

Accelerating the Degradation of Polyolefins Through Additives and Blending

Xingxun Liu,^{1,2} Chengcheng Gao,^{1,3} Parveen Sangwan,³ Long Yu,^{1,3} Zhen Tong²

¹Center for Polymers from Renewable Resources, South China University of Technology, Guangzhou, China

²School of Materials Science and Engineering, South China University of Technology, Guangzhou, China

³Materials Science and Engineering, Commonwealth Scientific and Industrial Research Organisation, Melbourne, Australia

Correspondence to: L. Yu (E-mail: long.yu@csiro.au)

ABSTRACT: Polyolefins are popular because of their low price, useful properties, broad supply chains, and mature processing facilities, but they do not easily degrade in the natural environment, and hence, the development of degradable polyolefins has attracted increasing interest. Oxidative degradation and blending with natural polymers can accelerate the degradation of polyolefins in natural environments. In this article, we review the research and developments in the acceleration of the degradation of polyolefin blends and composites, including both the fundamental science, such as the degradation mechanisms and characterizations, and application techniques, such as the processing conditions and formulations. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40750.

KEYWORDS: biopolymers & renewable polymers; degradation; polyolefins

Received 20 September 2013; accepted 20 March 2014

DOI: 10.1002/app.40750

INTRODUCTION

Polyolefins have received significant attention recently because of their combination of flexibility, toughness, excellent barrier properties, easy manufacturing, and good chemical resistance; this has made them excellent materials for various packaging applications, especially in food packaging.^{1,2} However, the polyolefins do not easily degrade in the natural environment. It has been estimated that polyethylene (PE) would degrade less than 0.5% in 100 years and up to 1% if exposed to sunlight (UV) for 2 years before biodegradation.³ So, the study of the degradation of polyolefins has become a hot topic of research to manage such environmental problems. Figure 1 shows the number of articles on this subject by year of publication as indexed in Scopus over the 1970–2013 period. According to this figure, there has been 40 years of history in the preparation of degradable polyolefins, including a huge increase in the last 10 years.

The design of degradable polyolefin systems has already been well reviewed in several articles.^{1,4–9} It has been generally realized that the complete degradation process of polyolefin involves two stages: oxidative degradation (oxodegradation) and biodegradation. Oxodegradation incorporates oxygen into the carbon chain; this results in the formation of functional groups, such as carboxylic or hydrocarboxylic acids, esters, aldehydes, and alcohols, and thereby, the hydrophobic polyolefins are converted into hydrophilic polyolefin fragments. Once the molecular weight of a polymer is significantly reduced to a lower level

through oxodegradation, the oxidation products can then be biodegraded by microorganisms and converted into CO₂, H₂O, and biomass.^{10–12} In this article, we review the developments in the acceleration of the degradation of polyolefin/biopolymer blends and composites, including both the fundamental science, such as the degradation mechanisms and characterizations, and application techniques, such as the processing conditions and formulations. We also discuss the controlling factors during the degradation of polyolefin/biopolymers.

OXODEGRADATION AND BIODEGRADATION

The term *oxodegradation* is used to describe the two stages of the degradation of polyolefins: the abiotic oxidation of the carbon backbone into smaller molecular fragments and the biotic (microbial) degradation process.^{1,6} In the first stage, the oxidative degradation of polyolefin can be accelerated by UV or thermal degradation; this is critical for determining the degradation rate of the entire process.

The oxodegradation mechanism of PE at the molecular level is presented in Figure 2. The hydroperoxide group (CH—OOH) is the primary group, and it is unstable under both thermal and UV light. Its breakdown leads to the formation of several types of oxygen-containing products. One of the few differences between peroxidations initiated by heat and by light is that ketone products are stable under exposure to heat but not under exposure to UV light.^{1,6} The degradation at the chain

Xingxun Liu is currently a postdoc working in the field of polymers from renewable resources. He received his Ph.D. from South China University of Technology in 2011. His current research focuses on the relationship of the multisize structure and properties of natural polymers, and the degradation and stability of polymers during processing and application.



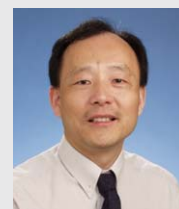
Chengcheng Gao is a Ph.D. candidate enrolled in South China University of Technology and is currently studying at Monash University and Commonwealth Scientific and Industrial Research Organization, Australia, and is supported by the China Scholarship Council. Her research project is about self-reinforced biocomposites.



Parveen Sangwan is an environmental microbiologist and has been working in the field of biopolymers and biodegradation for over 8 years. She applies her microbiological and material characterization skills to monitor changes in material physicochemical properties during exposure to the natural environment, identify agents that trigger plastic degradation, and develop lab-based tests for accelerating (bio)degradation processes. She is an active speaker at conferences and has more than 40 publications in peer-reviewed scientific journals, magazines, books, and a patent.



Long Yu is a principal scientist at Commonwealth Scientific and Industrial Research Organization, Materials Science and Engineering, Australia, and a professor at South China University of Technology. He received his Ph.D. from Monash University, Australia, and has working experience in universities, research organizations, and industries in the field of polymers from renewable resources. He has had more 120 papers published in various journals and has been cited over 3200 times. He is on the editorial boards of five scientific journals and has published seven books.



Zhen Tong is a professor at South China University of Technology. He received his Ph.D. from Osaka University, Japan, and has done cooperative research with universities in Japan, Germany, and the United States. His research field is the physical chemistry of macromolecules, especially polyelectrolytes and functional hydrogels. He has published more than 200 papers in journals and has been cited more than 2500 times. He is on the editorial or editorial advisory boards of four journals.



and aggregation structure levels was also studied by Hsu et al.,¹³ who used various characterization tools, and they reported that the main reaction was a chain-scission reaction. The results obtained in their study further indicated there were some crosslinking reactions with UV aging times because the molecular weight of the PE films decreased, but the polydispersity and gel content gradually increased with aging time. They observed further that the degree of crystallinity increased gradually; the crystallite size increased at first (in 14d) and then remained stable thereafter; this may have been due to the

recrystallization of mobile short-chain fragments produced from the chain-scission reaction. Small-angle X-ray scattering (SAXS) results showed that the crystalline phase thickness for PE did not change with UV aging, but the long period and amorphous phase decreased. The decrease in the molecular chain length due to the chain-scission reaction increased the chain mobility, and the chains recrystallized.¹³

Photodegradation is considered one of the primary mode of degradation of polyolefins in industrial practice. The principle

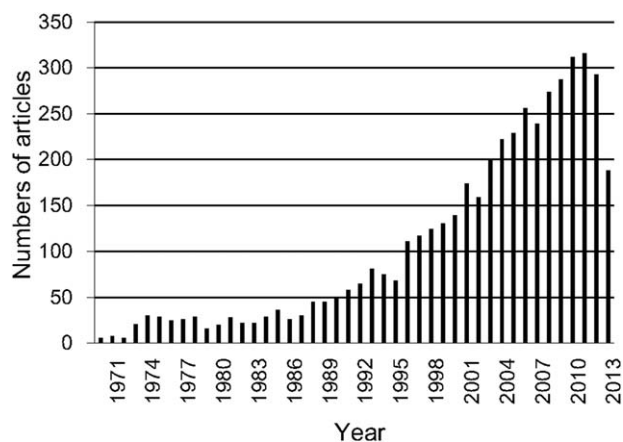


Figure 1. Annual number of articles on the degradation of polyolefins indexed in Scopus from 1970 to 2013.

of the photodegradation of polymers has been well reviewed.^{4,7,9} UV radiation has sufficient energy to cleave the C—C bond. The UV wavelength required for a specific plastic depends on the bonds present; for polyolefins, it is around 300 nm for PE and around 370 nm for polypropylene (PP).^{4,7,9} Some other parameters, such as the light intensity, temperature, volume, and depth, may also affect the degradation of polyolefins.^{12,14–16} Natural weathering (outdoor exposure) and artificial weathering (in-laboratory testing) conditions are used to assess the photodegradability of plastics. The main reactions during the photodegradation of PE include chain scission, crosslinking, oxidation, and recrystallization. The main degradation mechanism is the chain-scission reaction in the amorphous phase¹⁷ at the amorphous-lamellar interface, and the crystalline phase remains mostly inert. Chain scission involves the absorption of UV light, and this then leads to the generation of free radicals.¹³

The thermal oxidative degradation of polymers in the presence of an oxygen or air environment is important to practical industrial applications because most polymers are applied below their processing temperature and hardly degrade in an environment without oxygen. The deterioration of material properties in the natural environment is a result of reactions with oxygen.^{18,19} Oxygen can lower the decomposition temperature and activation energy (E_a) of polyolefins.^{20,21} The degradation of polyolefins always occurs at high temperatures in a screw.²² The degradation of PP and HDPE have been studied with multiple extrusions, and it has been reported that the molecular weight of PE decreased as a result of chain scission. However, the molecular weight of HDPE increased at first as the chain branched and crosslinked.²³ Pro-oxidants, such as cobalt stearate (CoSt), can also accelerate both the thermal and thermooxidative degradation of polyolefins, as indicated by lower E_a values and the reduced lifetime of low-density polyethylene (LDPE) in the presence of CoSt.²¹ Thermooxidative testing was also carried out in an air oven at different temperatures and times, such as at 70 and 100 °C.^{21,24,25}

Biodegradation is a degradation process in which microorganisms play an important role either under aerobic or anaerobic

conditions.²⁶ Biodegradation generally follows photodegradation or thermal degradation and chemical degradation. Unmodified polyolefins are resistant to biodegradation because of their hydrophobicity and high molecular weight; this renders their functional groups unsusceptible to attack by microbial enzymatic systems.²⁷ The biodegradation of polymers involves several steps. First is the attachment of microorganisms to the surface of the polymer followed by their growth and the utilization of the polymer as a carbon source. The next step is the primary degradation; that is, the main chain is cleaved, and this leads to the formation of low-molecular-weight fragments, dimers or monomers, and the final step is mineralization, that is, conversion into CO₂, water, and biomass.²⁸ It has been reported that to achieve significant biodegradation in a reasonable time period, the average molecular weight of an oxidized polyolefin should be less than 5000 Da.^{5,11} Thus, the development of an oxobiodegradation system would be a good method for the degradation of polyolefins. A detailed list of standards for the assessment of degradation and biodegradation was published in a recent review.¹

CHARACTERIZATION OF POLYOLEFIN DEGRADATION

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is used not only for identifying oxidation products from the γ -, photo-, and thermally initiated oxidation of polyolefins²⁹ but also for characterizing and quantifying the oxidation extent of polymers.^{14,29} The extent of oxidation could be expressed by the *carbonyl index* (CI), which is defined as the ratio between the integrated band absorbance of the carbonyl groups of carboxylic acids around 1714 cm⁻¹ and that of the PE-polymer bands at about 1470.¹⁴ Actually, the carbonyl bands assigned to C=C stretching vibrations contain aldehydes and/or esters (1733 cm⁻¹), carboxylic acid groups (1700 cm⁻¹), γ -lactones (1780 cm⁻¹), and ketones (1714 cm⁻¹),^{10,12,14,15} so the absorption peak range chosen for integration should contain those peaks. The influence of the UV exposure parameters on PP by FTIR spectroscopy has been discussed in detail.^{12,14–16} Attenuated total reflection is a useful technique for directly

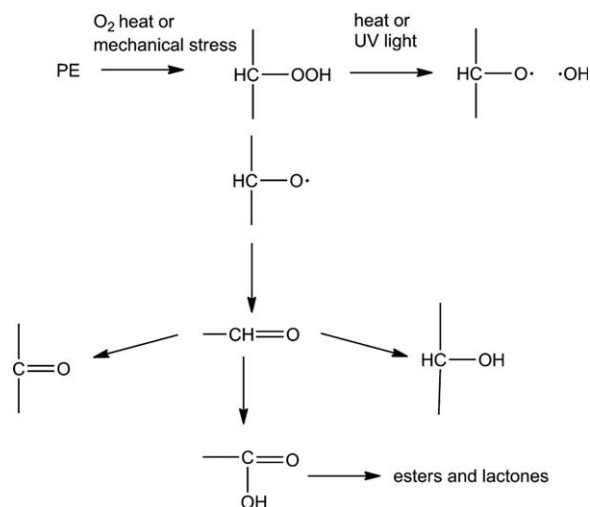


Figure 2. Simplified scheme showing the degradation pathways of PE. (Reprinted with permission from ref. 6. Copyright 2006 Elsevier, Ltd.).

examining surfaces without further sample preparation.^{12,18} A variable angle–attenuated total reflection technique developed by Gulmine et al.¹⁴ can be used to detect the UV oxidation extent in samples of distinct layers, from the surface down to different depths. Recently, Fourier transform infrared microscopy (FTIRM) has also been used to study the phase composition and interface of polymer blends.^{30,31} Synchrotron–FTIRM can improve the spatial resolution as a result of its high brilliance. Liu et al.¹² applied the synchrotron–FTIRM technique to study the accelerated degradation of PE by starch.

Gel Permeation Chromatography (GPC)

GPC is frequently used to determine the molecular weights and weight distributions of polymers and plastics.^{32,33} It allows the determination of the number-average molecular weight (M_n), weight-average molecular weight (M_w), polydispersity (M_w/M_n), and molecular weight distribution (MWD) of a wide range of polymers. Because highly crystalline polyolefin is soluble only at high temperatures, elevated temperatures are required to break down the ordered crystalline structure, and on cooling, the materials will recrystallize and precipitate from solution. Solvents for the analysis of polyolefin include 1,2,4-trichlorobenzene,^{33,34} decaline, and 1,2-dichlorobenzene,³⁵ and analysis is always performed at high temperatures between 135 and 160°C. Previous studies have reported that low dn/dc values of polyolefin limit the refractive index and light-scattering detector applications.³⁵ To obtain more information on the complex structures of polyolefins, such as the MWD, chemical composition distribution, and long-chain branching distribution, a number of different analysis methods have been used, namely, GPC with a multidetector, such as refractive index testing, FTIR spectroscopy, multi-angle laser light scattering, and viscometry.³⁶ DesLauriers et al.³⁷ used GPC–FTIR spectroscopy (mercury cadmium telluride (MCT) detector) to study the chemical composition (short-chain branching) distribution and the MWD of polyolefin. GPC–NMR is also a potential tool for obtaining MWD and chemical composition distribution information for polyolefins.³⁸ Recently, some innovative analytical methods, such as temperature-rising elution fractionation, have been used for isotactic polypropylene (iPP).^{39–41} Another technique called *crystallization analysis fractionation*⁴² was developed for the analytical separation of these polyolefins.

High-Performance Liquid Chromatography (HPLC)

HPLC is an important tool for the fast separation of complex polymers with regard to chemical composition. HPLC separations can be achieved via different separation mechanisms, including adsorption–desorption or precipitation–redissolution. A challenge to develop HPLC methods for the separation of polyolefins would be at temperature of 120°C and higher; this limits the application of HPLC in polyolefin characterization because the development of hardware for high-temperature HPLC is challenging. Recently, Macko and Pasch⁴³ designed a new chromatographic system for the adsorption and desorption of PE and PP; it was composed of a porous carbon-based material as the stationary phase, and the mobile phase was composed of 1-decanol and trichlorobenzene. The results show that this system enabled faster separation of the linear PE from isotactic PE and the separation of PP according to its tacticity. Roy

et al.⁴⁴ extended the high-temperature liquid gradient chromatography work for polyolefin separation. A two-dimensional, high-temperature liquid chromatography method was developed, in which separation was achieved on the basis of the composition of the first HPLC (with Hypercarb as the stationary phase) and the molecular size in GPC. Two-dimensional contour plots were constructed for samples, and this provided knowledge of both the apparent chemical composition and the molecular weight at the same time. Cong et al.⁴⁵ developed a new technique for characterizing the comonomer distribution in polyolefins by high-temperature thermal gradient interaction chromatography; this was based on the separation mechanism of the interaction of the polyolefin chains with the graphite surface during a temperature change in an isocratic solvent.

Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS)

The coupling of SEM and EDS can provide better information about the surface topography and the chemical composition of polyolefins during its degradation. Gulmine et al.¹⁴ used SEM–EDS to detect changes in the surface morphology and some residues of polyolefins after weatherometer degradation and purification. A detailed biodegradation process of composted PE–starch blends was studied by Vieyra et al.⁴⁶ with SEM.

Differential Scanning Calorimetry (DSC)

DSC has been recognized as one of the most convenient and useful techniques for studying the thermal behavior of polymeric materials, including the glass transitions, cold crystallization, crystallinity (PE used 293.1 J/g and PP used 209 J/g as heats of fusion for 100% crystallinity),^{26,47} melting, and effect of thermal treatment.^{48–50} Conventional DSC is not a suitable method for studying the thermal decomposition of natural polymers because the moisture will evaporate from the samples, and as a result, the glass transitions in the DSC curves will show overlapping predominant moisture loss peaks. Recently, some special DSC pans (high-pressure pans) that form a seal system were developed to monitor the thermal decomposition of starch,^{51,52} which is different from the open system. Yu et al.⁵³ added solid CO₂ (dry ice) to form a pressure seal system and studied the phase transition of polystyrene. High-pressure DSC can implement different pressures to the sample. Yu and coworkers^{49,50} used this kind of DSC to study the crystallization and glass transition of a semicrystalline polymer polylactic acid (PLA) as a function of the time and pressure. The successive self-nucleation and annealing technique consists of a series of heating and cooling cycles that are designed to produce thermal fractions as a function of the different linear sequence chain lengths (methyl sequence lengths). Later, they are usually present in ethylene/ α -olefin copolymers or in any branched PE as a consequence of its intramolecular and intermolecular branch distribution.⁵⁴

Thermogravimetric Analysis (TGA)

TGA, also called *thermogravimetry*, is a technique used to measure the mass of samples as a function of the temperature or time in which the sample is subjected to a controlled temperature program in a controlled atmosphere.¹⁸ TGA has been used widely as a method for studying the thermal stability and

decomposition of polyolefins and polyolefin-based materials. Differential thermogravimetry (DTG), the first derivative TGA, is a sensitive measurement and supplies the analyst with information of relative rates of volatilization and polymer decomposition. The peak maxima in the DTG curve represents the maximum rate of mass loss. Each step of weight loss corresponding to a peak in the DTG curve represents a separate event in a particular temperature range, and these parameters are used to evaluate the thermal decomposition behavior of polymers. Furthermore, some kinetics based on TGA will give E_a , the exponential factor, and the overall reaction order; this is important for predicting the product stability and thermal decomposition behavior.^{18,55} The kinetics based on the Flynn–Wall–Ozawa model were applied to obtain E_a of PE with and without the prodegradant after UV exposure.⁵⁶

SAXS and Wide-Angle X-ray Scattering (WAXS)

SAXS is able to probe nanostructure information, including the size (2–100 nm), shape, and orientation, of materials. SAXS measures variations in the electron density distribution of a material. For polyolefin systems, the scattering intensity of X-rays is proportional to the difference in the scattering length densities between the two phases (e.g., crystalline and amorphous phase). Depending on existing knowledge of the system, small-angle analysis may yield the size, shape, mass, and X-ray scattering length density from the scattering curve. For example, the correlation function is used to obtain information on the size of amorphous and crystalline layers in lamellae.⁵⁷ Synchrotron radiation is used to improve the resolution and intensity in scattering. This technique allow the coupling of WAXS with SAXS in SAXS beams, and various online techniques, such as heat or tensile testing, can be developed in this beamline. WAXS or X-ray diffraction is often used to determine the crystalline structure and relative content of polyolefins.

Mechanical Testing

The mechanical behavior observed from the stress–strain curves (e.g., tensile, shear, and flexural tests) and impact tests is important in evaluating polyolefin materials and studying the relationship between its structure and mechanical properties. For example, the annealing and orientation treatment of semicrystalline polymers improve their mechanical behavior.⁵⁸ Some parameters, such as the strength, elongation, modulus, and toughness, are frequently used to evaluate the mechanical behavior of polymers.

Dynamic mechanical analysis is also used to determine the mechanical and viscoelastic behavior, and is expressed in terms of a dynamic storage modulus, a dynamic loss modulus, and a mechanical damping term ($\tan \delta$). More parameters, including the glass-transition temperature, relaxation time, and time–temperature and temperature–frequency curves are given. Contat-Rodrigo and Ribes-Greus⁴⁷ used dynamic mechanical analysis to investigate the dynamic mechanical relaxation spectra of polyolefin with different biodegradable additives, after a 21-month outdoor soil burial test. The results from this study show that the β -relaxation was the most sensitive to the exposure time; this suggested that degradation started in the crystalline–amorphous interface.

Other techniques, such as NMR,⁵⁹ gas chromatography mass spectrometry,⁶⁰ and chemiluminescence,⁶⁰ are also used to identify the degradation products of polymers to explore the degradation mechanism of polyolefins.

ACCELERATING THE DEGRADATION OF POLYOLEFINS

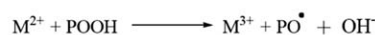
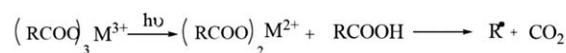
As mentioned before, polyolefins polymers containing long-chain C—C bonds are generally resistant to biodegradation because microbial enzymes are not able to access the C—C backbone because of their hydrophobic nature. To initiate the biodegradation of polyolefins, some principle strategies have been developed. The first is based on the introduction of a certain content of carbonyl groups directly into the PE chain or on the α -position of short branches during copolymerization processes. The second is the incorporation of pro-oxidants²⁵ or the direct incorporation of natural biodegradable polymers, such as starch, to enhance the potential biodegradability of PE. Different methods used to improve the biodegradation of polyolefin are reviewed in the following sections.

Adding Inorganic Degradation Agents

Light and heat are the primary initiators for the oxodegradation of PE-containing pro-oxidants. In their presence, pro-oxidants encourage polyolefin to degrade by a free-radical chain reaction involving oxygen from the atmosphere. The degradation pathways of PE containing pro-oxidant additives is presented in Figure 3.⁶¹ When PE-containing metal carboxylates absorb energy, electron transfer occurs in the three-dimensional subshell of the metal atom; this leads to the production of carboxylic acid free radicals ($R'COO\cdot$). These further decarboxylates to form R' , which transforms PE into a free radical. In the presence of heat and oxygen, hydroperoxides ($R'OOH$) are formed; they further decompose into radicals in the presence of metal salts, and this leads to chain scission and the production of low-molecular-mass oxidation products, such as carboxylic acids, alcohols, ketones, and low-molecular-mass hydrocarbon waxes. GPC results have shown that the M_n and M_w values of the oxidized PE were much lower than those of the original PE.^{61,62}

The most active pro-oxidants are transition-metal ion complexes added to polyolefins in the form of either stearates or other organic ligand complexes; they can yield two metal ions of similar stability and with oxidation numbers that differ by one unit only (e.g., Mn^{2+} and Mn^{3+}).^{33,63} Different kinds of metal ion complexes were referenced in a recent review article.¹ Stearate complexes of transition metals, such as zinc stearate,^{59,64} CoSt,^{65,66} manganese stearate (MnSt),⁶⁷ titanium stearate,⁶³ and chromium stearate, or alkaline earth metals, such as magnesium stearate⁶⁸ and calcium stearate (CaSt),^{64,67,69} have been studied widely. Some inorganic degradation agents recently used in polyolefins are presented in Table I.

The most commonly used transition metals include iron (Fe), cobalt (Co), and manganese (M_n). All of the metals ions (Fe^{3+} , Mn^{2+} , and Co^{2+}) can act as thermal catalysts and photocatalysts; however, Fe^{3+} is highly effective in accelerating photodegradation, whereas Mn^{2+} and Co^{2+} are sensitive to thermal degradation.^{25,70,71} Focke et al.⁷² compared the rate of photodegradation of polymers with different metal stearates and found that rates, as



Where M is Fe, Co and Mn

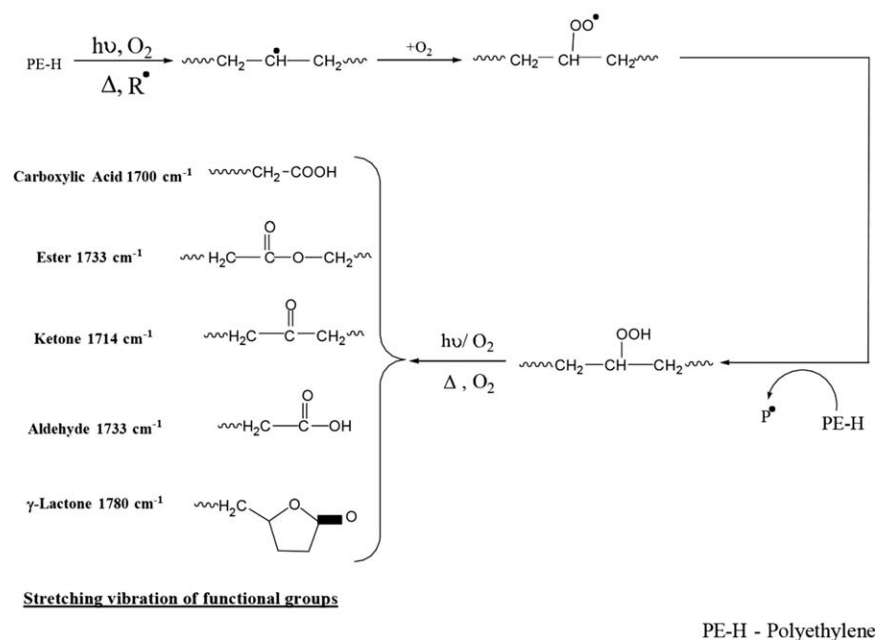


Figure 3. Degradation pathways of PE containing pro-oxidant additives. (Reprinted with permission from ref. 61. Copyright 2013 Elsevier, Ltd.).

expressed by CI, in the following order: Co(III) > Fe(II) ~ Fe(III) > Cu(II). These results agreed with a previous study that has reported that thermooxidative degradation in the presence of metal stearate followed the order: Cobalt > Manganese > Iron.²⁵ Roy et al.'s study²⁵ also revealed that the initial oxidation state (+2 and +3) of the metal did not affect its ability to initiate and accelerate degradation. Transition metals with an ability to switch between two oxidation states can result in the decomposition of hydroperoxides, and this can initiate the oxidation process. Once initiated under light and heat, the process continues, even under dark conditions.

The effect of iron stearate (FeSt) and CaSt on the photodegradation and biodegradation of PE was studied by Pablos and coworkers.^{60,70} In a later study, we found that both FeSt and CaSt accelerated the photodegradation of PE, and FeSt had a higher degradation compared to that of pure PE or CaSt PE. The study reported that three bacterial species, namely, *Bacillus cereus*, *Bacillus megaterium*, and *Bacillus subtilis*, which are common in soil, were found attached to the polymer surface. In another recent study, a mixture of these three *Bacillus* bacterial species (MIX) and *B. bartelensis* were used to evaluate the effect of a pro-oxidant on the biodegradation of highly photodegraded films.⁷⁰ After 90 days of incubation of PE films with the MIX and *B. bartelensis*, the GPC results revealed a significant change in MWD in the presence of FeSt. The average molecular weight decreases were

measured as 5.6 and 6% for MIX and *B. bartelensis* respectively; this suggested that the bacteria used in this study were able to degrade photodegraded low-molecular-weight compounds and molecular weight fractions of less than 5000 Da.⁷⁰

The effect of three cobalt carboxylates with different chain lengths, including CoSt₃, cobalt palmitate (CoPal₃), and cobalt laurate (CoLau₃) on the photodegradation, thermal degradation, and biodegradation of LDPE films were investigated by Roy et al. (Table II).^{24,73} The order of photodegradation reported was CoSt₃ > CoPal₃ > CoLau₃; thus, we concluded that in addition to the metal content, the chain length of carboxylate also played a vital role in PE degradation. A similar result was observed in the thermal oxidative degradation of PE; bacteria were found on UV-irradiated samples, and their number was found to grow.⁷⁴

Inorganic fillers are often added to polyolefins to form composites or nanocomposites in which the filler serves to enhance the mechanical properties. Montmorillonite (MMT) is commonly used to enhance the mechanical behavior of polyolefins, and it also used to accelerate the photooxidation of polyolefins (Table II).⁷⁵⁻⁷⁷ The lower efficiency of antioxidants, such as phenolic antioxidants and hindered amine light stabilizers, could result from interaction between the phenolic groups of the antioxidant and the MMT. Qin and coworkers^{78,79} have also studied the photooxidative degradation of PE/MMT nanocomposites, and they found that the effect of ammonium ions

Table I. List of Inorganic Degradation Agents

Polymer	Active components	Loading (wt %)	Process type	Degradation conditions			Reference
				Photodegradation	Biodegradation	Thermal degradation	
LDPE	CeSt ₃ , CeLau ₃ , CeOct ₃	6	M, SSE	Yes	No	No	129
PE	Al, Ti, Mg, Cr, Zr	0.002-0.1	CM	Yes	No	Yes	127
PE	MnSt		Film	No	Yes	Yes	33
iPP	MMT	5	TSE	Yes	No	No	77
iPP	MMT	5	TSE	Yes	No	No	75,76
LDPE	Fe ³⁺ -MMT, MMT	5	TSE	Yes	No	No	78,79
LDPE	CoSt ₃ , CoPa ₃ , CoLau ₃	0.05-0.2	TSE	Yes	Yes	Yes	17,24,73,74
LLDPE	Na-MMT, OMMT	2.5-5	TSE	Yes	No	No	82
PE	d2w		TSE	Yes	Yes		130
OBPE	OMMT	2	TSE		yes	yes	81
LDPE	OMMT	2-7	TSE	Yes	No	No	80
LDPE	CoSt ₂ , CoSt ₃ , MnSt ₂ , MnSt ₃ , FeSt ₂ , FeSt ₃	0.5	Blowing	Yes	No	Yes	25
LDPE, LLDPE	FeSt ₂ , CaSt ₂	0.2		Yes	Yes	No	60,70
LDPE	TiO ₂	0-0.75%	TSE	Yes	No	No	131
HDPE	MIs: Cr, 36%; Si, 8%; Al, 4%; Cl, 2%	0.5-2.0	SSE	Yes	No	Yes	132
LDPE	FeSt ₂ , CoSt ₂ , MnSt ₂	0.2		Yes	Yes	Yes	61

CM, compression-molded; M, mixer; OBPE, oxobiodegradable polyethylene; SSE, single-screw extruder; TSE, twin-screw extruder; TSE, cerium stearate; CeSt₃, cerium laurate; CeOct₃, Cerium octoate.

Table II. List of Studies That Have Reported Effects of Additives, Fillers, and Blends on Polyolefin Degradation

Modification	Effect on the total mass of the composites	Effect on polyolefin degradation	Reference
Additives/pro-oxidants			
Cobalt carboxylates: CoLau ₃ , CoPal ₃ , and CoSt	The molecular weight decreased.	The rate of thermooxidative degradation increased with concentration, and the chain length of the cobalt carboxylate additive increased.	24
FeSt and CaSt	There was a significant decrease in the molecular weights.	A higher percentage biodegradation was achieved on incubation with microbial cultures.	61
Manganese salt	There was a significant decrease in the molecular weights.	A higher biodegradation in soil (91%) was achieved compared to that in a compost (43%) environment.	62
Benzyl and CoSt	Not determined	No effect of benzyl was observed, but the thermal oxidation due to cobalt increased.	65
Metal stearates	Not determined	The rate of photodegradation increased.	72
Cobalt carboxylates: CoLau ₃ , CoPal ₃ , and CoSt	The molecular weight decreased on UV exposure.	The photooxidative degradation increased with increasing chain lengths of the cobalt carboxylates. The extent of the molecular weight reduction depended upon the type and amount of additive.	73
Proprietary pro-oxidant	Sunlight and thermal exposure led to an increased residual weight percentage.	The rate of degradation increased significantly (the differences in CI suggested an excess 20% oxidation).	83
Fillers			
MMT	Not determined	Faster photodegradation was observed. The induction time decreased in the presence of MMTs, and this effect was enhanced in the presence of an exfoliated nanocomposite.	75,76
OMMT	A significant decrease (94%) in M_w compared to neat PE (65%) was observed.	A significantly enhanced degradation was observed.	80
Compatibilizer PE-g-MA (added to improve the dispersion of OMMT)	Not determined	The rate of photooxidation of the compatibilized PE/PE-g-MA/OMMT nanocomposites was much higher than that of the PE/OMMT.	82,93
Blending			
Starch and catalyst/pro-oxidant	The weight loss was the highest (22.7%) in the catalyst blends; this was followed by the starch blends (11.3) and the unblended sample (1.5%).	The higher rate of degradation was observed with the starch blends kept under sunlight (10% loss in 60 days) compared to the catalysts blends.	71
Food-grade corn starch	A significant weight loss was observed.	Higher degradation rates were observed with the effect being proportional to the starch content.	46
Starch from agricultural waste	A significant weight loss was observed.	Higher degradation rates were observed.	86

Table II. Continued

Modification	Effect on the total mass of the composites	Effect on polyolefin degradation	Reference
Thermoplastic starch	Not determined	A faster degradation rate was observed.	106,107
Chemical starches and starch grafted with cholesterol moieties	Not determined	The degradation was higher for blends with modified starch on exposure to activated sludge but was relatively slower during the enzyme treatment.	108
Acetylated banana starch	A significant weight loss was observed.	The rate of degradation was faster (mostly in the starch fraction).	109
Propylated corn starch	There was an increase in the weight loss.	There was an increase in the degradation rate, which was proportional to the starch content.	110
Chitosan			
Acrylic acid modified chitosan	A lower weight loss was observed in the treated chitosan blends versus the untreated blends.	The treated chitosan blends had better thermal degradation resistance than the untreated ones.	117
Chitosan and palm oil hybrid reinforced LDPE	The weight loss increased with the chitosan content. Similarly, for palm oil, the weight loss was higher than that of the unplasticized films.	The degradation was higher for blends compared to that of the unplasticized samples.	118
Protein			
Soy-protein-grafted PE	The weight loss increased with time (and was 74% after 4 months of soil burial).	An increased rate of degradation was observed, and the PE fraction decreased over time.	119
Fibers			
PEG-plasticized KC/LDPE biocomposites	Not determined	An increase in the degradation with increasing KC content was observed.	120,121
Natural fibers: wood flour and kenaf fiber	Not determined	An accelerated weathering of the blends was observed.	122
PP/FC composite containing PEO/TiO ₂	Not determined	A linear increase in the degradation with increasing PEO content was observed.	126

was a primary one for degradation. In their study, they found no significant increase in PE degradation in samples with nanodispersion or microdispersion of MMT, but Fe³⁺-modified MMT was observed to accelerate the degradation of PE. Kumayaka et al.⁸⁰ reported that the decomposition of alkyl ammonium ions in MMT created olefins and acidic sites on the clay surface, and this led to accelerated radical formation in the PE matrix.

The effect of organically modified montmorillonite (OMMT) on the biodegradation of PE was investigated by Reddy and coworkers,^{11,81} and they observed that the thermal oxidation of PE was influenced significantly by the pro-oxidant but not by OMMT. However, OMMT could provide a favorable environment for the growth of the microorganism and their utilization of the polymer surface and the bulk of the polymer volume.

Dintcheva et al.⁸² studied the effects of the compatibilizer polyethylene-grafted maleic anhydride (PE-g-MA) on the photooxidation of linear low-density polyethylene (LLDPE)/MMT

and found that PE-g-MA could accelerate the photooxidation rate of PE/PE-g-MA/OMMT nanocomposites compared with a pure polymer and PE/OMMT (Table II). The major reason seemed to be the thermal degradation products of alkyl ammonium surfactant; this ultimately resulted in more polymer peroxidation and gave rise to pro-oxidant effects and a lower stability in the compatibilized nanocomposites, that is, the photolytic instability of the anhydride ring and the catalytic effect of the metal-ion impurities present in naturally occurring clays.

Adding Organic Degradation Agents

Although transition-metal salts are widely used as prodegradant additives in oxodegradable polyolefins, as reported in the literature, there are some prodegradant additives that do not contain any transition metals; these include ketone copolymers, 1,2-oxohydroxyl groups, unsaturated alcohols or esters, benzophenones, γ -pyrones, β -diketones, polyisobutylene, and selected amines and peroxides. Detailed information can be found in a recent review article.¹

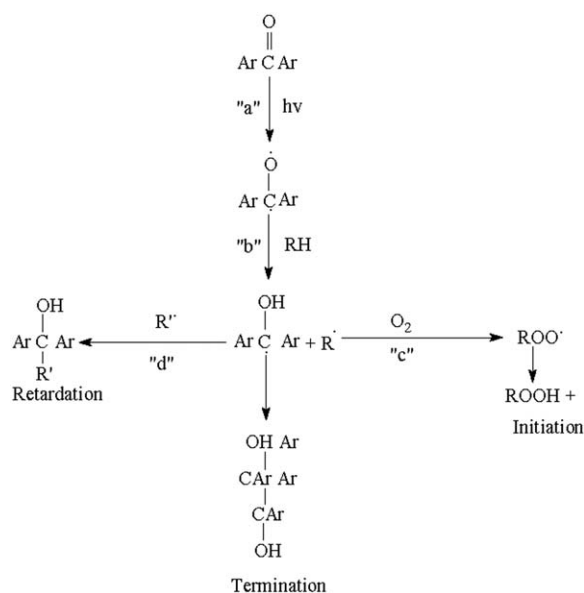


Figure 4. Photoinitiation due to aromatic ketones. (Reprinted with permission from 65. Copyright 2005 Elsevier, Ltd.).

The effect of benzyl and CoSt on the thermal degradation, photodegradation, and natural weathering degradation of LDPE films was investigated by Roy et al.⁶⁵ They investigated the tensile properties, CI, and apparent density to characterize the degradation behavior and found that benzyl's effectiveness was lower than that of transition-metal complexes; this limits its commercial success. However, when it was used in combination with CoSt, the rate of degradation was enhanced, and this depended on the amount of CoSt (Table II). The accelerated degradation mechanism of benzyl is presented in Figure 4; it was suggested that a more stable structure was formed, and this lowered or terminated the degradation reaction.⁶⁵

Another way to initiate the degradation of polyolefins is to introduce certain weak sites, such as carbonyl groups, dithiocarbamates, and carbon monoxide, into the hydrocarbon backbone/side chain. The addition of olefinic bonds during polymerization has also been used before, but it has a higher cost.^{9,83}

Blending with Natural Polymers

The direct incorporation of natural polymers, such as starch, to enhance the potential biodegradability of polyolefins has recently been used. The microbial assimilation of natural polymers in blends was observed to increase the surface area of synthetic bulk materials and to render them more susceptible to degradation. The underlying mechanism is a complex interaction of abiotic- and biotic-mediated oxidative processes.^{2,12,46,84–87} The blending of PE with different natural polymers are described in the following sections.

Blending with Starch. Starch is considered one of the most important renewable polymers; it has potential as a material to replace large quantities of petroleum-derived plastics.⁸⁵ A lot of fundamental work has been done on the microstructure,^{88,89} phase transition,^{18,51,90–92} rheology,^{93–95} and process properties,⁹⁶ and some starch-based functional materials^{30,31,97–100} have been developed.

The biodegradation of PE and its blending with starch have been widely studied,^{46,86,101–106} and it is clearly understood that the initial stage of the biodegradation of PE blends is mainly due to the starch phase. A more continuous starch phase content could improve the accessibility of the PE matrix. Photoradiation treatment can also enhance and accelerate the rate of biodegradation of PE/starch blends by increasing or creating an oxidized starch surface area.

The UV degradation of oxodegradable PE/thermoplastic pea starch (TPPS) blends¹⁰⁷ showed that TPPS could accelerate the photooxidative degradation of PE (Table II). In this study, the degradation process of blends was promoted by pro-oxidant (TPPS) addition into PE. During the first few weeks, the crystallinity of the PE matrix increased with the UV-irradiation time because of the preferential cleavage of the branching points of PE. After 13 weeks, the UV degradation proceeded directly through the main backbone, and this led to a decrease in the degree of crystallinity. When TPPS was added, starch was also subject to degradation because of some preferential cleavage of α (1–4) and α (1–6) bonds.

The biodegradation of starch-blended oxodegradable PE was compared in three different environments, such as soil, marine, and direct sunlight environments.⁷¹ Exposure to sunlight showed the highest weight loss, and samples buried in soil showed the lowest weight loss. Pro-oxidant blended HDPE showed a higher weight loss compared to other starch-blended samples. Direct sunlight (UV) was a good way to initiate the abiotic degradation/deterioration of polyolefins. Pro-oxidant blending appears to be a better alternative than starch blending (in the case of HDPE) for achieving higher degradation. There is a need for the development of degradable PEs suitable for degradation in the marine environment and in soil so that they can degrade faster than they have done in the studies reported in the literature.

Different chemical starches have been used to improve the compatibility of PE,^{108,109} and their biodegradation behaviors have been studied. Starch-grafted cholesterol moieties were used to improve the dispersion, tensile strength, and elongation. The PE/modified starch films showed improvements in biodegradability with the activated sludge method because of the increased accessibility of the microbes to the cholesterol moieties (Table II).¹⁰⁸ Acetylated modified starch accelerated the biodegradation of LDPE films, whereas oxidized starch slowed the biodegradation compared with native starch. We can explain these results by highlighting the fact that the oxidation starch destroyed the amorphous regions and increased the starch crystalline area, whereas acetate destroyed the ordered crystalline structures.¹⁰⁹ The biodegradability of propylated¹¹⁰ starch/LDPE films increased with increasing starch concentration, but it decreased with increasing degree of substitution. These results were similar to those observed with fatty acid esters of starch.¹¹¹

The effects of γ radiation on the biodegradation of LDPE/starch has also been reported in the literature. Radiation-processed thermoplastic starch (RTPS) improved the processability of blends and made the process less energy intensive. The

biodegradation of LDPE/RTPS was inhibited by an increase in the dose imparted to starch, and this was attributed to the poor connectivity of the starch domain in the LDPE phase and to the increased crystallinity of the LDPE domain when RTPS was used.¹¹² γ radiation promoted a certain fragility in the starch, especially in the amorphous region. This increased the susceptibility of the fungi to consume the starch in the blend as a nutrient source. An increase in the speed of the degradation of the polymer material was also reported by Ferreira et al.¹¹³

Blending with Chitosan. Chitosan is a high-molecular-weight polymer formed by *N*-acetyl-D-glucosamine units with β (1–4) glycosidic bonds. The cationic nature of the chitosan is due to the free amino groups of chitin. It can form transparent films to enhance the quality and extend the storage life of food products.^{85,114–116} Chitosan was observed to reduce the tensile strength of PP composites, although it increased the Young's modulus. On the other hand, the impact strength was observed to increase with the addition of chitosan. The chemically treated PP/chitosan composites were found to have a higher tensile strength, higher Young's modulus, and improved impact strength compared to untreated composites. This might have been due to the better dispersion of the chitosan in the PP composites and the enhanced interfacial adhesion between the chitosan and the PP matrix (Table II).¹¹⁷

The improvement in the biodegradability of LDPE with palm oil as a plasticizer and chitosan as a filler was studied by Sunilkumar et al.¹¹⁸ The biodegradability of the samples was studied by the inoculation of the films with *Aspergillus niger* on a potato dextrose agar media and incubation at room temperature (25°C) for 21 days. The biodegradation rate was found to increase with increasing chitosan loading in the matrix (Table dII). The plasticized samples showed a better biodegradability rate and hydrophilicity compared to the unplasticized ones. Chitosan and palm-oil-hybrid-reinforced LDPE have proven to be a novel combination with an increased biodegradation rate of LDPE and have invoked potential applications in food packaging, bioseparation, and drug delivery.

Blending with Protein. The biodegradation behavior of soy-protein-grafted PE was studied with the soil burial method by Gautam et al.¹¹⁹ The results suggest that the weight loss increased with the exposure period, and a microanalysis of the soil containing the samples also showed an increase in the microbial colonies with increasing number of days (Table II). The effect of the degradation of the grafted samples on the growth of plants (wheat and soybean) showed that the products of degradation were not harmful to the growth of the plants.

Reinforced by Natural Fibers

Natural (plant) fibers have attracted increasing research interest because of their advantages, which include renewability, biodegradation, low cost, low density, high strength properties, ease of separation and recyclability, carbon dioxide sequestration, and biodegradability.^{120,121} Fiber-reinforced polymeric composites have received widespread attention in recent years because of their high specific strength and modulus together with their low cost and biodegradability. Natural plant fibers contain cellulose, lignin, and hemicellulose. For lignocellulosic materials,

photodegradation leads to the breakdown of lignin, hemicelluloses, and cellulose and the loss of fibrous material. The degradation of the fiber, matrix, or the interface caused by weathering can reduce the ability of the composite to effectively transfer stress between these components, and this results in lowered mechanical properties.¹²²

The photodegradation and biodegradation of PE/natural fiber blending has been well studied.^{122,123} It has been found that blends are less stable than pure polymers or natural fiber, and the degradation of blends depends on the blend composition and irradiation time. The mechanical behavior decreased significantly with increasing exposure time. It was also found that the degradation depth increased with increasing exposure time.

Tajeddin et al.¹²⁰ found that poly(ethylene glycol) (PEG) plasticized kenaf cellulose (KC)/LDPE biocomposites showed improved fiber–matrix adhesion and processability. The rate of the biodegradation of LDPE and KC blends was low but was sufficient for breakdown in the environment, and the addition of PEG increased the biodegradation rate a little. The water absorption values in the composites were higher than those of pure LDPE. The addition of PEG reduced the water absorption of the composites; this means that PEG had a protective effect against the penetration of water.

The water absorption behavior of PE reinforced with pineapple-leaf fibers (pineapple leaf fiber/LDPE composites) was investigated by George et al.,¹²⁴ who found that the uptake of water increased with fiber loading because of the increased cellulose content. The chemically modified fiber composite exhibited a reduction in the water uptake because of better interfacial bonding. The fiber/matrix bonding became weak with increasing moisture content; this resulted in interfacial failure. They found that the relative decrease in the tensile strength was lower in untreated fiber composites. The flexural strength and modulus of the composite samples after exposure to UV showed a small decrease.

The photodegradation and biodegradation of ethylene–propylene (EP) copolymer was enhanced by treatment with jute fiber with 3% NaOH (J1C) and jute fiber with 17.5% NaOH (J2C), and blends with microcrystalline cellulose powder (MC) were prepared by melt mixing with a maleated EP copolymer as a compatibilizer.¹²⁵ Detailed study reported photoresistance in the order: Neat EP > MC > J2C > J1C, whereas the bioaccessibility was reported as follows: Neat EP < J1C < J2C < MC. The observed results might have been due to the complex reaction of the fiber composition and the better dispersion of MC. However, composites were less durable under both abiotic and biotic conditions in comparison to the neat polymer matrix.

A novel iPP/fibrous cellulose (FC) composite containing a poly(ethylene oxide) (PEO)/TiO₂ was prepared, and its oxobiodegradation behavior was studied by Miyazaki et al.¹²⁶ TiO₂ acted as a radical initiator for both PP auto-oxidation and PEO degradation. PEO was photocatalytically degraded by TiO₂, and this produced acid and aldehyde compounds. These products accelerated hydroperoxide decomposition. After the UV irradiation, TiO₂ and the PEO played the roles of the initiator and the

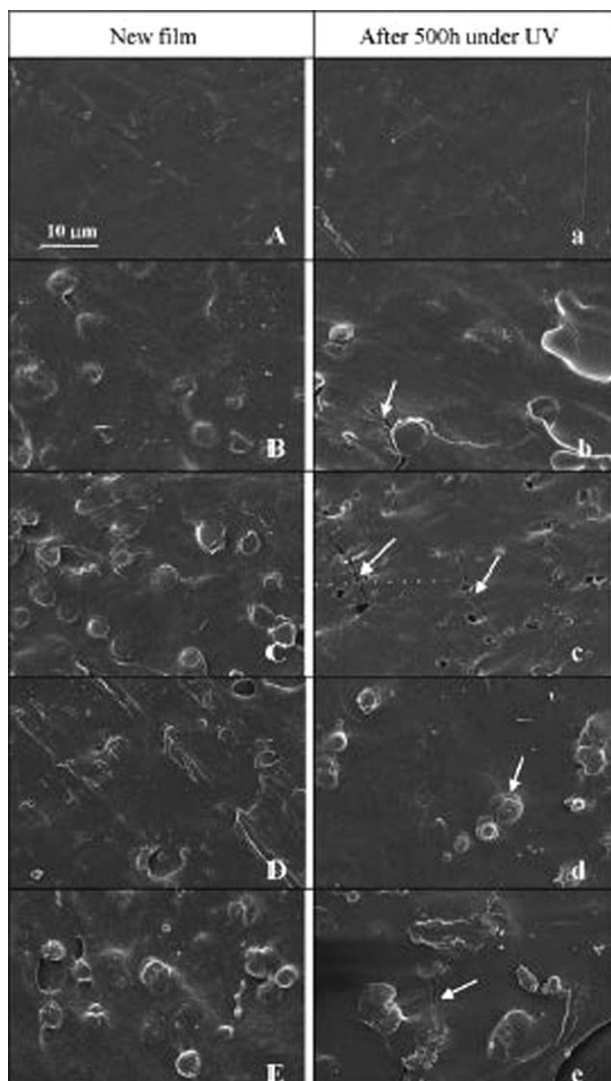


Figure 5. SEM macrographs of the film surfaces with the same scale before and after 500 h of UV exposure: (A,a) pure PE film, (B,b) HDPE/Co/starch, (C,c) (HDPE/Co)/starch, (D,d) HDPE/Fe/starch, and (E,e) (HDPE/Fe)/starch. (Reprinted with permission from ref. 10. Copyright 2013 John Wiley & Sons, Inc.).

accelerator of PP auto-oxidation, respectively. In addition, even at a lower PEO content, the accelerator effect was found to be supplemented by the spreading of the degraded PEO component from other places by the enhancement of the film thickness. The biodegradability of the photodegraded composite was confirmed by the soil burial test, and the attachment of the filamentous fungus was observed on the surface.¹²⁶

CONTROLLING THE DISTRIBUTION OF DEGRADATION AGENTS

The effect of prodegradant (Fe and Co-based) distribution in hybrid PE/starch blends was first studied by Yu et al.¹⁰ The distribution of prodegradants in the different phases was varied by a dual-step process with a side feed on a reactive extruder. The variation in the mechanical properties and the evaluation of carbonyl groups by FTIR spectroscopy were conducted to inves-

tigate the effect of degradation after exposure to photooxidative (UV) degradation. It was found that the variation in the mechanical properties was higher when the prodegradants were distributed in the PE phase. The concentration of carbonyl groups increased as a function of UV exposure, and the concentration of carbonyl groups was higher when the prodegradants were distributed in the PE phase. Microcracking was observed on the interface between starch and PE after the addition of the prodegradants (see Figure 5). The prodegradants prefer to stay with starch as they both have polar surfaces. When the prodegradants were distributed in the high-density polyethylene (HDPE) phase, the microcracks mainly appeared in the HDPE matrix, and the density of the microcracks was higher. In general, the function of prodegradants in PE/starch blends is enhanced when their distribution was varied within the HDPE phase.

The enhancement of the photodegradation and biodegradation of polyolefins by natural polymers has been widely reported. The effect of the natural polymer structure, content, chemical modification, and processing addition on photodegradation and biodegradation have been reviewed before, but the underlying mechanism and the exact role played by natural polymers in accelerating polyolefin parts is still not completely understood. The increases in the CI, crystallinity, and degradation ratio and the decreases in the mechanical properties and thermal stability have been widely reported; however, the mass or the molecular weight changes during limited times (1 year) either have been reported as no change or have not been determined in most studies. Vieyra et al.⁴⁶ reported that a starch/neat PE blend containing 40% starch is expected to last 4375 days (11.98 years) before it undergoes complete degradation. The contribution of natural polymers in the acceleration of the degradation of polyolefins needs to be studied more extensively in the future.

SUMMARY AND FUTURE PERSPECTIVES

The study and utilization of polyolefins have rapidly evolved over several decades, primarily because of a combination of their flexibility, toughness, and excellent barrier properties, easy manufacturing, and good chemical resistance. However, the polyolefin do not easily degrade under the natural environment, so the design of degradable polyolefin systems is necessary. Modern technologies provide powerful tools for characterizing the products of degradation and exploring the degradation mechanism of polyolefin.

In this review, we outline recent developments in the acceleration of the degradation of polyolefin/biopolymer blends and composites, the degradation mechanisms and characterization methods, and the application of techniques, such as the processing conditions and formulations, were well reviewed. Preliminary oxidative degradation and blending with natural polymers, such as starch and plant fibers, can enhance their biodegradability in natural environments. Various methods have been used to control the degradation rate. In summary, some of the key issues that should be considered during design include

1. The choice of polyolefin. For example, the thermal stability was found to follow the order HDPE > *m*-PE > LLDPE,

whereas in photooxidation they followed the order $m\text{-PE} > \text{HDPE} > \text{LLDPE}$.¹²⁷ Degradation under natural weathering followed the same order.¹²⁸

- The choice of metal. As mentioned before, the thermal catalytic or photocatalytic activity is different, so the right one, on the basis of its end use, should be chosen.
- The ratio of prodegradant to antioxidant. Both are commonly used in commercial polyolefins, and a balanced mixture of them could lead to the desired rate of degradation;⁷²
- Modified natural polymers. Different chemical function groups were used to increase or decrease the polyolefin-based composition degradation rate.
- Others additives, such as pigments and dyes. The use of different kinds of metal salts would also effect the degradation rate.
- The rate of degradation of the biopolymer. A controlled rate of degradation of the biopolymer would expand the fields of application.

Although there have been rapid developments in the design of degradable polyolefin systems and polyolefin/biopolymer blends and composites, some challenging questions, such as the understanding of the underlying mechanism of accelerated polyolefin degradation by the addition of natural polymers and incompatibility between natural polymers and hydrophobic polyolefins, should be explored in the future. The degradation mechanism of polyolefin/polyester blending should be studied; this would provide a longer shelf life for end use and allow the controlled degradation for some special applications, such as food packaging.

ACKNOWLEDGMENTS

The authors from South China University of Technology acknowledge research funds from the National Natural Science Foundation of China (contract grant numbers 31301554, 21174043), GNSF (contract grant number S2012040006450), and Chinese Postdoc Funding (contract grant number 2013M531854). One of the authors (C.G.) acknowledges the financial assistance provided by the China Scholarship Council (through the State Scholarship Fund) for her study in Australia.

REFERENCES

- Ammala, A.; Bateman, S.; Dean, K.; Petinakis, E.; Sangwan, P.; Wong, S.; Yuan, Q.; Yu, L.; Patrick, C.; Leong, K. H. *Prog. Polym. Sci.* **2011**, *36*, 1015.
- Scott, G.; Wiles, D. M. *Biomacromolecules* **2001**, *2*, 615.
- Khabbaz, F.; Albertsson, A. C. *J. Appl. Polym. Sci.* **2001**, *79*, 2309.
- Feldman, D. J. *Polym. Environ.* **2002**, *10*, 163.
- Zheng, Y.; Yanful, E. K.; Bassi, A. S. *Crit. Rev. Biotechnol.* **2005**, *25*, 243.
- Wiles, D. M.; Scott, G. *Polym. Degrad. Stab.* **2006**, *91*, 1581.
- Singh, B.; Sharma, N. *Polym. Degrad. Stab.* **2008**, *93*, 561.
- Sivan, A. *Curr. Opin. Biotechnol.* **2011**, *22*, 422.
- Roy, P. K.; Hakkarainen, M.; Varma, I. K.; Albertsson, A.-C. *Environ. Sci. Technol.* **2011**, *45*, 4217.
- Yu, L.; Liu, X. X.; Petinakis, E.; Bateman, S.; Sangwan, P.; Ammala, A.; Dean, K.; Wong-Holmes, S.; Yuan, Q.; Siew, C. K.; Samsudin, F.; Ahamid, Z. *J. Appl. Polym. Sci.* **2013**, *128*, 591.
- Reddy, M. M.; Deighton, M.; Gupta, R. K.; Bhattacharya, S. N.; Parthasarathy, R. *J. Appl. Polym. Sci.* **2009**, *111*, 1426.
- Liu, X.; Yu, L.; Xie, F.; Petinakis, E.; Sangwan, P.; Shen, S.; Dean, K.; Ammala, A.; Wong-Holmes, S. *J. Appl. Polym. Sci.* **2013**, *130*, 2282.
- Hsu, Y.-C.; Weir, M. P.; Truss, R. W.; Garvey, C. J.; Nicholson, T. M.; Halley, P. J. *Polymer* **2012**, *53*, 2385.
- Gulmine, J. V.; Janissek, P. R.; Heise, H. M.; Akcelrud, L. *Polym. Degrad. Stab.* **2003**, *79*, 385.
- Philippart, J. L.; Sinturel, C.; Arnaud, R.; Gardette, J. L. *Polym. Degrad. Stab.* **1999**, *64*, 213.
- Girois, S.; Audouin, L.; Verdu, J.; Delprat, P.; Marot, G. *Polym. Degrad. Stab.* **1996**, *51*, 125.
- Roy, P. K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *J. Appl. Polym. Sci.* **2008**, *108*, 2726.
- Liu, X.; Wang, Y.; Yu, L.; Tong, Z.; Chen, L.; Liu, H.; Li, X. *Starch* **2013**, *65*, 48.
- Gijsman, P. *e-Polymers* **2008**, *65*, 1.
- Peterson, J. D.; Vyazovkin, S.; Wight, C. A. *Macromol. Chem. Phys.* **2001**, *202*, 775.
- Roy, P. K.; Surekha, P.; Rajagopa, C.; Choudhary, V. *eXPRESS Polym. Lett.* **2007**, *1*, 208.
- Mendes, A. A.; Cunha, A. M.; Bernardo, C. A. *Polym. Degrad. Stab.* **2011**, *96*, 1125.
- Hinsken, H.; Moss, S.; Pauquet, J. R.; Zweifel, H. *Polym. Degrad. Stab.* **1991**, *34*, 279.
- Roy, P. K.; Surekhal, P.; Rajagopal, C.; Choudhary, V. *J. Appl. Polym. Sci.* **2007**, *103*, 3758.
- Roy, P. K.; Surekha, P.; Raman, R.; Rajagopal, C. *Polym. Degrad. Stab.* **2009**, *94*, 1033.
- Khabbaz, F.; Albertsson, A. C.; Karlsson, S. *Polym. Degrad. Stab.* **1999**, *63*, 127.
- Chiellini, E.; Corti, A.; Swift, G. *Polym. Degrad. Stab.* **2003**, *81*, 341.
- Tharanathan, R. N. *Trends Food Sci. Technol.* **2003**, *14*, 71.
- Lacoste, J.; Vaillant, D.; Carlsson, D. J. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 715.
- Liu, X.; Wang, Y.; Yu, L.; Zhang, N.; Shanks, R. A.; Liu, H.; Tong, Z.; Chen, L. *Chin. J. Polym. Sci.* **2013**.
- Zhang, N.; Liu, X.; Yu, L.; Shanks, R.; Petinakis, E.; Liu, H. *Carbohydr. Polym.* **2013**, *95*, 649.
- Liu, X.; Yu, L.; Dean, K.; Toikka, G.; Bateman, S.; Nguyen, T.; Yuan, Q.; Filippou, C. *Int. Polym. Proc.* **2013**, *2013*, 64.
- Jakubowicz, I. *Polym. Degrad. Stab.* **2003**, *80*, 39.
- Yau, W. W. *Macromol. Symp.* **2007**, *257*, 29.
- Pasch, H. *Macromol. Symp.* **2001**, *165*, 91.
- Soares, J. B. P. *Macromol. Symp.* **2007**, *257*, 1.

37. DesLauriers, P. J.; Rohlfling, D. C.; Hsieh, E. T. *Polymer* **2002**, *43*, 159.
38. Pasch, H.; Malik, M. I.; Macko, T. In *Polymer Composites—Polyolefin Fractionation—Polymeric Peptidomimetics—Collagens*; Abe, A., Kausch, H. H., Moller, M., Pasch, H., Eds.; Springer: New York, **2013**.
39. Yau, W. W.; Gillespie, D. *Polymer* **2001**, *42*, 8947.
40. Nakatani, H.; Matsuoka, H.; Suzuki, S.; Taniike, T.; Boping, L.; Terano, M. *Macromol. Symp.* **2007**, *257*, 112.
41. Ortin, A.; Monrabal, B.; Sancho-Tello, J. *Macromol. Symp.* **2007**, *257*, 13.
42. Monrabal, B. *J. Appl. Polym. Sci.* **1994**, *52*, 491.
43. Macko, T.; Pasch, H. *Macromolecules* **2009**, *42*, 6063.
44. Roy, A.; Miller, M. D.; Meunier, D. M.; deGroot, A. W.; Winniford, W. L.; Van Damme, F. A.; Pell, R. J.; Lyons, J. W. *Macromolecules* **2010**, *43*, 3710.
45. Cong, R.; deGroot, W.; Parrott, A.; Yau, W.; Hazlitt, L.; Brown, R.; Miller, M.; Zhou, Z. *Macromolecules* **2011**, *44*, 3062.
46. Vieyra, H.; Aguilar-Mendez, M. A.; San Martin-Martinez, E. *J. Appl. Polym. Sci.* **2013**, *127*, 845.
47. Contat-Rodrigo, L.; Ribes-Greus, A. *J. Appl. Polym. Sci.* **2000**, *78*, 1707.
48. Gao, C.; Ma, H.; Liu, X.; Yu, L.; Chen, L.; Liu, H.; Li, X.; Simon, G. P. *Polym. Eng. Sci.* **2013**, *53*, 976.
49. Yu, L.; Liu, H. S.; Dean, K.; Chen, L. *J. Polym. Sci. Part B: Polym. Phys.* **2008**, *46*, 2630.
50. Yu, L.; Liu, H.; Dean, K. *Polym. Int.* **2009**, *58*, 368.
51. Liu, X.; Yu, L.; Liu, H.; Chen, L.; Li, L. *Polym. Degrad. Stab.* **2008**, *93*, 260.
52. Liu, X. X.; Yu, L.; Liu, H. S.; Chen, L.; Li, L. *Cereal Chem.* **2009**, *86*, 383.
53. Yu, L.; Liu, H. S.; Chen, L. *Polym. Eng. Sci.* **2009**, *49*, 1800.
54. Benítez, A.; Sánchez, J. J.; Arnal, M. L.; Müller, A. J.; Rodríguez, O.; Morales, G. *Polym. Degrad. Stab.* **2013**, *98*, 490.
55. Liu, X.; Yu, L.; Xie, F.; Li, M.; Chen, L.; Li, X. *Starch* **2010**, *62*, 139.
56. Klein, J. M.; Ramos, G. R.; Grisa, A. M. C.; Brandalise, R. N.; Zeni, M. *Prog. Rubber Plast. Recycling Technol.* **2013**, *29*, 39.
57. Sun, Y.; Fischer, S.; Jiang, Z.; Tang, T.; Funari, S. S.; Gehrke, R.; Men, Y. *Macromol. Symp.* **2012**, *312*, 51.
58. Yu, L.; Liu, H. S.; Xie, F. W.; Chen, L.; Li, X. X. *Polym. Eng. Sci.* **2008**, *48*, 634.
59. Belfiore, L. A.; Pires, A. T. N.; Wang, Y.; Graham, H.; Ueda, E. *Macromolecules* **1992**, *25*, 1411.
60. Pablos, J. L.; Abrusci, C.; Marín, I.; López-Marín, J.; Catalina, F.; Espí, E.; Corrales, T. *Polym. Degrad. Stab.* **2010**, *95*, 2057.
61. Abrusci, C.; Pablos, J. L.; Marín, I.; Espí, E.; Corrales, T.; Catalina, F. *Int. Biodeter. Biodegrad.* **2013**, *83*, 25.
62. Jakubowicz, I.; Enebro, J. *Polym. Degrad. Stab.* **2012**, *97*, 316.
63. Konduri, M. K. R.; Koteswarareddy, G.; Rohini Kumar, D. B.; Venkata Reddy, B.; Lakshmi Narasu, M. *J. Appl. Polym. Sci.* **2011**, *120*, 3536.
64. González-Ortiz, L. J.; Arellano, M.; Jasso, C. F.; Mendizábal, E.; Sánchez-Peña, M. *J. Polym. Degrad. Stab.* **2005**, *90*, 154.
65. Roy, P. K.; Surekha, P.; Rajagopal, C.; Chatterjee, S. N.; Choudhary, V. *Polym. Degrad. Stab.* **2005**, *90*, 577.
66. Roy, P. K.; Surekha, P.; Rajagopal, C.; Raman, R.; Choudhary, V. *J. Appl. Polym. Sci.* **2006**, *99*, 236.
67. Burman, L.; Albertsson, A.-C. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 4537.
68. Ulutan, S.; Gilbert, M. *J. Mater. Sci.* **2000**, *35*, 2115.
69. Rosa, D. S.; Grillo, D.; Bardi, M. A. G.; Calil, M. R.; Guedes, C. G. F.; Ramires, E. C.; Frollini, E. *Polym. Test.* **2009**, *28*, 836.
70. Abrusci, C.; Pablos, J. L.; Corrales, T.; López-Marín, J.; Marín, I.; Catalina, F. *Int. Biodeter. Biodegrad.* **2011**, *65*, 451.
71. Muthukumar, T.; Aravinthan, A.; Mukesh, D. *Polym. Degrad. Stab.* **2010**, *95*, 1988.
72. Focke, W. W.; Mashele, R. P.; Nhlapo, N. S. *J. Vinyl Addit. Technol.* **2011**, *17*, 21.
73. Roy, P. K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *Polym. Degrad. Stab.* **2006**, *91*, 1980.
74. Roy, P. K.; Titus, S.; Surekha, P.; Tulsí, E.; Deshmukh, C.; Rajagopal, C. *Polym. Degrad. Stab.* **2008**, *93*, 1917.
75. Morlat-Therias, S.; Mailhot, B.; Gonzalez, D.; Gardette, J.-L. *Chem. Mater.* **2005**, *17*, 1072.
76. Morlat, S.; Mailhot, B.; Gonzalez, D.; Gardette, J.-L. *Chem. Mater.* **2004**, *16*, 377.
77. Mailhot, B.; Morlat, S.; Gardette, J.-L.; Boucard, S.; Duchet, J.; Gérard, J.-F. *Polym. Degrad. Stab.* **2003**, *82*, 163.
78. Qin, H.; Zhao, C.; Zhang, S.; Chen, G.; Yang, M. *Polym. Degrad. Stab.* **2003**, *81*, 497.
79. Qin, H.; Zhang, Z.; Feng, M.; Gong, F.; Zhang, S.; Yang, M. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 3006.
80. Kumanayaka, T. O.; Parthasarathy, R.; Jollands, M. *Polym. Degrad. Stab.* **2010**, *95*, 672.
81. Reddy, M. M.; Deighton, M.; Bhattacharya, S.; Parthasarathy, R. *J. Appl. Polym. Sci.* **2009**, *113*, 2826.
82. Dintcheva, N. T.; Al-Malaika, S.; La Mantia, F. P. *Polym. Degrad. Stab.* **2009**, *94*, 1571.
83. Corti, A.; Muniyasamy, S.; Vitali, M.; Imam, S. H.; Chiellini, E. *Polym. Degrad. Stab.* **2010**, *95*, 1106.
84. Yu, L.; Liu, X.; Petinakis, E.; Dean, K.; Bateman, S. *Advances in Natural Polymers*; Sabu Thomas, Aji. P. Mathew, Visakh. P. M., Eds.; Springer: New York, **2013**, *4*, 121.
85. Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *31*, 576.
86. Pang, M. M.; Pun, M. Y.; Ishak, Z. A. M. *J. Appl. Polym. Sci.* **2013**, *129*, 3237.
87. Elanmugilan, M.; Sreekumar, P. A.; Singha, N. K.; Al-Harathi, M. A.; De, S. K. *J. Appl. Polym. Sci.* **2013**, *129*, 449.

88. Chen, P.; Yu, L.; Simon, G. P.; Liu, X.; Dean, K.; Chen, L. *Carbohydr. Polym.* **2011**, *83*, 1975.
89. Chen, P.; Li, Y. Z.; Wu, X. H.; Liu, X. X. *Adv. Mater. Res.* **2012**, *391*, 719.
90. Liu, P.; Xie, F.; Li, M.; Liu, X.; Yu, L.; Halley, P. J.; Chen, L. *Carbohydr. Polym.* **2011**, *85*, 180.
91. Liu, X.; Yu, L.; Liu, H.; Chen, L.; Li, L. *Cereal Chem.* **2009**, *86*, 383.
92. Liu, X.; Ma, H.; Yu, L.; Chen, L.; Tong, Z.; Chen, P. *J. Therm. Anal. Calorim.* **2013**, *115*, 659.
93. Li, M.; Liu, P.; Zou, W.; Yu, L.; Xie, F.; Pu, H.; Liu, H.; Chen, L. *J. Food Eng.* **2011**, *106*, 95.
94. Xie, F. W.; Xue, T.; Yu, L.; Chen, L.; Li, X. X.; Zhang, X. M. *Macromol. Symp.* **2007**, *249*, 529.
95. Xie, F. W.; Yu, L.; Su, B.; Liu, P.; Wang, J.; Liu, H. S.; Chen, L. *J. Cereal Sci.* **2009**, *49*, 371.
96. Qiao, D.; Zou, W.; Liu, X.; Yu, L.; Chen, L.; Liu, H.; Zhang, N. *Starch* **2012**, *64*, 821.
97. Zou, W.; Yu, L.; Liu, X.; Chen, L.; Zhang, X.; Qiao, D.; Zhang, R. *Carbohydr. Polym.* **2012**, *87*, 1583.
98. Zhang, N.; Liu, H.; Yu, L.; Liu, X.; Zhang, L.; Chen, L.; Shanks, R. *Carbohydr. Polym.* **2012**.
99. Zhang, L.; Wang, Y.; Liu, H.; Yu, L.; Liu, X.; Chen, L.; Zhang, N. *Carbohydr. Polym.* **2013**, *98*, 73.
100. Zou, W.; Liu, X.; Yu, L.; Qiao, D.; Chen, L.; Liu, H.; Zhang, N. *J. Polym. Environ.* **2013**, *21*, 359.
101. Abd El-Rehim, H. A.; Hegazy, E.-S. A.; Ali, A. M.; Rabie, A. M. *J. Photochem. Photobiol. A* **2004**, *163*, 547.
102. Li, G.; Sarazin, P.; Orts, W. J.; Imam, S. H.; Favis, B. D. *Macromol. Chem. Phys.* **2011**, *212*, 1147.
103. Zuchowska, D.; Steller, R.; Meissner, W. *Polym. Degrad. Stab.* **1998**, *60*, 471.
104. Inceoglu, F.; Menciloglu, Y. Z. *J. Appl. Polym. Sci.* **2013**, *129*, 1907.
105. Pushpadass, H. A.; Weber, R. W.; Dumais, J. J.; Hanna, M. A. *Bioresour. Technol.* **2010**, *101*, 7258.
106. Schlemmer, D.; Sales, M. J. A.; Resck, I. S. *Carbohydr. Polym.* **2009**, *75*, 58.
107. Raquez, J. M.; Bourgeois, A.; Jacobs, H.; Degee, P.; Alexandre, M.; Dubois, P. *J. Appl. Polym. Sci.* **2011**, *122*, 489.
108. Kang, B. G.; Yoon, S. H.; Lee, S. H.; Yie, J. E.; Yoon, B. S.; Suh, M. H. *J. Appl. Polym. Sci.* **1996**, *60*, 1977.
109. Torres, A. V.; Zamudio-Flores, P. B.; Salgado-Delgado, R.; Bello-Perez, L. A. *J. Appl. Polym. Sci.* **2008**, *110*, 3464.
110. Garg, S.; Jana, A. K. *J. Appl. Polym. Sci.* **2011**, *122*, 2197.
111. Thiebaud, S.; Aburto, J.; Alric, I.; Borredon, E.; Bikiaris, D.; Prinos, J.; Panayiotou, C. *J. Appl. Polym. Sci.* **1997**, *65*, 705.
112. Dubey, K. A.; Chaudhari, C. V.; Raje, N.; Panickar, L.; Bhardwaj, Y. K.; Sabharwal, S. *J. Appl. Polym. Sci.* **2012**, *124*, 3501.
113. Ferreira, F. G. D.; Lima, M.; de Almeida, Y. M. B.; Vinhas, G. M. *J. Polym. Environ.* **2010**, *18*, 196.
114. Vasile, C.; Darie, R. N.; Cheaburu-Yilmaz, C. N.; Pricope, G.-M.; Bračić, M.; Pamfil, D.; Hitruc, G. E.; Duraccio, D. *Compos. B* **2013**, *55*, 314.
115. Martinez-Camacho, A. P.; Cortez-Rocha, M. O.; Graciano-Verdugo, A. Z.; Rodriguez-Felix, F.; Castillo-Ortega, M. M.; Burgos-Hernandez, A.; Ezquerro-Brauer, J. M.; Plascencia-Jatomea, M. *Carbohydr. Polym.* **2013**, *91*, 666.
116. Kurek, M.; Brachais, C. H.; Nguimjeu, C. M.; Bonnotte, A.; Voilley, A.; Galic, K.; Couvercelle, J. P.; Debeaufort, F. *Polym. Degrad. Stab.* **2012**, *97*, 1232.
117. Amri, F.; Husseinsyah, S.; Hussin, K. *Compos. A* **2013**, *46*, 89.
118. Sunilkumar, M.; Francis, T.; Thachil, E. T.; Sujith, A. *Chem. Eng. J.* **2012**, *204*, 114.
119. Kaur, I.; Bhalla, T. C.; Deepika, N.; Gautam, N. *J. Appl. Polym. Sci.* **2009**, *111*, 2460.
120. Tajeddin, B.; Rahman, R. A.; Abdulah, L. C. *Int. J. Biol. Macromol.* **2010**, *47*, 292.
121. Nakatani, H.; Iwakura, K.; Miyazaki, K.; Okazaki, N.; Terano, M. *J. Appl. Polym. Sci.* **2011**, *119*, 1732.
122. Lundin, T.; Cramer, S. M.; Falk, R. H.; Felton, C. *J. Mater. Civil Eng.* **2004**, *16*, 547.
123. Oldak, D.; Kaczmarek, H.; Buffeteau, T.; Sourisseau, C. *J. Mater. Sci.* **2005**, *40*, 4189.
124. George, J.; Bhagawan, S. S.; Thomas, S. *Compos. Sci. Technol.* **1998**, *58*, 1471.
125. Kumar, A. P.; Singh, R. P.; Sarwade, B. D. *Mater. Chem. Phys.* **2005**, *92*, 458.
126. Miyazaki, K.; Shibata, K.; Nakatani, H. *J. Appl. Polym. Sci.* **2013**, *127*, 854.
127. Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S.; Fontan, E. *J. Photochem. Photobiol. A* **2002**, *147*, 213.
128. Ojeda, T.; Freitas, A.; Birck, K.; Dalmolin, E.; Jacques, R.; Bento, F.; Camargo, F. *Polym. Degrad. Stab.* **2011**, *96*, 703.
129. Lin, Y. *J. Appl. Polym. Sci.* **1997**, *63*, 811.
130. Ojeda, T. F. M.; Dalmolin, E.; Forte, M. M. C.; Jacques, R. J. S.; Bento, F. M.; Camargo, F. A. O. *Polym. Degrad. Stab.* **2009**, *94*, 965.
131. Yang, R.; Christensen, P. A.; Egerton, T. A.; White, J. R.; Maltby, A. *J. Appl. Polym. Sci.* **2011**, *119*, 1330.
132. Jeyakumar, D.; Suresh, G.; Mukesh, D. *J. Appl. Polym. Sci.* **2012**, *125*, 2790.