrease gradually on prolonged exposure, the rate of reduction in the case of the ECO polymer, A2, at this stage was much slower. The behavior of A2 suggests that the degree of degradation in this case is strongly dependent on the initial carbonyl concentration in the degradable polymer. An important finding is that when the ECO (A2) and the FeDRC (B01) containing polymers were photofragmented (in the S/B cabinet well beyond embrittlement) to the same extent in terms of molecular weight reduction, to about 96% of their original value (MW decreases from 254,200 to 9,600 and from 240,600 to 5,800, respectively) and the total carbonyl content was compared in the fully fragmented samples, it was found that the ECO polymer, A2, had a lower overall carbonyl content compared to the FeDRC polymer; A2 contained only 63% of the total carbonyl content of the FeDRC-containing polymer sample, B01. The lower content of carbonyl products in the ECO polymer, A2, makes the fully fragmented polymer more hydrophobic than the B01 sample degraded to the same extent, and this can account for the observed [4] rapid microbial growth in the FeDRC-containing polymers compared to the ECO polymer which showed faster initial degradation (in MW reduction) but underwent much slower biodegradation.

Degradation Products of Photodegradable Polyethylene Films

It was shown earlier (see Fig. 1) that all the photodegraded polymers examined gave large amounts of carbonyl-containing compounds: primarily acids, esters (acyclic and cyclic), and ketones. Although these are generally known to be nontoxic to animals, there is public concern [3] about the lack of information on the possible hazards associated with the degradation products of degradable plastics. To address the question of whether the oxidation products of photooxidized and fragmented PE-based degradables could be removed from the polymer under environmental leaching conditions, samples B5 (Ni/FeDRC system) and B7 (FeAcAc) were exposed to the sun and rain, and the liquid washing the surface of the polymer samples was removed at intervals and examined for residues after evaporation; no aqueous extraction was observed from either sample. Furthermore, it was found that even for very heavily photooxidized samples (in S/B cabinet well beyond embrittlement), the oxidation products could not be extracted with water alone, nor was it possible to extract any significant amount of degradation products in the aqueous layer after dilute alkaline (0.01–0.1 M NaOH) treatment. However, the photofragmented (high carbonyl content) films did swell in water and could be readily suspended in a dilute alkaline solution due to their modified highly hydrophilic nature. It was concluded that the carboxylic acids and ester groups formed in the surface layers of the polymer are substantially aliphatic in nature with long alkyl chains and hence resistant to aqueous leaching. However, although normal groundwater cannot remove these low molecular weight oxidation products, it was shown [4] that microorganisms can remove these oxidation products which are located in or near the surface of the photofragmented films (they do so even in a nutrient-starved medium).

The nature of the degradation products was therefore further examined by modifying the extraction treatment; more concentrated (1 M) aqueous alkaline solution was found to remove the low molecular weight degradation compounds. Figure 6 shows the functional groups region (carbonyl and unsaturation, from FT-IR and solid-state ^{13}C NMR) of the ECO polymer A3 before exposure (A3-A), after photofragmentation in S/B cabinet (beyond embrittlement at a point where 96% reduction in MW has taken place, A3-B, and after photofragmentation and aqueous alkali extraction, A3-E). Photoxidation (A3-B) leads to the formation of acids, esters, γ-lactone, and ketones. The alkaline extraction leads to sharp reduction in the carbonyl absorption and the appearance of a carboxylate peak at 1574 cm^{-1}, following the conversion of acids (1715 cm^{-1}) and esters (1739 cm^{-1}) upon treatment with NaOH; ketones and aldehydes are unaffected by this treatment, see A3-E. Solid-state ^{13}C-NMR spectra of samples of the photofragmented, A3-B, and photofragmented and alkaline treated, A3-E, Fig. 6, support this and show clearly a shift in the carbonyl peak (broad) from the 169–175 ppm region (in A3-B) characteristic of carboxylic acids and esters to 181 ppm (in A3-E) attributable to the carboxylate group. Further resonance signals at δ = 114 and 139 ppm and 74 ppm appear in both samples; these are attributable to unsaturated carbons of the vinyl group formed via Norrish-type II photolysis of the ketone carbonyls in the ECO polymer, and to secondary alcohols which may be formed from hydrogen abstraction and further oxidation of the active methylene next to the vinyl group, see Scheme 2 and Fig. 6. These results support the important role played by the Norrish II reaction (compared to Norrish I) in ECO polymers [17].

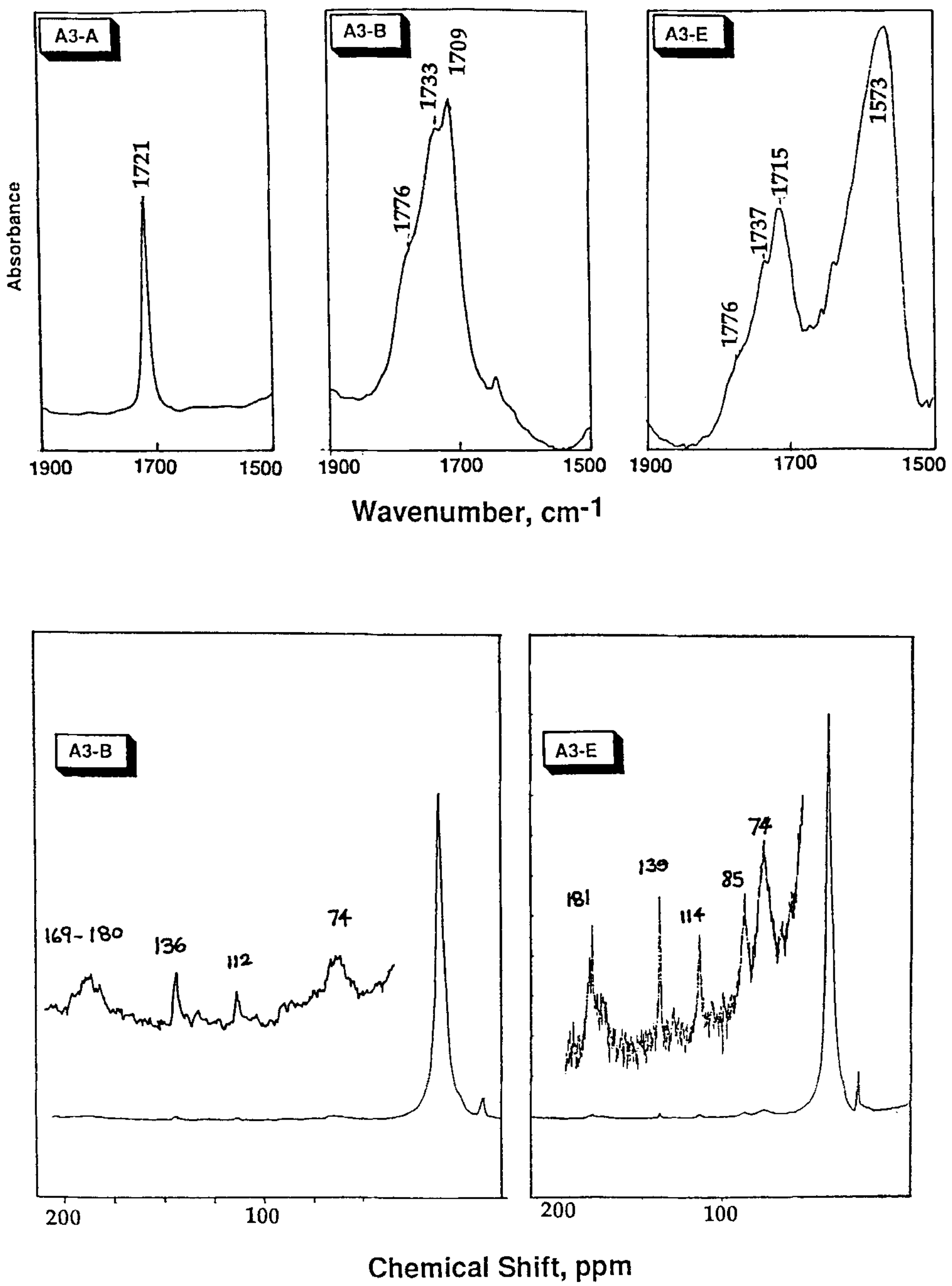


FIG. 6. IR and solid-state ^{13}C-NMR spectral regions for the ECO polymer A3 before UV exposure (A), after photofragmentation (B), and after photofragmentation and alkaline extraction (E).

Figure 7 shows FT-IR spectra in the carbonyl region of the photofragmented (in S/B cabinet, M_w decreased to 97% of its initial value) FeDRC-containing polymer film, B01, before B01-B and after B01-E with the same aqueous alkaline treatment, as well as that of the aqueous extract after neutralization and extraction in organic solvent, B01-D. Only about 10% of the total carbonyl products present in this photofragmented (M_w 5800) sample was found to be present in the aqueous alkaline extract; this is taken to suggest also the level of the extractable (in aqueous alkaline solution) low molecular weight oxidation products. FT-IR and ^{13}C and ^{1}H NMR (in carbonyl and hydroxyl regions) of extracted photooxidation products (after similar aqueous alkaline treatment) from photofragmented laboratory-prepared PE film containing a combination of FeDRC, 0.03%, and NiDRC, 0.01%, Bs3-D (i.e., "similar" to the commercial film B5) are also shown in Fig. 7. The extracted low molecular weight products in both cases (B01-D and Bs3-D) are shown to be composed mainly of carboxylic acid(s) (IR absorbance at 1712 cm^{-1} for B01 and at 1709 cm^{-1} for Bs3, as well as a ^{13}C-NMR signal at 180 ppm attributable to acid carbonyl) and to a lesser extent, alcohol (^{1}H signal at 8.5 ppm and a broad strong IR absorption peak at 3416 cm^{-1} attributable to strongly hydrogen-bonded OH group), see Fig. 7. The major contribution of the carboxylic acid to the final degradation product composition was confirmed from SF_4 treatment of photoembrittled laboratory-prepared PE-containing FeDRC samples, as shown earlier, see Fig. 3.

These results show clearly two major differences in the level of the oxidation products formed in the photofragmented samples of ECO (A3) and FeDRC (B01) polymers (degraded to the same level of MW reduction of about 96%), whereas the total carbonyl formed in A3 was (as shown earlier) about 60% of the amount formed in B01. The vinyl content in B01 was about 10% of that formed in A3. This finding clearly illustrates the greater contribution of the Norrish II photolysis in the ECO polymer, see Scheme 2, while photooxidation by Norrish I accounts for the formation of the final photodegradation products (mainly carboxylic acids) in the case of the commercial FeDRC-containing polymers, see Scheme 1. Furthermore, it can be concluded that the formation of these photooxidation products in all the degradable PE samples examined is of paramount importance as they not only lead to physical breakdown of the polymer, as evidenced by the loss of polymer strength, reduction in molecular weight, and photofragmentation, but also to making the originally hydrophobic polymer much more hydrophilic after degradation, hence accessible to the action of microorganisms during the biodegradation stage. The importance of the initial abiotic degradation and its role as a controlling step for subsequent biodegradation has been discussed recently [20].

Recyclability of Degradable Plastics

Recycling polymer products made from high value engineering plastics back to the original application, e.g., car bumpers to car bumpers [21], is a viable approach to the preservation of plastics; there is certainly no prospect for degradable materials in this form of recycling. However, low cost commodity plastics, e.g., polyolefins, are often recycled into products with inferior properties. A major problem of recycling in this case is the level of contaminants present, especially transition metal ions, which are potent catalytic degradants. To address the question

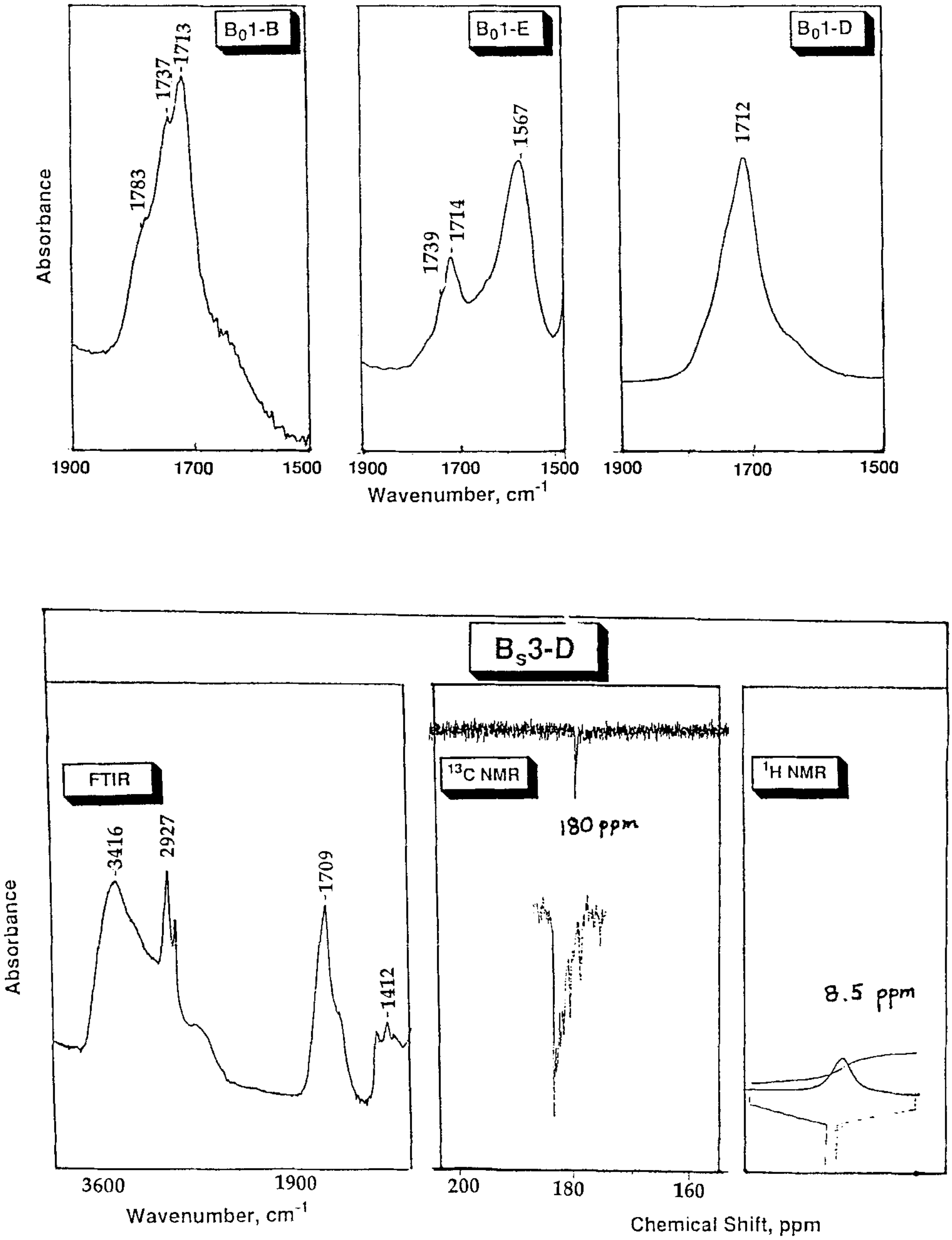
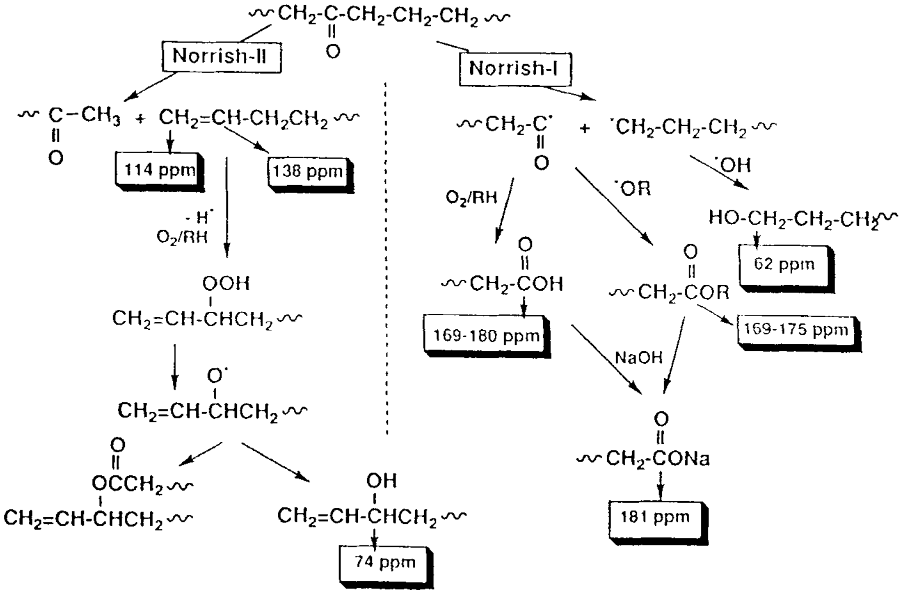


FIG. 7. Carbonyl absorption in the IR spectra of the FeDRC-containing polymer B01 after photofragmentation (B), after photofragmentation and alkaline extraction (E), and for the aqueous liquid extract of the photofragmented sample (D). IR and specific regions of ^{13}C- and ^{1}H-NMR spectra of the liquid extract of a laboratory-extruded Ni/FeDRC-containing polymer treated in the same way (Bs3-D) are also shown.



SCHEME 2. Photooxidation products of the ECO copolymers. The numbers are observed ^{13}C chemical shifts; see Fig. 6.

of whether homogeneous or heterogeneous (mixed) plastics waste can still be recycled if it was contaminated with small amounts of a degradable polymer, we have examined the recyclability of both homo- and heterogeneous polyolefin blends containing 10% of either nonoxidized or photooxidized degradables.

Compared to nonoxidized degradable polymer containing FeSt-starch filled, C2, and ECO copolymer, A3, the dithiocarbamate-containing polymers, B5 and B01, showed the least adverse effects on the recyclability of "homogeneous" blends with PE (see Fig. 8a) and "heterogenous" blends with PE:PP:EPDM (see Fig. 8b) since very little change was observed in the initial carbonyl index and melt stability (MFI) of the blends even after four processing passes. This is almost certainly due to the thermal antioxidant effect of the dithiocarbamate ligand [15, 16, 18, 19]. Multiple extrusion in SSE of nonoxidized degradables in PE, e.g., A3 and C2 (see Fig. 8c), has led to an increase in the molecular weight of the polymer (crosslinking) at lower temperatures (180°C), but this did not greatly affect the initial mechanical performance of the blends (see Fig. 8d). However, multiple extrusion of the same blends at higher temperature, e.g., 210°C, caused a progressive reduction in molecular weight (chain scission) together with a detrimental effect on the initial mechanical properties of the blends; controlling the processing parameters can therefore minimize the adverse effects of these degradables on the final properties of polymer blends. Figure 9 shows the effect of the presence of degradables which have been initially photooxidized on the reprocessibility of homogeneous (series II, PE) and heterogeneous (series IV, PE:PP) blends. The behavior of recycled blends containing the photooxidized Fe/NiDRC system, B5, is quite interesting since this shows that they can withstand the effect of reprocessing (up to four passes), whereas analogous blends containing FeSt-starch filled polymer, C2, and the ECO copoly-

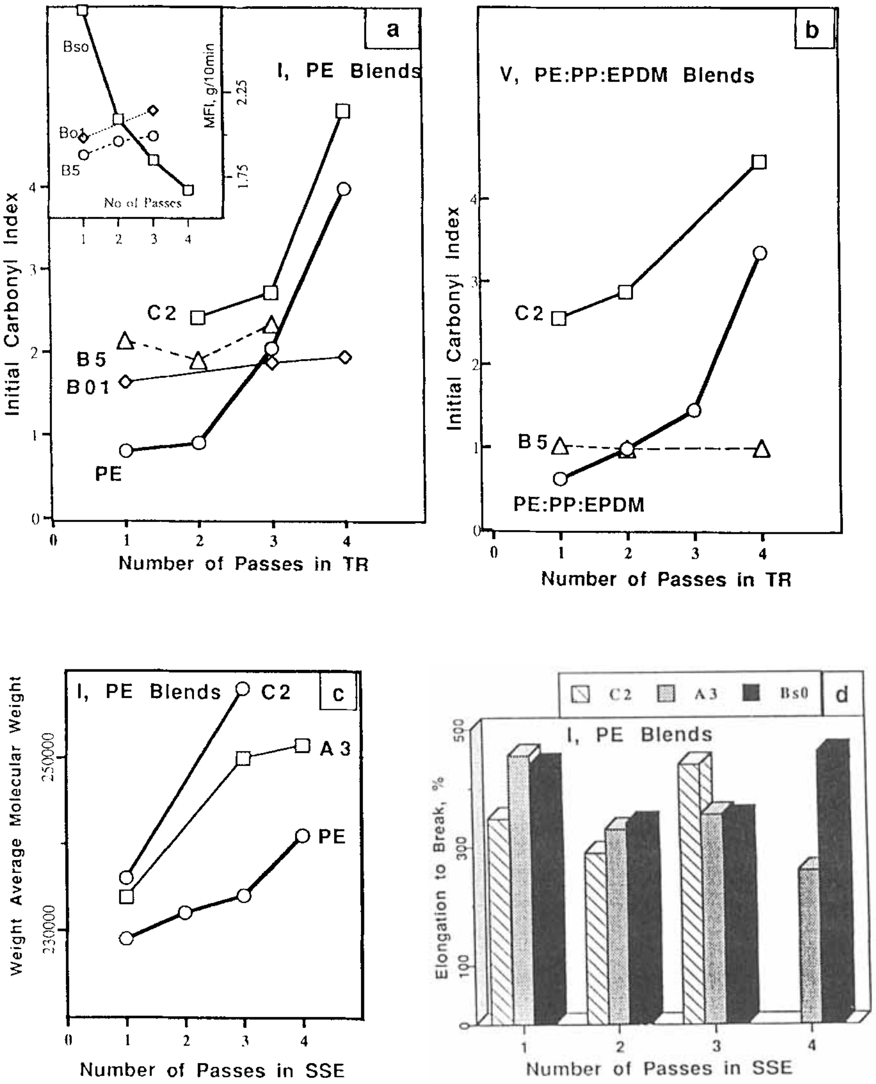


FIG. 8. Effect of multiple processing in internal mixer (TR) and single screw extruder (SSE) at 180°C on melt stability (MFI and MW), carbonyl and elongation to break of blends containing 10% nonphotooxidized degradables.

mer, A3, showed severe oxidation (see Fig. 9). Multiple processing of blends containing degradables has generally led to a decrease in the vinylidine group (887 cm^{-1}) content with a concomitant increase in carbonyls and a decrease in MFI (i.e., increased molecular weight), but with relatively small change in the vinyl (909 cm^{-1}) concentration, especially during the first two or three passes; see, for example, Fig. 9a inset for blends containing photooxidized C2. This confirms [22] the importance of vinylidine hydroperoxide thermolysis and subsequent crosslinking reactions (decrease in MFI) of the derived alkoxyl or alkyl radicals, see Scheme 1

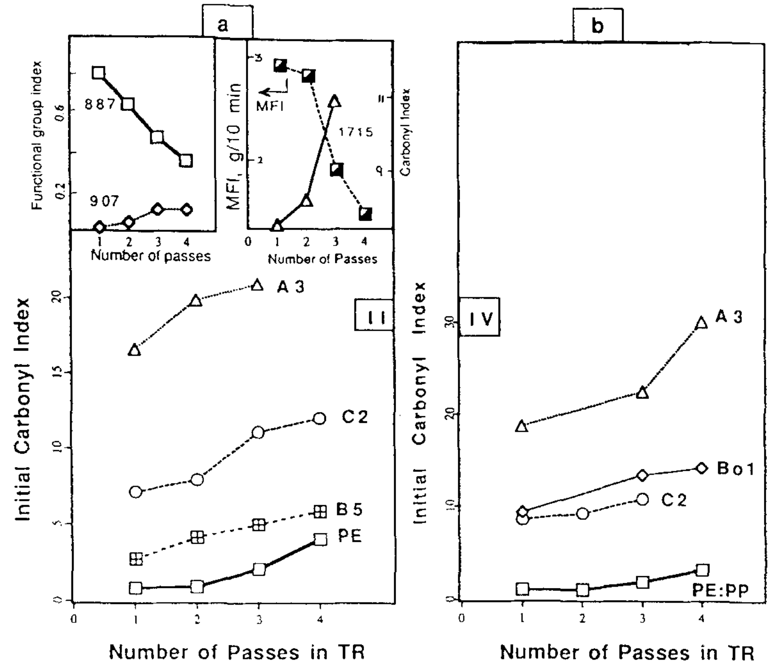


FIG. 9. Effect of multiple processing in internal mixer (TR) at 180°C on melt stability (MFI) and changes in functional group concentrations of blends (Series II PE and Series IV PE:PP) containing 10% photooxidized degradables, except for C2-III in Inset b, which contains nonphotooxidized C2.

(a, b, l, m, n). The thermolysis of the ketones formed (Scheme 1c) via a Norrish II reaction gives rise to vinyl groups and does not seem to play a major role during processing.

The photooxidative stability of PE and PE:PP blends containing initially photooxidized degradables is shown in Fig. 10. Again the Ni/FeDRC-containing polymer (B5) was least detrimental to the "weathering" behavior of blends containing it, even though this was an initially photooxidized B5 sample, Fig. 10a. However, in general, all blends containing photooxidized degradables showed inferior performance compared to the nonoxidized degradable analogues, both during processing and subsequently on exposure to UV light (see, for example, Fig. 10c and d for sample C2); sample B5-II (photooxidized B5 in PE) which contains Ni/FeDRC was least detrimental to the photostability of the PE blend. Furthermore, processing severity increases the extent of photooxidation of these blends (inset Fig. 10a). It is interesting to note, however, that compared to blends containing photooxidized degradables, those containing nonphotooxidized degradables showed very little adverse effect on their UV stability (i.e., when compared to the stability of the polymer control), see Fig. 10c (curves PE and PE-containing nonphotooxidized and oxidized C2). However, the final photooxidative stability of plastics containing degradables depends on the oxidizability of the virgin polymer(s) used. For example, PE:PP blends are more sensitive to thermal and photooxidation than PE alone (due to higher oxidizability of PP), see inset Fig. 10c, and the weatherability of

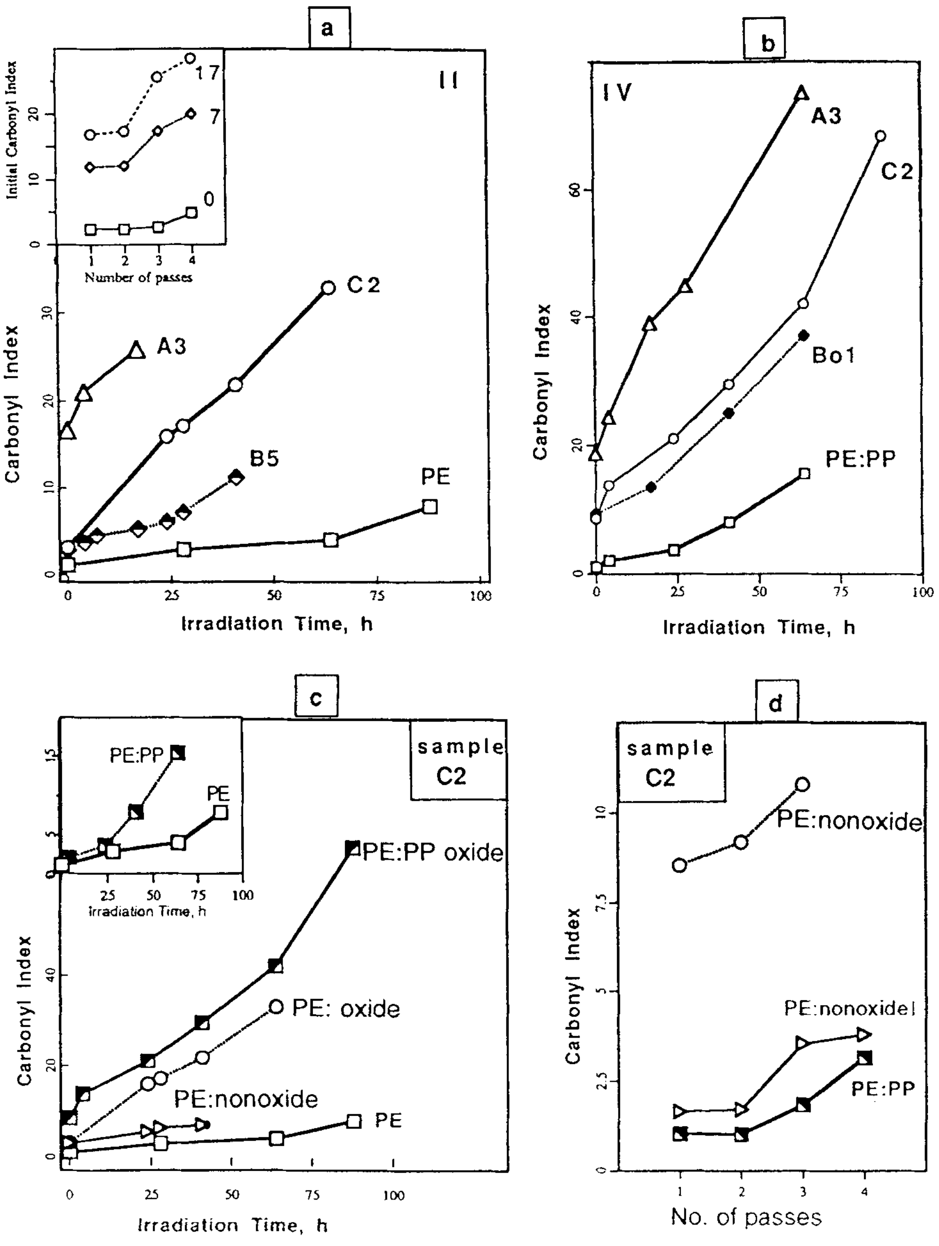


FIG. 10. Photooxidative stability (exposed in SEPAP 12-24) of PE (Series II) and PE:PP (Series IV) blends containing 10% photooxidized degradables processed for one pass (a–c; in c the effect of PE containing nonoxidized C2 is also shown). Effect of multiple processing on initial carbonyl index of PE:PP blends containing oxidized and nonoxidized C2 is shown in d.

these blends (containing photooxidized degradables) is consequently more severely affected compared to PE containing the same photooxidized degradable samples, see Fig. 10c. These results show that while thermal reprocessing (recycling) of plastics waste containing small amounts of degradables can still be performed, especially if the process temperature is controlled, recyclates containing photooxidized degradables suffer more severely and will, in general, benefit from the use of additional photoantioxidants (and possibly thermal antioxidant) for improved outdoor performance as was demonstrated in the case of blends containing the degradable sample B5 which contains a very small concentration of a photoantioxidant.

CONCLUSIONS

1. Photooxidation of all degradables examined leads to the build-up of high concentrations of carbonyl compounds concomitant with a reduction in molecular weight. The rate of photooxidation depends on the sensitizing mechanism: starch-filled PE (containing no FeSt) showing the lowest rate and starch-FeSt-containing polymer showing much higher rates comparable to FeDRC-containing polymer. All the degradables showed faster photooxidation than a control LDPE (with no additives) and without an induction period except for the case of Fe/NiDRC (Scott-Gilead polymers) which gave an IP but without adversely affecting the subsequent rapid photooxidation which leads to embrittlement. In all cases the initial abiotic degradation is essential for the subsequent biodegradation process.

2. The rate of reduction in molecular weight of all degradables during the initial stages of UV exposure was rapid but slowed down at later stages; the ECO polymer, A3, showed the fastest initial rate of reduction in MW compared to the slower and more progressive reduction in the case of the iron-containing polymers (B1, B5, C2).

3. Photooxidation imparts hydrophilicity to the initially hydrophobic LDPE-based degradables. The low molecular weight photofragmented polymers were shown to contain high concentrations of carboxylic acids and, to a lesser extent, esters, ketones, and alcohols. When photofragmented to the same level of reduction in MW, the ECO polymer (A3) gave only about two-thirds of the total carbonyls formed in an FeDRC-containing polymer (B01) but showed a ninefold increase in vinyl absorption. This leads to the conclusion that photooxidation of A3 is dominated by a Norrish II photolysis of ketones and that its degradation is dependent on the initial amount of carbonyl available, while the Norrish I process is more important in the case of B01 with the formation of carboxylic acids as the major final degradation product. The lower total level of carbonyls in the photofragmented ECO polymer may account for the slower biodegradation observed compared to FeDRC-containing polymer.

4. Homogeneous and heterogeneous polymer blends can be recycled in the presence of a small concentration of nonoxidized degradables, and the adverse changes in polymer properties can be kept to a minimum by controlling the recycling conditions, e.g., temperature. The Fe/NiDRC-containing degradable polymers do not show adverse effects on recyclate properties both during processing and weathering due to the excellent antioxidancy of the dithiocarbamates. However, if plastics

waste becomes contaminated with photooxidized degradables, then both the processing and weathering stability of the recyclates will be severely affected, and antioxidants should be added during the recycling process to ensure long term performance of the blends in subsequent lives.

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