Degradation of Enhanced Environmentally Degradable Polyethylene in Biological Aqueous Media: Mechanisms During the First Stages

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SYNOPSIS

Degradation of LDPE films containing a biodegradable starch filler and a pro-oxidant formulation was performed in aqueous media inoculated with bacteria or fungi at ambient temperatures for 1 year. The samples were characterized with the aim of elucidating the mechanisms that occur during the first stages and that are responsible for initiating the degradation of the LDPE matrix. Two interactive mechanisms were observed: The basal salt medium (water containing trace elements) triggered autoxidation of the pro-oxidant through decomposition of trace hydroperoxides, which, in synergistic combination with biodegradation of the starch, eventually initiated autoxidation of the LDPE matrix as monitored by chemiluminescence (CL), differential scanning calorimetry (DSC), and confocal scanning laser microscopy (CSLM). The length of the induction period was dependent on the sample thickness and on the activity of the microbiological system. Up to 48% of the starch was consumed during the first year as revealed by polarized-light microscopy.

INTRODUCTION

Relatively inert synthetic polymers, e.g., polyethylene, can be rendered enhanced degradable by introducing prodegradant additives into the matrix. These additives provide the plastic materials with different potential degradation mechanisms that can be triggered upon environmental exposure. Several techniques in which starch is used as a biodegradable additive have been patented since the 1970s. The main problem associated with the use of starch as a filler is its hydrophilic nature and the generally hydrophobic nature of the polymer matrix. The starch particle size limits the amount to be incorporated if the composition is to be blown to a thin film, but this is not such a limitation for sheets or injection-molded articles. The starch can be used in its natural granular form, in the gelatinized form, or in the destructurized form.

Griffin has invented formulations based on granular starch. In his early patents,[1,2] the starch was surface-treated in order to improve the compatibility between the starch and the synthetic polymer matrix, whereas in a later patent,[3] the starch is used together with a thermoplastic elastomer that functions both as a compatibilizer and as an autoxidant. Willett[4] presented in a recent patent a composition that includes granular starch and a copolymer carrier resin. Starch in its gelatinized form is utilized in formulations developed by Otey and Westhoff.[5,6] Together with the complexing agent, ethylene acrylic acid copolymer (EAA) and ammonia, it is possible to incorporate up to about 60% gelatinized starch in blown films. Bastioli et al.[7] patented a technology based on destructurized starch. By combining synthetic thermoplastic polymers and copolymers and destructurized starch to which a boron compound has been added, a material is obtained that can be used as film, sheet, or fiber. The starch

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level can be varied from 20 to 70%. Suominen,[8-10] in several patents, claimed to have overcome the constraints on starch loadings due to particle size by enzymatically degrading the filler to the desired size, thereby allowing 10–60% of the biopolymer to be incorporated. In addition, microbes in the form of spores are incorporated.

We have studied polyethylene (LDPE) in which corn starch and pro-oxidants have been included in the form of a masterbatch (MB) according to the Griffin technology. These materials have the potential for multiple degradation pathways such as biodegradation and chemical degradation. The behavior on exposure to the environment of polymers with an enhanced degradability cannot be isolated as being due to one single mechanism but involves a complex pattern of degradation mechanisms. The initiation and extent of these mechanisms are governed by environmental factors such as temperature, sunlight, supply of oxygen and water, living organisms, and pollutants[11] as well as by properties of the material itself such as polymer composition, surface/volume ratio,[12] and additives.[13,14]

We previously investigated the susceptibility of LDPE–MB materials to thermal and photooxidation and established the capability of these mechanisms to initiate degradation.[15] The samples were highly affected by the thermal treatment (up to 10 days at 100°C). Degradation of the PE matrix was observed by the detection of surface carbonyl groups, changes in crystallinity and melting behavior, molecular weight reduction, surface morphology, and the formation of volatile low molecular weight degradation products after an induction period of 5 days. The induction period is a crucial property in that it ensures that the material has a certain shelf life since degradation is not desirable during the lifetime of the material.

In this work, the degradation studies on the LDPE–MB materials are continued by exploring the effect of a biotic environment on the degradation. The samples have been subjected to aqueous microbiological environments at ambient temperature. The aim has been to clarify the mechanisms that occur during the first stages of degradation and are responsible for initiating degradation of the PE matrix and also to compare these with the mechanisms of abiotic aging. Chemiluminescence (CL) in combination with oxidative differential scanning calorimetry (DSC) proved to be very sensitive methods for following early oxidative reactions. Changes in starch content were monitored by polarized-light microscopy. The reported results are from the first year of an ongoing long-term degradation study.

EXPERIMENTAL

Materials

LDPE films with thicknesses of 30 and 80 μm were used in this study. These films were made by a conventional blown-film process using a Betol extruder with a 25 mm screw of $L : D$ 20 : 1 and a blow-up ratio of about 2.5 : 1. The die temperature was set to 185°C. The polymer used was a conventional LDPE grade of MFI 2 acquired from ATO (France) that incorporated a conventional thermal stabilizer of undisclosed composition. Most of the samples contained additives that in different ways promote degradation. Samples without these additives were used as a control (referred to as pure LDPE in the text). The prodegradant additives were introduced into the LDPE matrix in the form of a master batch (MB) in the amounts of 10, 15, and 20%. The master batch consisted mainly of corn starch, LLDPE, styrene–butadiene copolymer (SBS) and manganese stearate. In addition, samples with only corn starch (3.85, 5.77, and 7.70%) corresponding to the amounts in the MB samples were studied. All samples were kindly provided by EPRON Industries Ltd.

Degradation Procedure

Biodegradation was performed in flasks containing basal salt media where the polymer samples constituted the sole carbon source. The nutrient medium contained per liter of distilled water the following: 1.0 g $(NH_4)_2C_4H_4O_6$, 0.2 g KH_2PO_4, 0.205 g $MgSO_4 \cdot 7H_2O$, 0.166 mL of a 1% solution of $FeCl_3 \cdot 6H_2O$, and 1.6 mL of a 1% solution of $ZnSO_4 \cdot 7H_2O$. One series of samples was inoculated with the bacterium *Arthrobacter paraffineus* (*A. paraffineus*) (alkane- and starch-degrading species) after the pH had been adjusted to 7.0 by the addition of NaOH, a second series with the fungi *Verticillium lecanii* (*V. lecanii*) (alkane-degrading species), and *Verticillium nigrescens* (*V. nigrescens*) (starch-degrading species), pH adjusted to 5.5 with HCl, and a third series was kept sterile by adding 0.02% NaN_3 to autoclaved nutrient medium, pH 5.5. Each series comprised three replicates of each sample type. Incubation took place at ambient temperature for 52 weeks during which samples were removed at intervals for analysis.

Polarized-Light Microscopy

Starch contents were calculated from photographs obtained from a polarized-light microscope Leitz

Ortholux POL BK II equipped with crossed polarizers. Thanks to the birefringent properties of the starch granules, they were easily distinguished provided the films were thin enough and were counted from photographs representing an area of 0.12 mm^2 in the sample. The starch content was then calculated according to a calibration curve obtained from the original samples containing different known starch levels. The values presented are the means of three independent measurements on each sample.

Chemiluminescence (CL)

Chemiluminescent intensity was measured with a chemiluminescence detector, CLD 100, from Tohoku Electronic Industrial Co., Japan. Circular discs with a diameter of 13 mm were cut from the sample films and the CL intensity was recorded at 100°C in a nitrogen atmosphere during 3 min for each sample. At least three independent measurements were performed on each sample. Due to the construction of the instrument, it was not possible to achieve a complete nitrogen atmosphere from the very beginning of each measurement. To explore whether the measured intensity was simply an effect of oxidation in the instrument, samples that had been saturated with nitrogen overnight were subjected to measurements. The CL intensity was, however, not significantly decreased.

Differential Scanning Calorimetry (DSC)

The thermal stability was measured by means of a Perkin-Elmer DSC-2 on 2 mg samples encapsulated in standard aluminum pans with three holes in each pan cover. The samples were purged with oxygen (flow rate: 50 mL min^{-1}) while being heated from 50 to 200°C at a rate of 5°C min^{-1}. The temperature corresponding to the onset of the exothermic oxidation, T_{ox}, was taken as the intersection of the extrapolated scanning base line and the tangent at a point on the curve that deviated 0.5 mW from the scanning base line. At least six independent measurements were performed on each sample.

Confocal Scanning Laser Microscopy (CSLM)

Oxidation of the samples was imaged by a PHOIBOS confocal scanning laser microscope developed at the Department of Physics IV at the Royal Institute of Technology in Stockholm, Sweden.[16] The light source was a coherent Innova 70 Ar^{2+} laser, $\lambda = 458$ nm. A microscope objective 100×, N.A. 1.3, was used. The recorded images were from the bulk of the sample, at a depth of approximately 15 μm with a resolution of 0.8 μm in depth and 0.2 μm laterally. Each recorded image comprised 512 × 512 image points (pixels), which corresponds to 100 × 100 μm in the specimen.

RESULTS AND DISCUSSION

Several degradation mechanisms may interact during environmental degradation, working toward a total destruction of the material. The different mechanisms that occurred in the additives and in the LDPE matrix during incubation with microorganisms in aqueous environments will be revealed and discussed in the following sections.

Biodegradation of Starch

The changes in starch content as monitored by polarized-light microscopy during 1 year of degradation are shown in Figures 1(a) and (b). Starch in samples containing pro-oxidants was consumed to a greater extent than in samples containing only starch. Similar results obtained by FTIR have been reported by Ianotti et al.[17] who performed initial degradation studies in different biotic environments for periods up to 24 weeks. Since the pro-oxidant (SBS) functions as a compatibilizer, it is supposedly distributed mainly at the interface between the starch and the PE matrix and easier penetration by the enzymes through the SBS phase could explain this observation. Figure 2 presents a compilation of data on the amount of starch consumed after 1 year in the different samples in different microbiological environments. The samples inoculated with the bacteria *A. paraffineus* showed a greater starch removal than that of the samples inoculated with the fungi strains *V. lecanii* and *V. nigrescens*. This could be due to the shorter generation time of the bacteria, which gives these a greater activity than that of the fungi.

The role of the starch depends largely on the amount incorporated. Wool and co-workers[18,19] applied a percolation theory regarding the connectivity of the starch particles in the polymer matrix at different starch concentrations. A threshold concentration (the percolation threshold) can be calculated, above which continuous biodegradation takes place, leaving behind a disintegrated polymer matrix. Griffin and Nathan[20] found that enzyme diffusion can take place through very thin films of polyethylene, suggesting that a somewhat larger portion of

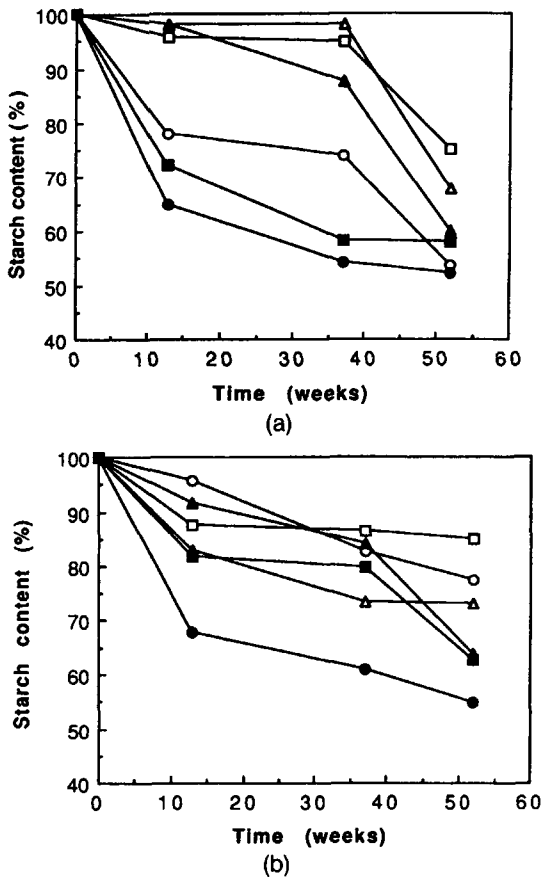


Figure 1 Starch content as a function of time for samples aged in a basal salt medium inoculated with (a) the bacterium *Arthrobacter paraffineus* and (b) the fungi *Verticillium lecanii* and *Verticillium nigrescens*. The values were calculated from photographs obtained by polarized-light microscopy. Starch contents in samples with only starch correspond to the amounts in the MB samples. Sample thickness = 30 μm. (—△—) 3.85% starch; (—□—) 5.77% starch; (—○—) 7.70% starch; (—▲—) 10% MB; (—■—) 15% MB; (—●—) 20% MB.

the starch than that calculated from the percolation theory can be accessible to continuous enzymolysis.

Our samples contain a maximum concentration of 7.70% w/w starch, which is well below the percolation threshold of approximately 41% w/w. Except in the case of hyphal penetration from fungi, which can occur deeper into the sample, microbial invasion is principally limited to surface or near-surface accessible particles. This does not immediately lead to disintegration of the LDPE matrix but weakens it and enhances the permeability, which, in turn, can speed up the autoxidation process. Several other researchers report the effects of incorporating additives that are more easily degraded than is the matrix. These reports include the work done by Tanna et al.[21] and by Holland et al.[22,23] showing the greater degradation of matrices of hydroxybutyrate–hydroxyvalerate copolymers when polysaccharides are used as fillers. Tanna et al. observed that the addition of 5–10% starch accelerated the degradation of the matrix by almost 15% under aerobic composting conditions.

Autoxidation Process

In a previous paper,[15] we concluded that the autoxidation process during accelerated aging is initiated predominantly in the SBS phase. The oxidation of the SBS generates free radicals, which, subsequently, initiate oxidation of the LDPE according to the classical oxidation scheme for polyolefins.[24] Sensitive methods are required to observe the very early oxidative reactions. A technique that we have previously used is to measure the weak light emission that accompanies oxidation called chemiluminescence (CL). There is some dispute concerning the origin of the CL, but it is generally accepted that it comes from phosphorescence of an excited ketone.[25] Possible mechanisms are the bimolecular termination of alkyl peroxy radicals,[25,26] the direct decomposition of hydroperoxides,[25,26] or the decomposition of hydroperoxides through intermediate dioxetanes.[27] Regardless of the mechanism, the CL intensity parallels the oxidation rate. Hydroperoxides are important intermediate products in the oxidation scheme and their decomposition rate greatly affects the overall oxidation rate. The total CL measured when pre-aged samples are heated in an inert at-

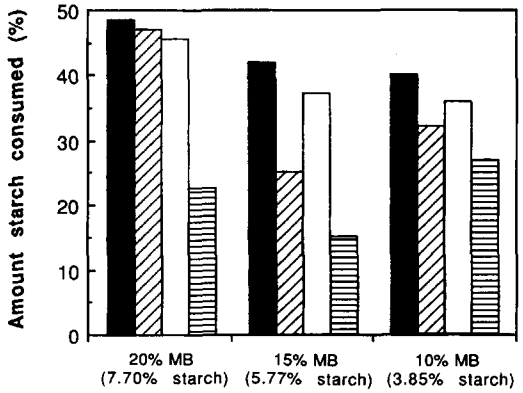


Figure 2 The amount of starch consumed after 1 year. The figure shows a compilation of the results from Figure 1(a) and (b). (■) LDPE + MB, with bacteria; (□) LDPE + MB, with fungi; (▨) LDPE + starch, with bacteria; (▤) LDPE + starch, with fungi.

mosphere can thus be associated with the hydroperoxide content built up in the samples.

Figures 3(a) and (b) show CL records from samples aged for 1 year in nutrient media inoculated with bacteria and fungi, respectively. After an induction period of a couple of weeks during which the stabilizer interferes with the oxidation and eventually has been depleted, CL is detected from all pro-oxidant-containing samples. The CL intensity is dependent on sample thickness and on MB content. Kihara and Hosoda[28] used the peak-top area from CL measurements in an inert atmosphere as an indication of the oxidation history of polymer materials. We attribute the fact that CL is observed at this early stage of degradation to traces of hydroperoxide impurities present in the materials from the beginning. Exposure to the nutrient medium apparently had a triggering effect on the decomposition of the hydroperoxides. Henry and Garton[29] showed that water alone or solutions of nontransition metal salts affect the oxidation rate and attributed it to catalysis of the hydroperoxide decomposition step of the oxidation mechanism. It is well known that transition metal salts work in this way according to the mechanisms shown in Scheme 1.[30] Apart from manganese stearate, which is already included in the samples, the nutrient medium provides additional transition-metal salts like those of iron and zinc as well as nontransition-metal salts. To explore further whether trace hydroperoxides were responsible for the first detected CL, we removed them from some samples by heating in an inert atmosphere, followed by cooling to ambient temperature in the same atmosphere. The samples were then exposed to the inoculated basal salt medium for a period of 8 weeks. Samples removed during this period showed no significant increase in CL, as shown in Table I.

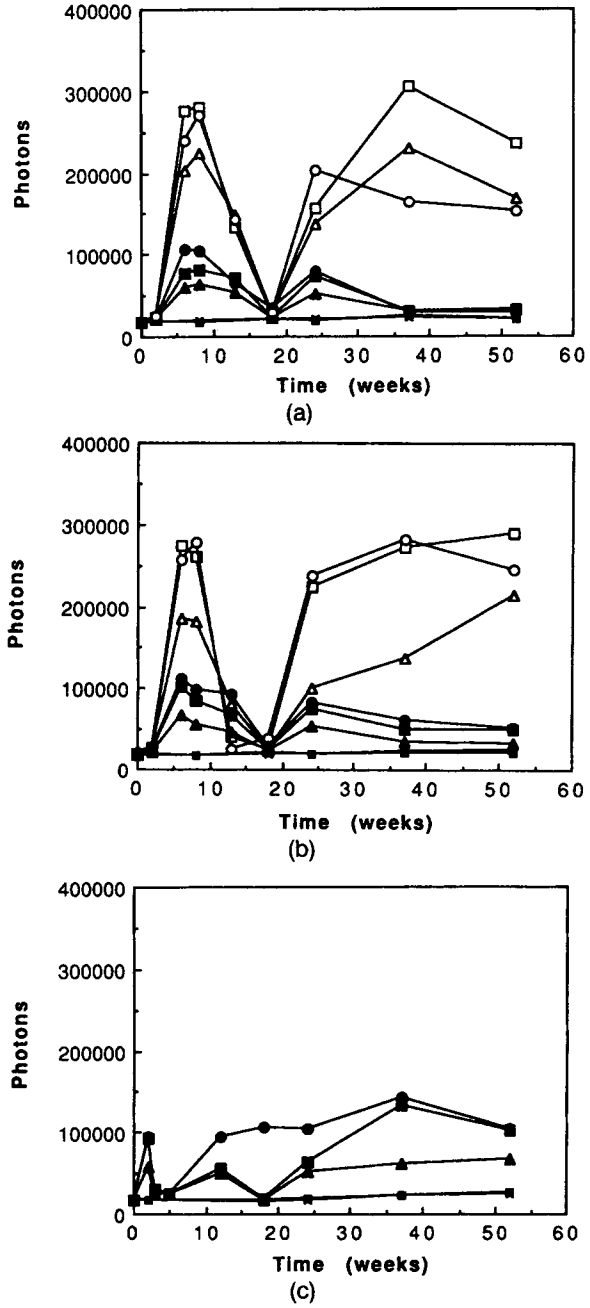


Figure 3 Chemiluminescence, measured in a nitrogen atmosphere at 100°C, as a function of time for samples aged in a basal salt medium inoculated with (a) the bacterium *A. paraffineus;* (b) the fungi *V. lecanii* and *V. nigrescens;* (c) sterile. (—△—) 10% MB (80 μm); (—□—) 15% MB (80 μm); (—○—) 20% MB (80 μm); (—▲—) 10% MB (30 μm); (—■—) 15% MB (30 μm); (—●—) 20% MB (30 μm); (—▪—) 7.70% starch (30 μm); (—x—) LDPE.

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

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

$$2ROOH \xrightarrow{Me^{n+}/Me^{(n+1)+}} ROO\bullet + RO\bullet + H_2O \quad (c)$$

Scheme 1 Examples of reactions of metal catalysts with hydroperoxides.

The influence of hydroperoxides as initiating species on subsequent oxidation processes has been described by Chakraborty and Scott.[31] The SBS phase is the most oxidizable component of the samples due to its large content of unsaturated bonds. The decomposition of trace hydroperoxides therefore induced autoxidation preferentially in this phase. This can be seen in the CL records as a second

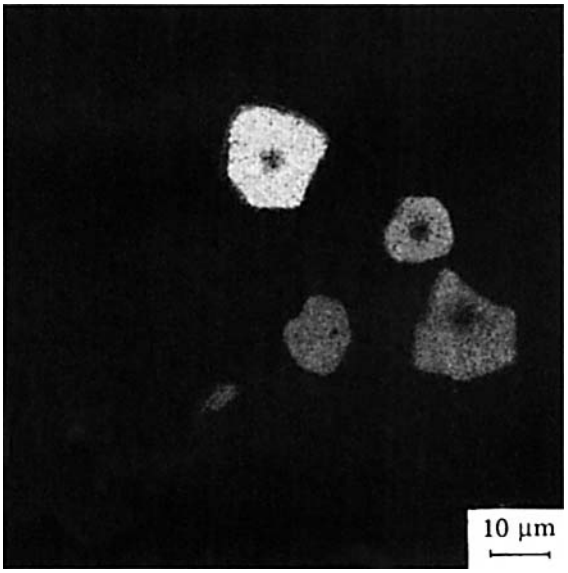
Table I Chemiluminescence, Measured in a Nitrogen Atmosphere at 100°C, for 20% MB Samples (80 μm) Aged in a Basal Salt Medium Inoculated with the Bacterium *A. paraffineus*

Sample Pretreatment	Photons[a]	Photons[b]	Photons[c]
Untreated	19,240	239,306	270,108
Hydroperoxides removed	15,162	27,333	30,466

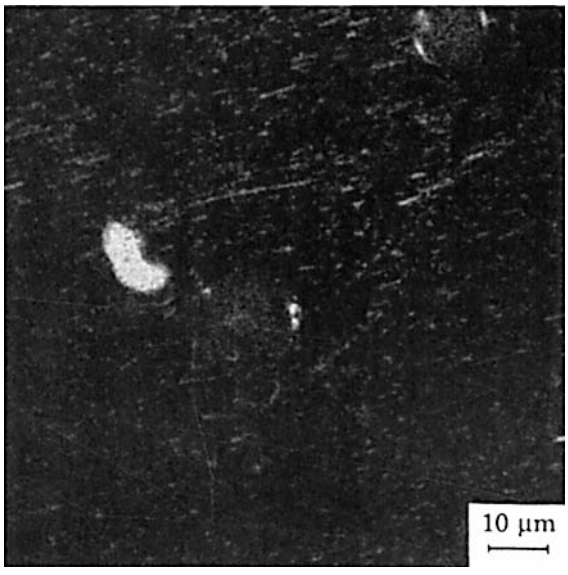
[a] Before degradation.
[b] After 6 weeks' aging.
[c] After 8 weeks' aging.

increase in intensity after 18 weeks. The concentration of hydroperoxides passes through a maximum in the 30 μm samples, whereafter it ceases upon depletion of the SBS. The decomposition of these hydroperoxides generates free radicals, which, in turn, initiate autoxidation of the LDPE matrix. In the 80 μm samples, the autoxidation of SBS was not quite complete, but was on its way toward initiating degradation of the LDPE matrix. According to recent results[32,33] obtained by liquid scintillation countings on equivalent ^{14}C-labeled samples, the LDPE matrix starts degrading after a period of somewhere between 300 and 400 days. It is impossible to establish an exact time since the microbiological activity always differs between systems. The CL intensity was almost proportional to sample thickness, indicating that it originates from both surface and bulk. Deviation in a few cases from the correlation between the CL intensity and MB content can be explained by difficulties in averaging the CL intensity over the whole sample due to the inhomogeneous nature of the oxidation, a phenomenon that we have observed by means of confocal scanning laser microscopy [Fig. 4(a) and (b)]. The images are recorded from sections, approximately 0.8 μm thick, from the interior of the film, wherefore the observed effects are bulk phenomena. The fluorescent particles seen in Figure 4(a) are starch particles. In Figure 4(b), after 1 year in a basal salt medium inoculated with *A. paraffineus*, these have decreased in amount but many small fluorescent spots can be seen that probably are due to localized oxidation. The phenomenon was not observed in samples containing starch as the sole additive. The oxidation starts in localized centers, leading to local variations in oxidation rate, which necessitates many repeated independent measurements. Reasons for localized oxidation are reviewed by Scheirs et al.,[34] the most important reasons in the present case being heterogeneous distribution of MB in the samples and variations in oxygen permeability in the bulk.

The corresponding CL records for the sterile samples as shown in Figure 3(c) exhibit the same



(a)

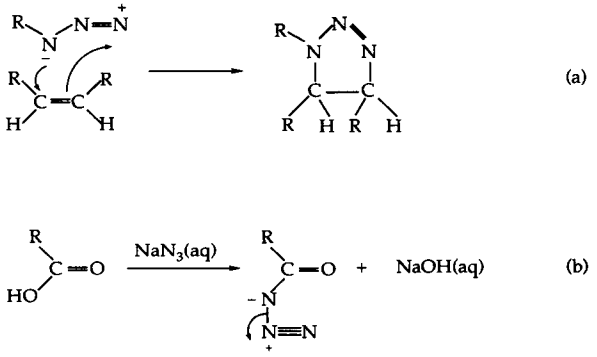


(b)

Figure 4 Micrograph obtained by confocal scanning laser microscopy of a 20% MB sample (30 μm): (a) original; (b) after 1 year in a basal salt medium inoculated with *A. paraffineus*.

general pattern, although some discrepancies can be noted that may have several causes. The lack of microbial consumption of starch eliminates the possibility of increased oxygen permeability as in the inoculated samples. The significance of increased oxygen permeability on the oxidation rate is demonstrated by comparing Figure 3(a) and (b). The *A. paraffineus*-inoculated samples of Figure 3(a) in which a greater starch removal was observed have a slightly faster autoxidation rate. Accordingly, the sterile samples show an overall slower autoxidation rate. The addition of sodium azide (NaN_3) to keep the samples sterile may also interfere with the autoxidation. Azide compounds are known to undergo several reactions such as 1,3-dipolar addition to double bonds,[35] shown in Scheme 2(a), or reaction with carboxylic acid,[36] Scheme 2(b). The reaction with intermediate carboxylic groups with the formation of NaOH(aq) could possibly account for the increase in pH to 6.5 of the sterile nutrient media that we observed.

In an attempt to relate the obtained CL data to measurements of the oxidative stability after various aging times, differential scanning calorimetry (DSC) was applied. DSC can be used either in the isothermal mode to measure the induction time or in the dynamic mode to measure the temperature of the onset of oxidation, T_{ox}.[37] Figure 5 shows T_{ox} as a function of aging time. For the 80 μm and the sterile samples, no significant change in T_{ox} can be seen, but for the 30 μm samples, T_{ox} is markedly reduced somewhere between 24 and 37 weeks of aging when the SBS is depleted and oxidation of the LDPE matrix can commence. This is also illustrated in Figure 6 showing DSC scans obtained in the isothermal mode. The isothermal mode is even more sensitive to differences in composition than is the dynamic mode.[38] The peak observed for the unaged sample and for the sample aged for 18 weeks originates from



Scheme 2 Examples of reactions of azides.

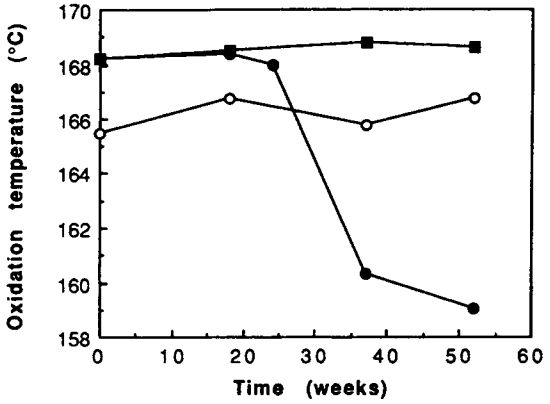


Figure 5 Oxidation temperature, obtained by dynamic DSC measurements, as a function of time for samples aged in a basal salt medium inoculated with the bacterium *A. paraffineus*. (—○—) 20% MB (80 μm); (—●—) 20% MB (30 μm); (—■—) 20% MB (30 μm), sterile.

the SBS. Not shown (from considerations of space) is the ensuing lengthy oxidation of the LDPE. The thermogram from the sample aged for 37 weeks shows that the SBS is virtually depleted and oxidation of the LDPE starts almost immediately, whereas the corresponding thermogram for the 52 weeks aged sample indicates an immediate oxidation

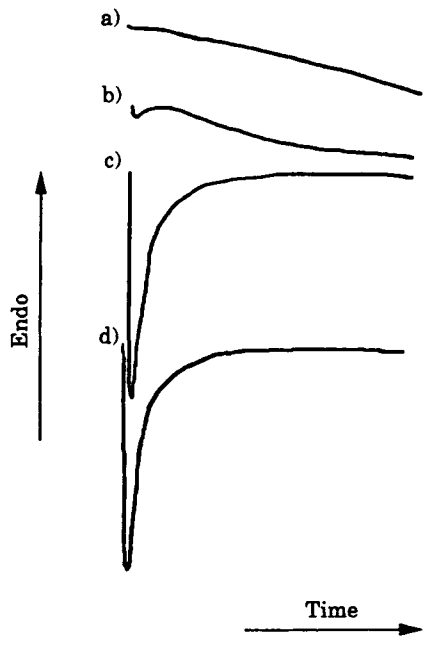


Figure 6 Isothermal (175°C) DSC scans of a 20% MB sample aged in a basal salt medium inoculated with the bacterium *A. paraffineus* for (a) 52 weeks; (b) 37 weeks; (c) 18 weeks; (d) unaged.

of the LDPE. No effects were observed, either by CL or by DSC, in the samples containing only starch or in those consisting of pure LDPE.

Abiotic and Biotic Aging

Previously published results[15] from thermal oxidative (100°C) and photooxidative studies on MB–LDPE samples confirmed the formation of carbonyl compounds in the surface as well as reductions in molecular weight once autoxidation of the LDPE matrix had started. The accelerated treatments triggered autoxidation of the pro-oxidant, which, in turn, in a matter of hours in the case of photooxidation or days in the case of thermal oxidation, generated radicals that started attacking the LDPE matrix. Under ambient conditions in the dark, there is no defined trigger for the autoxidation process. However, in the aqueous medium, the presence of the basal salt composition as well as of the water itself triggered autoxidation at a rather early stage, but the subsequent autoxidation of the pro-oxidant occurred in a matter of weeks, even though it was enhanced due to microbiological consumption of the starch filler. The rate of degradation is thus overall slower in aqueous media at ambient temperatures than is the accelerated aging in air, so that we have not yet observed any significant changes in surface functional groups as monitored by ATR–FTIR or in molecular weight as monitored by SEC.

CONCLUSION

We have clearly demonstrated the greater susceptibility to degradation of the LDPE matrix of the MB-containing samples than of samples containing only starch or of pure LDPE samples. The mechanisms responsible for initiating degradation of the LDPE matrix in aqueous biological environments at ambient temperature are found to be hydroperoxide-catalyzed autoxidation of the pro-oxidant in synergistic combination with biodegradation of the starch particles. Decomposition of already built-in hydroperoxides was catalyzed upon contact with the basal salt medium. This triggering factor initiated autoxidation of the pro-oxidant, which, in turn, initiated autoxidation of the LDPE matrix. The induction time was dependent on sample thickness and on the activity of the microbiological system. No signs of degradation of the LDPE matrix were observed in the pure LDPE samples or in the samples containing only starch. Up to 48% of the starch was consumed, where samples containing pro-oxidant displayed the highest values, possibly due to easier penetration of enzymes through the SBS phase. The bacteria *Arthrobacter paraffineus* was found to be slightly more efficient than was the fungi mixture of *Verticillium lecanii* and *Verticillium nigresens,* which could be attributed to the shorter generation time of the bacteria, which gives these a greater activity than that of the fungi.

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