Polyolefin Fibres

Structure, Properties and Industrial Applications

Second Edition

Edited by Samuel C. O. Ugbolue

Polyolefin Fibres

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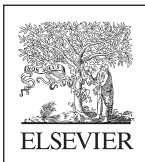
Second Edition

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Contents

Part II   Improving the functionality of polyolefins   187

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Preface

Since publishing the First Edition of polyolefin fibres: industrial and medical applications tremendous advances have been made in polymer science and engineering particularly in the important fields of nanocomposites and biomaterials. The import of polyolefins remains very strong and concerted demands have led to the publishing of the second edition of the book titled, Polyolefin fibres: Structure, Properties and Industrial Applications. Polyethylene and polypropylene (PP) are very important polyolefin polymers and the fastest growing polymer family. Polyolefins cost less to produce and process than many other plastics and materials they replace. Indeed, PP is a versatile and widely used synthetic polymer for hygienic applications like food packaging, surgical masks, diapers, hygiene bands, filters, automotive parts, and medical devices. Polyolefins are also important for fibres and films; PP fibres are used widely in upholstery fabrics, geotextiles, and carpet backing. Evidently, because of the low cost, high strength, high toughness, and resistance to chemicals, PP fibres find a broad spectrum of use in the industrial, home furnishing sectors, and medical applications. Thus our knowledge in engineering nanocomposite polyolefin materials has proved invaluable in improving the range of commercially available products. However, PP fibres do not enjoy comparable popularity in the apparel sector of the textile industry; one of the main reasons being lack of dyeability.

Specifically, this Second Edition is made up of three parts, namely: Part I: Structure and properties of polyolefin fibres with special emphasis on the types of polyolefin fibres, their structure and chemical properties, detailed discussion on the structural mechanics of polyolefin fibrous materials and nanocomposites, polyolefins and the environment, the use of polyolefins in industrial and medical applications, and advances in polyolefin-based fibres for hygienic and medical applications.

Part II: Improving the functionality of polyolefins places emphasis primarily on the production methods for polyolefin fibres, enhancing the hygiene/antimicrobial properties of polyolefins, improving their use in nonwovens, testing and quality control of polyolefins, the current status of polyolefin nanocomposite fibres and films and efforts geared towards improving the coloration/dyeability of polyolefin fibres.

Part III: Enhanced applications and uses of polyolefin fibres focus on various topics dealing with improving the wear resistance of polyolefins; improving thermal and flame resistance properties of polyolefins; discussions about the various polyolefin automotive components, the use of polyolefins in geotextiles and engineering

applications; the increasing use of polyolefins in biomedical applications and also the use of polyolefins in hygienic applications.

I am most grateful to all the contributors for their time, determination, and enthusiasm in insuring that the deadline of the editorial team was met. I am indebted to all the members of my family for their support, interest, and encouragement in the realization of this book project. Many of my graduate students and visiting scientists from various universities across the globe have made contributions through our shared research projects over the years and their efforts are duly acknowledged.

I believe this book provides excellent information not only for researchers, academics, and professionals in the biomaterials, nonwoven, and medical areas but also for technologists, engineers, product designers, marketers, and mangers in the polymer, textile, and allied industries.

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Part I

Structure and properties of polyolefin fibres

Polyolefins and the environment

4

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4.1   Introduction

4.1.1   Polyolefins

Polyolefins (PO) are the leading and largest volume industrial polymer in the world and they are used for the production of a wide range of commercial products that are used in nearly every aspect of our daily lives, such as household bottles, pipes, automobile parts, packaging films, etc. [1]. PO derive their physical properties from the arrangement or the entanglement of the atoms in the chain molecules. Branching caused by radical transfer influences the physical properties as well as the molecular distribution [2]. They are based on low-cost petrochemicals or natural gas and the required monomers are produced by cracking or refining of crude oil and therefore, resource depletion may become a determining factor in the future production of PO [3]. It is, therefore, highly desirable that PO material does not have any negative effect on the environment during its transformation into articles or components or during service [4]. It is important to avoid any negative effects at the end of the life cycle of PO (see Fig. 4.1).

PO are saturated hydrocarbon polymers, based on ethylene; high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), propylene and higher α-olefins or combinations of these monomers. PO also take great advantage of their chemical nature, being composed by carbon and hydrogen only, with respect to other plastics, such as poly(vinyl chloride) (PVC), polyamides, and polyurethanes [5]. PO, intended as polymers and copolymers of ethylene and propylene, represent more than 40% of plastics produced every year, with a clear tendency to increase such percentage. As the use of the material widens, so does the amount of waste disposed off into the environment [5]. Therefore PO play a major role in environmental issue and every progress achieved for them is a substantial progress for the whole issue [6]. Chemical and biological inertness of polyolefins were seen, originally as advantages. The high stability of these compounds and resistance to degradation has led to their accumulation in the environment, considerably increasing visible pollution and contributing to the clogging of drains during heavy rains, among other problems [7−10]. Environmental appearance is becoming an important factor that impacts on the market position of polyolefins, thus the appearance depends on the raw materials and
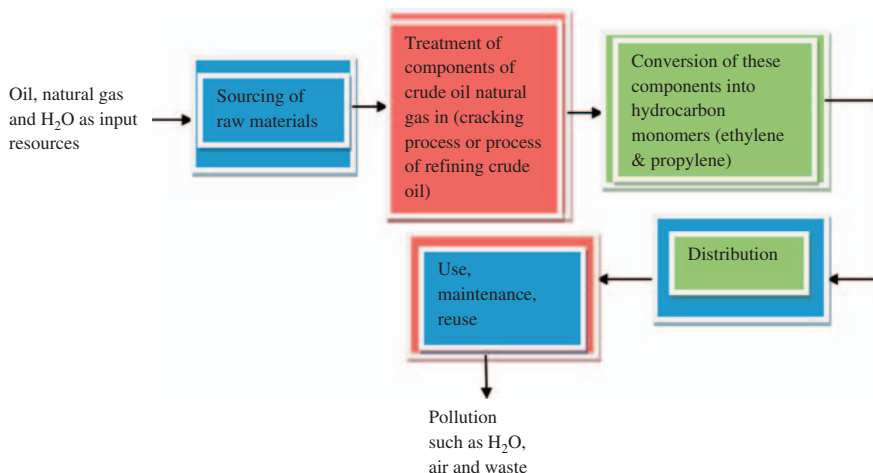
Figure 4.1 Polyolefins product life cycle.

the processes employed for the manufacture of these materials. Furthermore, product recyclability or biodegradability and the use of renewable resources need to be considered.

4.1.1.1 Polyethylene

Polyethylene (PE), a member of the important family of polyolefin resin, is the most widely used plastic in the world. They are prepared by the catalytic polymerization of ethylene [11]. It is a thermoplastic polymer consisting of long chains, produced by combination of the monomer molecules, i.e., ethylene. Depending on the mode of polymerization, three basic types of PE are frequently used: linear HDPE, branched LDPE, and LLDPE [12]. PEs are crystalline thermoplastics that possess toughness, excellent chemical resistance and excellent electrical insulating properties, near-zero moisture absorption, low coefficient of friction and ease of processing. Their heat deflection temperatures are reasonable but not high.

HDPE possesses greater stiffness, rigidity, improved heat resistance, and increased resistance to permeability than LDPE and LLDPE. HDPE has a low degree of branching and thus greater intermolecular forces and tensile strength. It can be produced by chromium/silica catalysts, Ziegler-Natta catalysts or metallocene catalysts [13]. HDPE is produced in molecular weights (MWs), ranging from 10,000 to several million. It has a linear polymeric chain (see Fig. 4.2), combined with a high density and melting point [14]. HDPE is used in the production of milk jugs, detergent bottles, margarine tubs, garbage containers, toys, and water pipes and in packaging.

Low-density PE is manufactured under high temperature and pressure using peroxide initiators. On the other hand, LLDPE is manufactured under low pressure. LLDPE is prepared by introducing short branching via copolymerization with
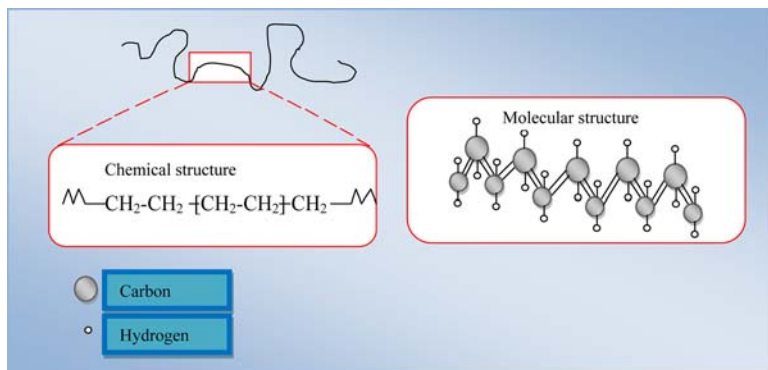
Figure 4.2 High-density polyethylene.
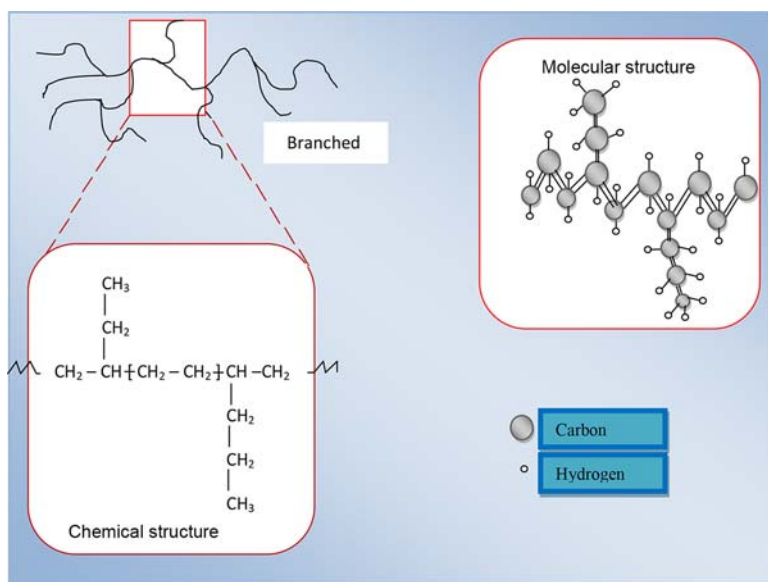
Figure 4.3 Low-density polyethylene.

a small amount of long-chain olefin. It is linear (see Fig. 4.3), but have a significant number of branches introduced by using comonomers, such as butene-1 or octene-1. Usually the comonomer content is between 8% and 10% at a density of 920 g cm^{-3}. The linearity provides strength, while the branching provides toughness. The modulus and ultimate tensile properties of LLDPE are significantly improved over the branched LDPE [14]. The branching in LLDPE and LDPE decreases the crystallinity and lowers the density [15]. LDPE or LLDPE form is preferred for film packaging and for electrical insulation.

4.1.1.2   Polypropylene

Polypropylene (PP) is a synthetic resin produced via the polymerization of propylene. PP films are widely used in packaging, textile, stationaries, and in a variety of other applications due to their great potentials in such areas as barrier properties, brilliance, dimensional stability, and processability. In many aspects, PP is similar to PE, especially in respect to their electrical properties and dissolution behavior. The properties of PP depend on the MW and molecular weight distribution (MWD), crystallinity, type and proportion of comonomer (if used). The mechanical properties of PP are strongly dependent on its crystallinity. Increasing crystallinity enhances stiffness, yield stress, and flexural strength; however, toughness and impact strength decrease [13]. The PP manufacturing process consists of a raw material, refining process, polymerization process, after treatment process, and granulation process. Propylene can also be polymerized with ethylene to produce an elastic ethylene−propylene copolymer. A large proportion of PP production is melt-spun into fibres. PP fibre is a major factor in home furnishings, such as upholstery and indoor−outdoor carpets [16]. The propene molecule is asymmetrical (see Fig. 4.4).

When polymerized, three basic chain structures can be formed and they are dependent on the position of the methyl groups: two are stereo-regular (isotactic and syndiotactic) and the third does not have a regular structure and it is termed atactic, as shown in Fig. 4.5 [17].

4.1.2   Polyolefin degradation

The negative change of properties (tensile strength, color, etc.) of a polymer or a polymer-based product under the influence of one or more environmental factors is known as polymer degradation. Naturally the degradation of plastics is a very slow process and it is a function of environmental factors such as temperature, humidity of air and moisture in the polymer, pH, and solar energy; polymer properties and biochemical factors. Degradation gives rise to changes in material properties such as optical, mechanical, or electrical characteristics which are evidenced as crazing, cracking, erosion, discoloration, and phase separation. The most problematic plastics are polyolefins as they are resistant to microbial attack (fungi and bacteria, etc.), due to the absence of any active functional groups [18]. This means that the surface of polyolefin material or articles made from polyolefins are hydrophobic, thus inhibit the growth of microflora on them [19]. Depending on the environmental factor, types of polyolefin degradation have been classified as photo-oxidative degradation, thermal degradation, ozone-induced degradation, mechanochemical degradation, catalytic degradation, and biodegradation [20].

$$H{\diagdown}{\diagup}CH_3$$
$$C = C$$
$$H{\diagup}{\diagdown}H$$
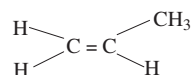
Figure 4.4 Propene molecule.
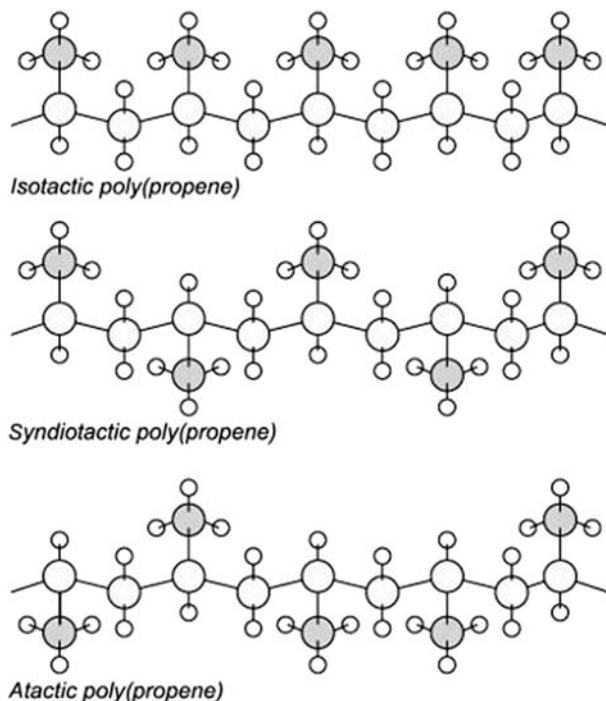
Figure 4.5 Molecular structures of polypropylene [17].

4.1.2.1 Thermal degradation

During the process of polymeric materials degradation and oxygen diffusion prevalently occur in the amorphous regions, linking degradability to the thermal history of the material [21]. A process whereby the action of heat or elevated temperature on a material, product, or assembly causes a loss of physical, mechanical, or electrical properties is known as thermal degradation. The rate of thermal degradation directly depends on the temperature, with high degradation values achievable at high temperatures [22]. At high temperature the components of the long-chain backbone of the polymer can begin to separate (molecular scission) and then react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical property changes that are relative to the initially specified properties. Generally, thermal degradation involves changes in the MW and the MWD of the polymer. Other property changes include: chalking, color changes, cracking, reduced ductility, and embrittlement [23].

The thermal degradation of polymers has become a progressively important method for the conversion of waste plastics into valuable chemicals and fuel. It is thus, important to have a good knowledge of the thermal degradation kinetics of polymers in order to improve their thermal behavior. Studies on pyrolysis kinetics

of polyolefin wastes have been carried out and most of these studies have been developed on the assumption that the reaction can be described by an *n*th order reaction model [24−30]. The assumption of an *n*th order reaction model would result in the Arrhenius parameters deviating from the real models [31]. A method of estimating the Arrhenius parameters as well as the reaction model of the pyrolysis of PP from isothermal kinetic results was described by some researchers [32,33]. They introduced a custom-made thermobalance that is able to record weight decrease with time under pure static condition. A best fit of experimental reduced-time-plot to theoretical models led to a conclusion that the pyrolysis reaction model and the Arrhenius parameters of PP vary with reaction temperature.

Mechanism of thermal degradation

In the last six decades, many investigations have been undertaken in order to clarify the degradation mechanism of polyolefins. The mechanism of polymer degradation is immensely complex, involving the simultaneous formation and decomposition of hydroperoxides. Degradation is promoted by oxygen, humidity and strain and results in such flaws as brittleness, cracking, and fading [34]. The thermal degradation of polymers consists of two distinct reactions, which occur simultaneously in the reactor. One is a random scission of links, causing a MW reduction of the raw polymer and the other is a chain-end scission of C−C bonds, generating volatile products [35].

The chain-end scission occurs at the gas−liquid interface in the working reactor. A continuous flow reactor for the thermal degradation of PE, PP, and polystyrene (PS) has been investigated and discussed as a typical example for the chain-end scission mechanism [36]. The nature and composition of the pyrolysis products provide important and profitable information about mechanism of thermal degradation [37]. The chain-end degradation begins from the end of the chain and successively releases the monomer units. The route of this type of degradation is also known as depolymerization reaction. The reaction involves successive release of monomer units from the chain ends. Such reactions are the opposite of the propagation step in addition polymerization and they occur through free radical mechanism [35]. The MW of the polymer in this type of degradation decreases slowly and large quantity of the monomer is liberated simultaneously. Generally, chain-end degradation takes place when the backbone bonds are weaker than the bonds of the side groups and only with polymer molecules, carrying active chain ends with a free radical, cation, anion, etc.

The degradation mechanism that is often attributed to the pyrolysis of a wide number of polymers is random scission. In the random scission mechanism the backbone of the polymer will break randomly; this can occur at any position of the backbone, as a result of the rapid decrease in the MW. As new free radicals with high reactivity are formed, monomers cannot be a product of this reaction; furthermore, intermolecular chain transfer and disproportion termination reactions can occur. For random degradation to occur the polymer chain does not necessarily require to carry any active site [38]. The mechanism of thermal degradation of PE has also been discussed as an example for random scission type reactions [39]. PE

also undergoes random degradation through migration of a hydrogen atom from one carbon to another thus generating two fragments [40]. The kinetics of decomposition of PP and PE are very significant, they serve as an example of a complicated radical chain mechanism and design of waste incineration and other recycling procedures. This is because PP and PE are respectively used in high amounts for packaging and they constitute the main components of plastic waste from domestic refuse.

Direct pyrolysis−mass spectrometry (Py−MS) is also applied in order to determine the primary structure of macromolecules and to further investigate selective thermal degradation mechanisms. This technique allows the thermal decomposition products of the polymer sample to be observed directly in the ion source of the mass spectrometer, so that the evolving products are ionized and continuously detected by repetitive mass scans almost simultaneously with their formation [41].

Methods of thermal degradation

Thermogravimetric analysis (TGA) method is one of the methods of thermal analysis techniques used in characterizing a wide variety of materials. TGA is used to measure the amount and rate of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used mainly to determine the thermal and oxidative stabilities of polymeric materials and their compositional properties [42]. The rate of degradation in TGA $(d\alpha/dt)$ is defined as the rate of change of the degree of conversion. The degree of degradation or conversion can be calculated in terms of mass as shown below [43]:

$$\alpha = \frac{w_o - w}{w_o - w_\infty} \tag{4.1}$$

where w_o, w, and w_∞ are the initial weight, the actual weight at each point of the curve, and the final weight measured at the end of the degradation process, respectively. In a TGA instrument, sample is submitted to constant heating rate from room temperature to 600°C or more, under the nitrogen flow. The reaction products can be analyzed by gas chromatography [35]. TGA was used to investigate the kinetic analysis of thermal degradation of polyolefin mixture between PP and LDPE under pyrolysis atmosphere at different compositions [30]. It was found that thermal degradation process of polyolefin mixture was a triple step process and an addition of PP reduced the degradation temperature.

Pyrolysis−gas chromatography−mass spectrometry (Py−GS/MS) method is an instrumental method of chemical analysis in which the sample is heated to decomposition in order to produce smaller molecules and more analytical useful fragments that are separated by gas chromatography and detected using mass spectrometry [44]. As Py−GC/MS decomposes instantly, aggregates of pyrolysates and other side products rarely occur. Thus chemically unchanged pyrolysates can be examined. Py−GC/MS can be used to examine the composition of polymer materials that are difficult to dissolve in a solvent, investigate resin deterioration, and analyze volatile additives [45]. This method of analysis involves putting the sample in the

inactivated sample holder of the microfurnace, dropping the sample holder into the reactor core, which is wrapped with high frequency coils, and filled with helium as the carrier gas using a switch, and then pyrolyzing it. The pyrolysis results are rather stable due to the comparatively low dispersion temperature changes resulting from the sample holder's small capacity [46].

Batch reactor method: Chemical reactions take place almost everywhere in the environment; nonetheless chemical reactors are defined as devices well designed to contain chemical reactions under controlled conditions toward specified products. These devices are designed to maximize the net present value of a given reaction. Reactor design also plays a fundamental role, as it has to overcome problems related to the low thermal conductivity and high viscosity of molten polymers [41]. The thermal degradation of waste plastic can take place in a glass reactor under atmospheric pressure with definite weight of sample that is loaded into bottom of the reactor for thermal degradation. The purging of the reactor with nitrogen gas at a flow rate of 10 mL/min at $120°C$ for 60 min is required to remove the physically adsorbed water from the plastic sample. After the nitrogen flow is stopped the reactor temperature is increased to the degradation temperature ($430°C$) at a heating rate of $3°C \ min^{-1}$ and the waste plastic bed temperature is taken as the temperature of the degradation. The gaseous products can be condensed (using a cold-water condenser) to liquid products and trapped in a measuring jar [35]. The compositions of the pyrolysis products of pure LDPE and PS and their mixtures were investigated over a temperature range from 300 to $500°C$. The pyrolysis experiments were carried out in a closed batch reactor pressurized autoclave under inert nitrogen atmosphere in order to study the effects of reaction temperature and residence time. The main objective was to convert the waste plastics to oil products for use as a hydrocarbon fuel oil or raw chemical feedstock. The effects of temperature and residence time were studied in order to ascertain the optimum conditions necessary for the production of oil and to investigate the effects of these parameters on the compositions of reaction products, with a special emphasis on the oil. LDPE was thermally degraded to oil at $425°C$ and the thermal cracking of LDPE in a batch reactor resulted in production of a broad range of hydrocarbon compounds where the yield of aromatics and aliphatics (olefins and paraffins) deeply depended on the pyrolysis temperature and residence time [47]. As waste, HDPE was pyrolyzed in a batch reactor at a temperature of between $400°C$ and $550°C$ at a heating rate of $20°C/min$ with the aim of optimizing the liquid product yield at a temperature range of between $400°C$ and $550°C$. The results of the pyrolysis experiments showed that, at a temperature of $450°C$ and below, the major product of the pyrolysis was oily liquid which became a viscous liquid or waxy solid at temperatures above $475°C$. The yield of the liquid fraction obtained increased with the residence time for waste HDPE. The liquid fractions obtained were analyzed for composition using FTIR and GC−MS [48]. The kinetics of virgin and waste PP and LDPE were recently studied by a modified Coats-Redfern method. Afterward the thermal cracking of these materials in a semibatch reactor under atmospheric pressure in nitrogen was investigated. Both virgin and waste plastics are decomposed at $420 − 460°C$. In order to help in the understanding of the processes for polyolefin degradation the

main reaction paths and the mechanisms for the thermal cracking of polyolefins in a semibatch reactor under atmospheric pressure, though thermal reactions occurring in a reactor are complex and this investigated by Ya et al. [49]. Owing to the short residence time and atmospheric pressure in the pyrolysis process, the high yield of the gaseous product and high yield of unsaturated hydrocarbons in both gaseous and liquid products can be obtained in a semibatch reactor. The results confirmed that chain scission reactions are predominant degradation mechanisms in the thermal cracking process. They concluded that the reaction of the intramolecular hydrogen and the β-scission of the end or middle chain radicals are responsible for the reduction in gaseous and liquid products. In the case of LDPE the reaction of intermolecular hydrogen and β-scission, followed by intramolecular hydrogen reaction may be contributed to form the 1-alkane and 1-alkene with same carbon number.

4.1.2.2   Photo-oxidation degradation

A natural weathering that has great effect produced by oxygen and light radiation is technically referred to as photo-oxidation [50]. Photo-oxidation is therefore the degradation of the surface of a polymer/material in the presence of oxygen or ozone radiation. It is one of the leading chemical degradation mechanisms in photoactive materials and occurs when organic materials are exposed to air and light. Materials that are subjected to oxygen are degraded faster in the presence of radiation than in the absence. The chemical changes that occur during degradation cause disruption of the π conjugation of the polymers and reduce photo absorbance in a process called photo bleaching [51]. The effect is facilitated by radiant energy such as artificial or UV light. The chemical changes reduce polymer's MW and as a consequence of this change, the materials become more brittle with a reduction in its tensile, impact, and elongation strength.

The most common photoreaction for all materials is photo-oxidation. Usually free radicals are generated as transient species in photolytic processes. Since oxygen reacts readily with most free radicals, peroxyl radicals will be formed. Photolysis, therefore, can give rise to autoxidative free radical chain reaction. For example, the primary reaction steps for photo-oxidation of polyolefins are as shown in Eqs. (4.2)−(4.15). The steps involve initiation, propagation, chain branching, and termination.

During the mechanism of initiation, the absorption of UV light that has sufficient energy to break the chemical bonds in the main polymer is responsible for polymer degradation. It involves a radical chain mechanism for the formation of initial radical. For the photo initiated oxidation of many commercial polymers this reaction is considered to be very important due to the presence of peroxide groups as chemically bound impurities, originating from processing at a very high temperature in the presence of oxygen. In general, initiation reaction occurs by random chain scission or chain-end initiation. This step is followed by depropagation step forming monomer [35], as depicted below.

$$RH \xrightarrow{O_2} R, H_2 \overset{\bullet}{O}, H_2O_2 \tag{4.2}$$

$$H_2O_2 \rightarrow 2 \overset{\bullet}{O}H \tag{4.3}$$

$$\overset{\bullet}{O}H + RH \rightarrow H_2O + R^{\bullet} \tag{4.4}$$

The propagating reactions of auto-oxidation cycle are common to all carbon backbone polymers. Propagation is a process in which a reactive intermediate is continuously regenerated during the course of chemical reactions. These reactions lead to generation of hydroperoxide species and are not directly led to backbone cleavage but they are the key intermediates to stimulate reactions. The key reaction in the propagation sequence is the formation of polymer peroxy radicals (ROO•). The next propagation step is the abstraction of hydrogen atom by the polymer peroxy radicals (ROO•) in order to generate new polymer alkyl radical (R•) and polymer hydroperoxide (ROOH) [52]. Hydroperoxide species generated in the propagating step lead to backbone degradation through the cleavage of hydroperoxide O−O bond followed by β-scission [35].

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \tag{4.5}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \tag{4.6}$$

$$ROOH + RH \rightarrow R = O + H_2O + R^{\bullet} \tag{4.7}$$

$$R = O \rightarrow R_2C^{\bullet} = O + C^{\bullet}H_2R_2 \tag{4.8}$$

$$HO_2^{\bullet} + RH \rightarrow HOOH + R^{\bullet} \tag{4.9}$$

Branching in polymer occurs by the replacement of a substituent, e.g., a hydrogen atom, on a monomer subunit, by another covalently bonded chain of that polymer. In chain branching, polymer oxy radicals (RO•) and hydroxyl radicals (HO•) are formed by photolysis. The oxidation of polyolefin is a radical chain type mechanism. At processing temperature, above ambient temperature polymer radicals R• are formed. The radicals react with oxygen to form peroxide radicals ROO• which abstract hydrogen from the polymer backbone in order to form a hydroperoxide (ROOH) and other radicals [53].

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \tag{4.10}$$

Termination of polymer radicals occurs by a bimolecular recombination. The termination of photodegradation process is achieved by "mopping up" the free radicals in order to create inert products. This occurs naturally by combining free radicals or assisted by using stabilizers in the plastic [35].

In here, crosslinking is a result of the reaction of different free radicals with each other. When the oxygen pressure is high, the termination reaction almost occurs by the reaction in Eq. (4.13). At low oxygen pressure, other termination reactions occur to some extent [52].

$$R^{\bullet} + R^{\bullet} \rightarrow RR \tag{4.11}$$

$$ROO^{\bullet} + R^{\bullet} \rightarrow ROOR \tag{4.12}$$

$$2ROO^{\bullet} + R^{\bullet} \rightarrow R = O + H_2O + O_2 \tag{4.13}$$

$$2HO_2^{\bullet} \rightarrow HOOH + O_2 \tag{4.14}$$

$$RO_2^{\bullet} + HO_2^{\bullet} \rightarrow ROOH + O_2 \tag{4.15}$$
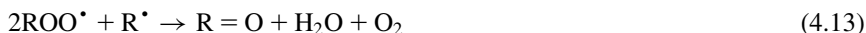
Hydroperoxide groups are formed in the propagation reaction as shown in Eq. (4.16). At wavelengths below 300 nm hydroperoxides are photolytically decomposed [54]. The most damaging UV wavelength for a specific plastic depends on the bonds present and maximum degradation therefore occurs at different wavelengths for different types of plastics, e.g., it is around 300 nm for PE and $\sim$370 nm for PP [35].

$$ROOH + h\nu \rightarrow RO^{\bullet} + {}^{\bullet}OH \tag{4.16}$$

PO are often used for outdoor applications. By virtue of the weather conditions the material age and therefore change their properties (cracking of the surface, color changes, embrittlement, decrease of the mechanical features, etc.). Weathering of polymers may be caused by various factors, for example mechanical stress, oxidation, heat-, or biodegradation. One of the most severe factors contributing to photo-oxidation degradation is ultraviolet (UV) radiation [54]. Most of the synthetic polymers are susceptible to degradation initiated by UV and visible light. Normally the near-UV radiations (wavelength 290−400 nm) in the sun determine the lifetime of polymeric materials in outdoor applications [55]. When PE and PP films are exposed to solar UV radiation, they readily lose their extensibility, mechanical strength, and mechanical integrity along with decrease in their average MW [56,57]. The deleterious effects of solar UV radiation in particular on biopolymers, and polymers are well known. The phenomenon is of special interest to the building industry, which relies on polymer building products that are routinely exposed to sunlight during use. Most of the common polymers used in such applications contain photo-stabilizers in order to control photo-damage and to ensure acceptable lifetimes under outdoor exposure conditions [58].

Photochemical oxidation degradation
Photochemical oxidation which is initiated by light is considered the reaction of a chemical change in a substance which causes it to lose electrons. Photochemical

oxidation processes generally involve the generation and use of relatively powerful nonselective transient oxidizing species, primarily the hydroxyl radical ($\cdot$ OH) and in some cases the singlet oxygen which can be generated by photochemical means. The following processes can be considered photochemical oxidation process.

- UV/oxidation processes
- Vacuum ultraviolet (VUV) photolysis
- The photo-fenton process
- Sensitized photochemical oxidation processes

Research on polymer degradation has proof that practically all polymers and polymer-based materials are oxidized by atmospheric oxygen. The reactions induced in polymers by UV irradiation depend on different factors such as internal and external impurities, physical state of the sample, chain structure and characteristics of the radiation source, etc. Hydrogen atom abstraction could occur to a certain extent when impurities in the polymer create macroradical sites. These will react with oxygen, thus producing peroxy radicals and subsequently hydroperoxides, which are thermally and photochemically unstable and will induce further breakdown. Again, polymer degradation results in chemically irreversible reactions or physical changes, the knowledge of the processes involved is important to prevent the premature failure of these materials [59].

Oxidation processes based on the use of ozone (O_3), hydrogen peroxide (H_2O_2), and UV irradiation are currently employed for wastewater treatment as chemical oxidation processes (O_3/H_2O_2, O_3, H_2O_2/Fe^{2+}) or photochemical oxidation processes (H_2O_2/UV, O_3/UV) [60]. Some researchers have studied photochemical oxidation processes of some polymers. Sörensen et al. [61] investigated the degradation pathway for the oxidation of ethylenediaminetetraacetate (EDTA) in the UV/H_2O_2-process. In absence of iron ions the mineralization of EDTA was dominated by the reaction of the HO−radicals generated by the photolysis of H_2O_2. In the presence of iron ions, photolytic decarboxylation processes inside the complex get an important role during degradation, and the organic degradation products ethylenediaminetriacetate, ethylenediaminediacetate, ethylenediaminemonoacetate were found. By combining product studies with balances of carbon and nitrogen the degradation pathway in the UV/H_2O_2-process could be elucidated. No toxic degradation products were identified. Therefore the process was well suited for the elimination of EDTA in water treatment.

Kinetics of photochemical oxidation of polyolefins

The kinetics of decomposition of PE and PP are very important because they provide insight into a complex radical chain mechanism, relevant for the design of waste incineration and other recycling procedures. The kinetics of photochemical oxidation of polyolefin has been investigated by some researchers [62−64]. Photochemical oxidation can be described by a very close mechanistic scheme differing only by their initiation step. In any quantitative approach to the kinetics of photochemical oxidation of a polymer the control of the initiation rate is of major

importance. Polymers, in which the absorbing species are not identified, the absorption of light, are essentially dependent on the sample studied [65].

A mathematical expression for the oxidation rate was obtained through the conventional concepts of chemical kinetics by making four simplifying assumptions: (1) unicity of reactive site, i.e., oxidation occurs exclusively on the most labile CH bond; (2) low conversion ratios of oxidation process, i.e., concentration of reactive sites remains virtually constant; (3) constancy of initiation rate in the case of oxidation induced by an extrinsic factor; (4) steady-state for radicals concentrations in all oxidation cases, but also for hydroperoxides concentration in the case of pure thermal oxidation [66]. Cunliffe and Davis [67], Furneaux et al. [68], and Audouin et al. [69] developed kinetics model with the aim of describing other oxidation regimes of lower oxygen concentration than oxygen excess. These authors included other possible termination reactions such as bimolecular combinations of alkyl−alkyl and alkyl−peroxy radicals, to the previous mechanistic scheme. Long kinetic chain and the existence of an interrelationship between termination rate constants were assumed. They obtained a hyperbolic expression for the oxidation rate by making two additional simplifying assumptions; this was added to the previous four assumptions. With this model the oxygen concentration dependence of the oxidation rate of thin polymer films was described and the critical value of the oxygen partial pressure above which oxygen is in excess was determined. There are other new developed kinetic models. The introduction of a term of photo-induced initiation in a numerical model has been performed by Kiil [70] in the case of the photo-oxidation of epoxy coatings, but the corresponding initiation rate has been described through an empirical law.

Mechanism of photodegradation of polyolefins

Photo-oxidation is the result of the absorption of light, which leads to the formation of radicals that induce oxidation of the material. For polyolefins (PE and PP, especially), photo-oxidation is the dominating mechanism because these polymers do not have an inherent absorption at wavelengths present in terrestrial sunlight ($>290-400$ nm), therefore, photolysis cannot play an important role. Although, irradiation of these polymers with terrestrial wavelengths results in accelerated degradation; especially for PP, this can be attributed to the impurities that are formed during storage and processing. The steps of photo-oxidation have been described in Section 4.2.2.

The photodegradation mechanism [71,72] of PP occurs when primary events following irradiation of PP with UV light in vacuum are bond-scission and crosslinking as shown in Fig. 4.6.

$$
\begin{array}{ccccc}
CH_3 & CH_3 & & CH_3 & CH_3 \\
| & | & & | & | \\
-CH_2\text{-}CH\text{-}CH_2\text{-}CH & \rightarrow & -CH_2\text{-}CH\bullet & + & \bullet CH_2\text{-}CH\text{-}
\end{array}
$$
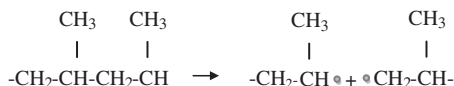
Figure 4.6 Chain scission of polypropylene.

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_3 \\
| & | & | & | \\
-CH_2\text{-}C^\bullet\text{-}CH_2\text{-}CH & \longrightarrow & -CH_2=CH & +^\bullet CH_2\text{-}CH\text{-}
\end{array}
$$
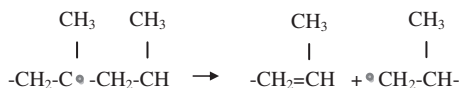
Figure 4.7 Dissociation of carbon−hydrogen bond.

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_3 \\
| & | & | & | \\
-CH_2\text{-}CH\text{-}CH_2\text{-}CH & \longrightarrow & -CH_2\text{-}C^\bullet + CH_2\text{-}CH\text{-}+H^\bullet
\end{array}
$$
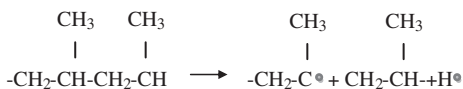
Figure 4.8 Chain scission of PP as a result of disproportionation reaction.

$$
\begin{array}{c}
CH_3 \quad CH_3 \\
| \qquad | \\
2\text{-}CH_2\text{-}C^*\text{-}CH_2\text{-}CH \longrightarrow -CH_2\text{-}C\text{-}CH_2\text{-}CH\text{-} \qquad \text{Recombination} \\
| \qquad | \qquad\qquad | \\
CH_3 \qquad CH_3 \qquad\quad -CH_2\text{-}C + CH_2\text{-}CH\text{-} \\
| \qquad | \\
CH_3 \qquad CH_3
\end{array}
$$

$$
\begin{array}{c}
CH_3 \quad CH_3 \\
| \qquad | \\
2\text{-}CH_2\text{-}C^*\text{-}CH_2\text{-}CH \longrightarrow -CH_2\text{-}C = CH_2\text{-}CH\text{-} \qquad \text{Disproportionation} \\
| \qquad | \qquad\qquad\quad + \\
CH_3 \qquad CH_3 \qquad -CH_2\text{-}C\text{-}CH_2\text{-}CH\text{-} \\
| \qquad | \\
CH_3 \qquad CH_3
\end{array}
$$
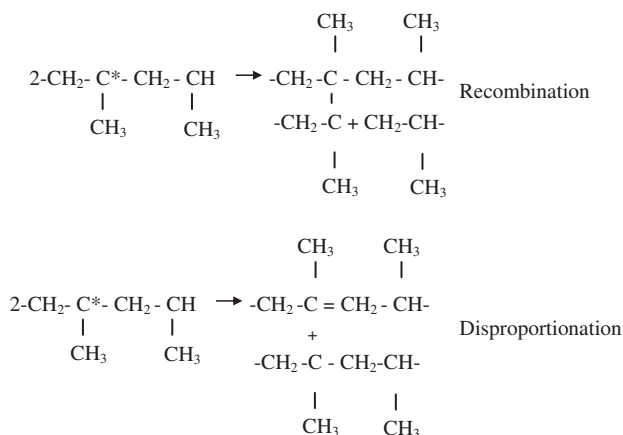
Figure 4.9 Crosslinking of polypropylene radicals [73].

The dissociation of carbon−hydrogen bonds at the tertiary carbon is another possible reaction (see Fig. 4.7).

This could lead to chain scission by a disproportionation reaction (see Fig. 4.8).

Crosslink is formed by the reaction of two propylene radicals (Fig. 4.9).

Pure PE is a relatively stable material in the absence of oxygen, under UV radiation. Chain scission and hydrogen abstraction occur after a long exposure to UV light of short wavelength (254 nm) in a nitrogen atmosphere or in vacuum. Crosslinking and evolution [72] of hydrogen can also be observed (see Fig. 4.10).

Methods of photodegradation

The most important factors of photodegradation are sunlight, atmospheric oxygen, air pollutants, moisture, and changes of temperature. Sunlight is of particular significance as it often triggers polymer degradation [74]. Since the weatherability of a material solely relies on its resistance to all weather factors, the radiation from the sun, especially the UV part is mainly responsible for limiting the lifetime of materials exposed to the environment. Therefore organizing the scope of weathering test

$$-CH_2- CH_2- CH_2 - CH_2 \longrightarrow - CH_2 - CH_2 \cdot + \cdot CH_2 - CH_2 -$$

$$\longrightarrow -CH_2 - CH \cdot - CH_2 - CH_2 - + H \cdot$$

$$-CH_2 - CH \cdot - CH_2 - CH_2 \qquad - CH_2 - CH + CH_2 - CH_2 -$$
$$+ \qquad \longrightarrow \qquad |$$
$$-CH_2 - CH \cdot - CH_2 - CH_2 - \qquad - CH_2 - CH - CH_2 - CH_2 -$$

$$H \cdot + \cdot H \longrightarrow H_2$$
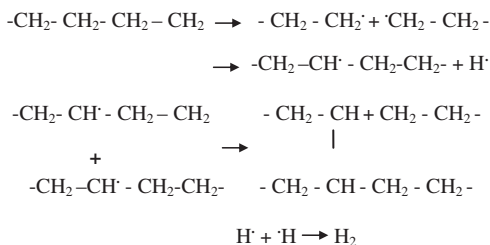
Figure 4.10 Chain scission and crosslinking of polypropylene.

methods into logical order will assist in visualizing the tools that are available for weathering tests.

Artificial weathering method Artificial weather testing process can be greatly accelerated through the use of specially designed weathering environmental chambers. Although this speeds up the time needed to get results, however, the conditions are not always representative of real-world conditions. Artificial light sources can also be used to approximately replicate outdoor conditions but with a greatly reduced test time under highly controlled conditions. The use of plastics in outdoor applications has greatly increased in the past six decades. With this increment, there is a great need of using a good method in for the prediction of the outdoor durability of potential outdoor product. One of the most common methods employed for this purpose is the artificial weathering devices. Most of the commercialized devices used are gas-discharged lamp, fluorescent lamp, and electric arc (carbon) in order to simulate/accelerate the effect of sunlight. These devices use a variety of light sources in combination with programmed spray cycle with the aim of simultaneously simulating and accelerating outdoor weathering conditions [75]. The accelerated weathering of fibre-filled PE composites has been studied in order to evaluate the relative durability of natural fibre-filled high-density polyethylene composites (NF-HDPE) intended for exterior roofing applications based on a single accelerated weathering protocol [76].

Natural weathering method Natural weathering test is conducted under natural environmental conditions and is done by placing of samples on inclined racks oriented towards the sun. The directions in which these racks are placed are very important. These racks are at an angle of 45°C in a Southerly direction of the Northern Hemisphere and 45°C in the Northerly direction of the Southern Hemisphere. The exposure to the full spectrum of solar radiation, from infrared to ultraviolet is established by this angle. Sites used for this type of testing should be areas with very high temperature. UV intensity and humidity are needed for maximum degradation. Ojeda et al. [10] studied the degradability of linear polyolefins under natural weathering in order to assess the abiotic degradability of HDPE, LLDPE, and PP extruded blown films with low or zero concentrations of antioxidant additives. They further studied the abiotic degradability of HDPE/LLDPE blend containing a prooxidant additive (oxo-biodegradable blend), during 1 year of

natural weathering period. Their study showed that the real durability of olefin polymers may be much shorter than centuries. In less than 1 year the mechanical properties of all samples decreased virtually to zero, as a consequence of severe oxidative degradation, that resulted in substantial reduction in molar mass accompanied by a significant increase in content of the carbonyl groups.

4.1.2.3 Ozone-induced degradation

Ozone is an immensely reactive form of oxygen occurring around electrical discharges. It is also present in the atmosphere, but in small quantities. The presence of ozone, even in very small concentrations, in the atmosphere significantly increases the rate of polymeric materials aging [77]. Atmospheric ozone usually causes the degradation of polymers under conditions that may be considered as normal; when other oxidative aging processes are very slow and the polymer retains its properties for a rather longer time [78−80]. Exposure of polyolefins to ozone gas causes change in the mechanical properties of LLDPE; oriented PP. Degradation can also be induced deliberately in order to assist in structural determination. This structural determination includes the specification of molecular geometry; when feasible and necessary, the electronic structure of the target molecule or other solids can be determined.

Mechanism of ozone-induced degradation

The oxidation mechanism of polyolefin and other polymers in the presence of ozone is well reported [81−83]. In the presence of oxygen, almost all polymers degrade faster than in an inert environment. The presumed ozone oxidation mechanism is due to the radical-based oxidation process where atomic oxygen is initially formed by degradation of ozone [82]. An atomic oxygen arising from ozone decomposition attacks polymers, thereby producing carbon and hydroxyl radicals. The carbon radicle reacts almost immediately with the oxygen molecule, giving a peroxyl radicle. The carbonyl oxide is considered to be the key intermediate in the $C = C$ bond ozonolysis mechanism. The produced peroxyl radicle further interacts with the PE to produce carbonyl groups in the chain [81]. The concentration of the peroxy groups depended on the ozone concentration and the exposure time of the surface to ozone [84].

Methods of ozone-induced degradation

Ozone testing is a method used to determine a rubber or polymers resistance to ozone degradation. The resistance level is determined by the physical appearance and the severity of the cracks on the surface of the material sample. The polymers samples are placed in a special chamber that exposes them to ozone at a specified concentration, temperature and duration by doing a specification testing or standard. A sample that does not stand up to the effects of ozone exposure will crack at the surface and sometimes break in two. During this test a material sample will undergo accelerated time/exposure ozone tests. The results of these tests are used to predict the reaction of a material sample under dynamic or static surface tensile strain conditions in an atmosphere containing specified levels of ozone. The extent of

reaction of polyolefins with ozone depends on the extent of agitation of the slurry, the slurry temperature, solid consistency, and ozone concentration in the gas. Because these tests are accelerated and only simulate long-term outdoor ozone exposure, actual real-world exposure results may vary [85,86].

4.1.2.4 Mechanochemical degradation

Mechanochemical degradation of polymers is an aspect of polymer degradation that takes place under mechanical stress and by strong ultrasonic irradiations. The molecular chains breakdown as a result of a mechanical force or under shear; this process is often aided by oxidation which is known as mechanochemical degradation. This type of degradation is common in machining process, such as mastication, grinding, and ball milling [87]. Rubber mastication, which leads to chain breakage and development of plasticity under shear, is an example of mechanochemical degradation. Mastication of rubber in the atmosphere of nitrogen at ordinary temperature does not change the plasticity and MW appreciably, but with the presence of oxygen, degradation occurs immediately and rapidly. Under mechanical shear the rubber molecules break into radicals and react with oxygen in the atmosphere leading to permanent chain breakage. In nitrogen, however, the primary radicals formed under shear immediately recombine to give no effective chain breakage [88].

Mechanism of mechanochemical degradation
It is known that input of mechanical energy to polymers does not only produce mechanical effects, it does produce chemical effect too. This effect is called the mechanochemical effect. Polymeric materials show an exceptional range of mechanical responses, which depend on the chemical and physical structure of the polymer chains. The mechanical response of thermoplastic polymers is highly influenced by the molecular mass, chain entanglements, chain alignment, and degree of crystallinity. High intensity ultrasounds can induce mechanochemical degradation in polymeric materials. Polymer in such a case is subjected to very high vibrations, which are only mechanical forces. As ultrasonic waves pass through the solution, the localized shear gradient produces tear of molecules leading to chain scission and decrease in MW [35].

It has been reported that the superposition of ultrasonic waves in extrusion could greatly decrease the viscosity of polymer melts and improve production rate [89−91]. Ultrasonic oscillations can also greatly enhance the compatibility and mechanical properties of HDPE/PS blends due to the in situ formation of interchain copolymer of PS−HDPE. The effects of ultrasonic irradiation intensity and the depth of ultrasonic irradiation on the mechanochemical degradation of HDPE have been discussed [92]. The development of MWD of HDPE melt during ultrasonic degradation was also studied. The average MW of HDPE decreases with increasing of ultrasonic intensity. A further increase in trends of under-graded HDPE was observed with the increase of distance from ultrasonic probe tip, indicating that attenuation of ultrasonic intensity in HDPE melt is very quick. It was

found that the weight average MW and MWD of HDPE depend, strongly on the time of irradiation [92].

Methods of mechanochemical degradation

The method of ball milling is a widely used process in which mechanical force is used to achieve chemical processing and transformations. In the past eight decades, some work in understanding the response of polymeric materials to mechanical stress was published by Staudinger and Bondy [93], who observed a decrease in the MW of polymers in response to mastication. It was suggested that the MW reduction resulted from the homolytic carbon−carbon bond cleavage due to mechanical force. This suggestion was supported by electron spin resonance (ESR) experiments of polymers cleaved by ball milling [93]. Sohma [94] stated that polymer molecules in a liquid phase are scissioned by mechanical actions, such as either ultrasonic waves or high-speed stirring. Although the main chain scissions generate free radicals (mechano radicals) of polymers in the liquid phase, however, the lifetimes of these mechano radicals in a liquid phase are too short to be detected by the conventional ESR technique.

Polymers in an extruder are in a molten state and are under strong shearing forces, i.e., the mechanical forces that will break the molecule of polymers. The molten state is something between two extremes, i.e., a solid phase and an ordinary liquid of considerably less viscosity [94]. It has been found that mechanical degradation reduces the average MW of the polymer [95]. The mechanochemical degradation response of polymers to mechanical force is characterized [93] by a variety of measures, including tensile strength, failure strain, stress, fracture toughness (resistance to crack growth), and elastic modulus (initial slope of the stress−strain curve).

4.1.2.5   Biodegradation

Biodegradation can be defined as nature's way of recycling wastes, or breaking down organic matter into nutrients that can be used by other organisms, i.e., biodegradation is the disintegration of materials by fungi, algae, bacteria, and other biological means. Biodegradation is considered a type of degradation involving biological activity. Biodegradation is expected to be the major mechanism of loss for most chemicals released into the environment. This process refers to the degradation and assimilation of polymers by living microorganisms in order to produce degradation products [96]. Biodegradable materials degrade into biomass, carbon dioxide, and methane. In the case of synthetic polymers, microbial utilization of its carbon backbone as a carbon source is required [97]. It has been stated that research has focused on developing biodegradable polymers since most of the polymers are resistant to degradation [98]. The newly developed polymers are degraded and catabolized ultimately to carbon dioxide and water by bacterial and fungi under natural environment. During the degradation process, they should not generate any harmful substances.

Polymers degrade in microbial environments either by anaerobic or aerobic bio-degradation and sometimes, a combination of the two. Aerobic biodegradation is the degradation of polymer material by microorganisms in the presence of oxygen with the subsequent conversion of carbon into carbon dioxide, biomass, and by-products. On the other hand, anaerobic biodegradation is the degradation of polymer material by microorganisms in the absence of oxygen with the subsequent conversion of carbon into carbon dioxide, methane or other hydrocarbons, biomass and by-products [97]. The biodegradation that occurs in each environment is characterized by the total carbon conservation. The mass balance equation for aerobic biodegradation of polymers [97] is given in Eq. (4.17):

$$C_T = CO_2 + C_R + C_B \qquad (4.17)$$

where C_T is the total carbon content of the polymer material, C_R is any residue of the polymer that is left or any by-product that is formed during the degradation process, CO_2 is the measurable gaseous product, and C_B is the biomass produced by the microorganisms through reproduction and growth. For the anaerobic environment the total carbon equation can be written as shown in Eq. (4.18).

$$C_T = CO_2 + CH_4 + C_R + C_B \qquad (4.18)$$

In this process the gaseous product is divided between carbon dioxide and methane. Both anaerobic and aerobic degradation can occur simultaneously in some environments. The process of mineralization occurs during the conversion of biodegradable materials or biomass to gases (such as carbon dioxide, methane, and nitrogen compounds), water, salts, minerals, and residual. Mineralization is complete when all the biodegradable materials or biomass are consumed and all the carbon is converted to carbon dioxide [99].

The important bacteria in the biodegradation process include, interalia, Bacillus (capable of producing thick-walled endospores that are resistant to heat, radiation, and chemical disinfection), Pseudomonas, Klebsiella, Actinomycetes, Nocardia, Streptomyces, Thermoactinomycetes, Micromonospora, Mycobacterium, Rhodococcus, Flavobacterium, Comamonas, Escherichia, Azotobacter, and Alcaligenes (some of them can accumulate polymer up to 90% of their dry mass) [97,100,101]. Fungi that are active in the biodegradation process are Sporotrichum, Talaromyces, Phanerochaete, Ganoderma, Thermoascus, Thielavia, Paecilomyces, Thermomyces, Geotrichum, Cladosporium, Phlebia, Trametes, Candida, Penicillium, Chaetomium, and Aerobasidium [102,103].

Polyolefin polymers are hydrophobic with high MW and are therefore not easily degraded by abiotic or biotic factors. These molecules are unable to enter microbial cells to be digested by intracellular enzymes due to their massive size and they are inaccessible to the action of extracellular enzymes produced by microorganisms due to their excellent barrier properties. Exposure to UV and heat is known to promote degradation of most polymers, however, polyolefins degrade very slowly under environmental conditions [104]. Abiotic and biotic degradation of PEs using

plastic bags of HDPE and LLDPE formulated with prooxidant additives as test materials have been evaluated. These packaging materials were exposed to natural weathering and periodically analyzed with respect to changes in mechanical and structural properties. After a year of exposure, residue samples of the bags were incubated in substrates (compost of urban solid waste, perlite, and soil) at 58°C and at 50% humidity. The biodegradation of the materials was estimated by their mineralization to CO_2. The molar mass of the prooxidant-activated PE decreased and oxygen incorporation into the chains increased significantly during natural weathering. These samples showed a mineralization level of 12.4% after 3 months of incubation with compost. Higher extents of mineralization were obtained for saturated humidity than for natural humidity. The growth of fungi of the genera Aspergillus and Penicillium was observed on PE films containing prooxidant additives exposed to natural weathering for 1 year or longer. Conventional PE films exposed to natural weathering showed marginally little biodegradation [105].

Oxo-biodegradations

Oxo-biodegradable process involves the transition of metals (some of which are regulated) that theoretically foster oxidation and chain scission in plastics when exposed to heat, air, and/or light. Thus oxo-biodegradable polymers contain prooxidants and pro-degrading compounds [105] that are integrated into the polymer chain in order to accelerate thermo or photo-oxidation [105,106]. These prooxidants are metal ions or oxides, such as titanium oxide, that catalyze photo- or thermo-oxidation of the polymer [105−108]. During photodegradation (pro-oxidant photocatalytic oxidation), free radicals obtained from the reactions catalyzed by pro-oxidant causes polymer chain scission [106,107], speeding up microbial degradation [106]. UV light serves as a catalyst that speeds up the process of photocatalytic oxidation [108]. Literature has reported that polymers that degrade by peroxidation followed by bioassimilation of the oxidation products (oxo-biodegradable polymers) are in general more environmental acceptable ("green") than some biologically produced hydro-biodegradable polymers [109].

Microbial degradation

The use of bioremediation and biotransformation methods to harness the naturally occurring ability of microbial xenobiotic metabolism to degrade, transform, or accumulate environmental pollutants is known as microbial degradation. PO are characteristically inert and are resistant to microbial attack, leading to their accumulation in the environment. Several studies have investigated the biodegradability of polyolefins containing pro-oxidants in the presence of microbial consortium present in the environment and the selected microbial species in defined medium under controlled laboratory conditions [110−114]. Microbial populations that have the ability of degrading contaminants in the subsurface depend on a variety of physical, chemical, and biological factors that influence their metabolic activity, their growth, and their existence. The characteristics and the properties of the environments in which the microorganisms function have a serious impact on the microbial population, the

rate of microbial transformations, the pathways of products of biodegradation, and, of course, the persistence of contaminants.

The microbial degradation process of polymers is initiated by the secretion of enzymes which cause a chain cleavage of the polymer into monomers [115]. During microbial activity, the microorganisms release protein structures [21], called enzymes; these enzymes are responsible for metabolism or transformation/ breakdown of a substance into another (enzymatic dissimilation of the macromolecules from the chain ends). The microorganisms participating in the degrading process attack the surface and settle in a biofilm-like colony, which produces alterations as it comes into contact with the polymer [116]. Biofilms are embedded in the polymer at source, consisting basically of extracellular polysaccharides, proteins, and microorganisms [21,116]. In general, bacteria, fungi, alga, and protozoa may be identified in biofilms. The formation of biofilms is a prerequisite to substance corrosion and/or material deterioration. Some polymers are susceptible to direct biodegradation via enzymes and/or microorganisms, while others may allow degradation only after a hydrolytic stage or scission of the oxidant chain [117].

Generally, an increase in the MW results in a decline of polymer degradability by microorganisms. In contrast, monomers, dimers, and oligomers of a polymer's repeating units are much easily degraded and mineralized. High MWs result in a sharp decrease in solubility making them unfavorable for microbial attack because bacteria require the substrate to be assimilated through the cellular membrane and then further degraded by cellular enzymes [118]. During degradation, exoenzymes from microorganisms breakdown complex polymers yielding smaller molecules of short chains, e.g., oligomers, dimers, and monomers, that are small enough to pass the semipermeable outer bacterial membranes to be utilized as carbon and energy sources. The process is called depolymerization [118]. It is now widely accepted that abiotic oxidative degradation of high MW polyolefin into low MW compounds is necessary to facilitate action of microorganisms and/or enzymes [104].

Enzymatic biodegradation

Enzymes are biological macromolecules that speed up chemical reactions without themselves undergoing any permanent change. The molecules at the beginning of the process upon which enzymes may act are called substrate and the enzyme converts these into different molecules, known as product. Enzymes are very selective in their choice substrates, so that they bind to the specific substrates, thereby lowering the activation energy and thus inducing an increase in the reaction rates in an environment otherwise unfavorable for chemical reactions. Some enzymes do not need any additional component for their optimal activity and others require nonprotein molecules called cofactors, to be bound for activity. Inorganic cofactors include metal ions such as sodium, potassium, magnesium, or calcium and organic cofactors, also known as coenzymes [104].

Substrates of MW higher than the cut off limit of the various transport systems have to be depolymerized by enzymes outside the cell membrane before entrance and terminal mineralization can complete the degradation process. Enzymes are transported across the membrane but those remaining in the periplasm or anchored

to the cell wall are called ectoenzymes, while those excreted into the surrounding media are called extracellular enzymes [119]. Extracellular enzymes may be excreted intentionally by living cells, enter the media by lysis or cell damage, or can result from grazing activity by zooplankton and protozoan [120]. High MW polymers are not easily susceptible to enzymatic biodegradation as they are unable to enter microbial cells due to their large size. In order to accomplish scission, microorganisms secrete specific enzymes or generate free radicals, which act on polymer chains and break them down into oligomers, dimers, and/or monomers [104].

Mechanism of biodegradation

Common mechanisms of biodegradation that involve bioassimilation from the ''ends'' of substrate molecules do exist. The primary mechanism for the biodegradation of polymer with high MW is the oxidation or hydrolysis by enzyme in order to create functional groups that improve its hydrophilicity. Consequently the main chains of polymer are degraded, thereby resulting in a polymer of low MW and feeble mechanical properties, thus, making it more accessible for further microbial assimilation [121]. Since commercial polyolefins have relatively high molar mass values, there are very few ends of molecules accessible on or near the surfaces of materials made from these resins [19]. It has however been observed that the oxidation products of polyolefins are biodegradable [122−124]. Such products have molar mass values that are significantly reduced, and they incorporate polar, oxygen-containing groups such as acid, alcohol, and ketone [125]. This is the basis for the term oxo-biodegradable polyolefins [19]. The biodegradation of polyolefins always follows photodegradation and chemical degradation.

PE is one of the synthetic polymers that exhibit high hydrophobic level and high MW. Naturally, it is not biodegradable. Therefore their use in the production of packing materials and disposal pose serious environmental problems. In order to make PE biodegradable, modification of its crystalline level, MW and mechanical properties that are responsible for PE resistance towards degradation is required [126]. This can be achieved by improving PE hydrophilic level and/or reducing its polymer chain length by oxidation in order to be accessible for microbial degradation [127]. The degradation of PE can occur by different molecular mechanisms; chemical, thermal, photo, and biodegradation [119]. It is known that biodegradation of PE occurs by two mechanisms: hydro-biodegradation and oxo-biodegradation. These two mechanisms agree with the modifications due to the two additives, i.e., pro-oxidant and starch used in the synthesis of biodegradable PE. In case of the pro-oxidant additive, biodegradation occurs following photodegradation and chemical degradation. If the pro-oxidant is a metal combination, after transition, metal catalyzed thermal peroxidation, biodegradation of low MW oxidation products occurs sequentially. The most commonly used additives are stearate (St) complexes of transition metals such as zinc (ZnSt), copper (CuSt), silver (AgSt), cobalt (CoSt), nickel (NiSt), manganese (MnSt), chromium (CrSt), and vanadium (VSt), or alkaline earth metals such as magnesium (MgSt). Starch blended with PE has a continuous starch phase that makes the material hydrophilic and therefore, catalyzed by

amylase enzymes. Microorganisms can easily access, attack, and remove this part. Thus the hydrophilic PE as matrix continues to be hydro-biodegraded [128].

PP films and bioriented polypropylene are widely used in packaging and in a variety of other applications due to their great potential in terms of barrier properties, brilliance, dimensional stability, and processability. As the use of the material widens so does the amount of waste disposed off into the environment [5,129]. PP biodegradation is possible by microorganisms; this process takes a long time, i.e., over hundreds of years to fully decompose. The amorphous regions of PP are the most susceptible to degradation and the impurities in the polymeric material can act as a catalyst for photodecomposition. The energy absorbed by means of heat, light, mechanical strain, etc. causes the β-scission, and the peroxide and hydroperoxides radicals generated catalyze the process [130−132]. Owing to the presence of hydrogen linked to a tertiary carbon in the backbone chain, PP degrades preferentially by chain scission with an overall shift of the MWD curve towards lower values [133]. As the total weight of the polymer used for gel permeation chromatography (GPC) measurements is kept constant the area under the MWD curve is also kept constant. The fragments of chains formed during scission are shorter than the original chains and so during the (GPC) run they will be excluded from the higher MW side, thereby reducing the weight fraction [dwt/d(MW)] at this point. They will be retained for a long time in the GPC, while columns elute with other short chains, thereby increasing the original weight fraction at this particular MW [133].

Methods of biodegradation

The usage of certain enzymes and organisms to degrade polymers are classified as methods of biodegradation of polymers [98]. Appropriate selection of test procedure based on the nature of plastic and the climatic conditions of the study environment are the most important factors in the determination of biodegradation. Respirometry tests can be used for aerobic microbes. During respirometry tests, a solid waste sample is first place in a container with microorganisms and soil, and then the mixture is aerated. Over the course of several days, microorganisms digest the sample bit by bit and produce carbon dioxide and the resulting amount of CO_2 serves as an indicator of degradation. Biodegradability can also be measured by anaerobic microbes and the amount of methane or alloy that they are able to produce. A lot of test methods have been developed by the International Standard Organization (ISO) in order to assess the potential biodegradability of plastics [134] and by the American Society for Testing and Materials (ASTM) [135].

Biodegradation can also be characterized with loss of weight. During degradation the mass of the material may undergo changes, and these changes can be monitored by comparing the mass before and after the degradation period. The material should be dried to a constant mass before measuring the initial weight of the sample in order to avoid residual moisture in the samples. The drying temperature should not exceed the temperature at which the materials undergo irreversible changes (e.g., melting temperature). After degradation the sample should be washed thoroughly with distilled or deionized water in order to remove traces of soluble degradation products, such as, enzymes, salts, or other impurities and then dried under

vacuum conditions until constant weight is attained. The extent of degradation is commonly determined by calculating the percentage weight loss [136].

4.1.2.6   Catalytic degradation

Catalytic degradation of plastic waste offers considerable advantages when compared to pure thermal degradation, as the latter demands relatively high temperatures and its products require further processing for their quality to be upgraded [137]. The advantages of catalytic degradation are (1) the low cracking temperature due to low activation energy and a short cracking time is required, (2) the high cracking ability of plastics, (3) the low concentration of solid residue in the product, and (4) the narrow product distribution with peaks of light hydrocarbons in the boiling point range of motor fuel and a high selectivity to liquid products [138]. Thus the extreme effect of catalyzed decomposition of polymers has necessitated wave of research in the area of catalysis and polymer degradation. Catalytic degradation occurs at considerably low temperatures [139] and forms hydrocarbons in the range of motor engine fuel [140,141] and thereby eliminating the necessity of further processing. In such a recycling process, liquid fuel is the most valuable product.

Catalytic cracking applied to the breakdown of polyolefins has focused mainly on polymer transformation into gaseous and liquid products of interest. For example, research has shown that for PE, the mesoporous material Al-MCM-41 produces hydrocarbons within the gasoline fraction while ZSM-5 governs the cracking towards light compounds with a large production of gaseous and aromatic hydrocarbons [142]. When Al-MCM-41 is used as a catalyst, the cracking occurs by a mechanism of random scission as a result of its large pore size and medium acidity. The zeolite HZSM-5, on the other hand, results in an end-chain cracking pathway as a result of its small pore size and strong acidity [142]. It has been proven that the catalyst's particle size is very important in catalytic degradation; this was confirmed by analyzing nanocrystalline zeolite ZSM-5 samples. A high cracking activity due to their large external surface and low diffusional constraint was observed [142]. Furthermore, researchers have studied beta zeolites and found that the particles with the smallest crystal size (~ 100 nm) give the best performance due to the bigger surface area and higher production of liquid compounds [143,144]. The addition of a catalyst not only improves the quality of products obtained from pyrolysis of plastic wastes, lowers the temperature of decomposition, but also enable a given selectivity to a certain product to be achieved [35].

Mechanism of catalytic degradation

Demirbas [145] investigated the catalytic degradation of polyolefin using the TGA as a potential method for screening catalysts and have found that the presence of catalyst led to a decrease in the apparent activation energy. Different mechanisms (ionic and free radical) for plastic pyrolysis proposed by different scientists are as given below.

Electrophilic catalysts cause marked changes in the kinetics of degradation of polyolefins. There is a change in the gross mechanism, accompanied by a considerable increase in the rate and selectivity of the process [146]. The electrophilic

catalytic degradation of polyolefins that occurs by a cationic mechanism [147] is very interesting from the theoretical viewpoint as an example of the decomposition of polymer products by terminal group or random mechanisms. In the last three decades, studies on the catalytic degradation of polyolefins in the presence of MAlCl$_4$ complexes, a cationic process mechanism, have been carried out and interpreted on the basis of a possible single-electron oxidation of primary radicals formed by the action of heat on the polymer [146].

1. Random thermal decomposition, with preference occurring at the weakest bonds, e.g. (Fig. 4.11)
2. A redox reaction with the formation of the polymer carbocation; it is a mechanism which would seem plausible only if M$^+$ is relatively easily reduced (Fig. 4.12).
3. Depolymerization of the macroions with formation of monomer (Fig. 4.13):
4. Chain transfer to polymer with further depolymerization of the macroions starting from end groups (Fig. 4.14):
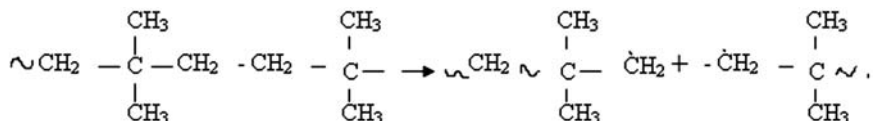
Figure 4.11 Random thermal decomposition at the weakest bond.
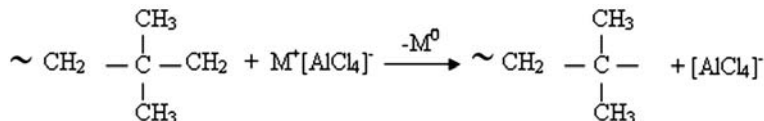
Figure 4.12 A redox reaction with the formation of the polymer carbocation.
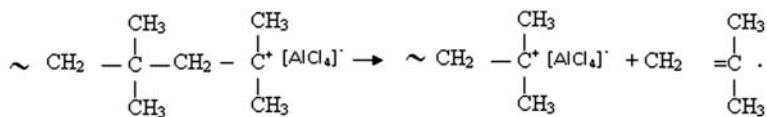
Figure 4.13 Depolymerization of the macroions with formation of monomer.
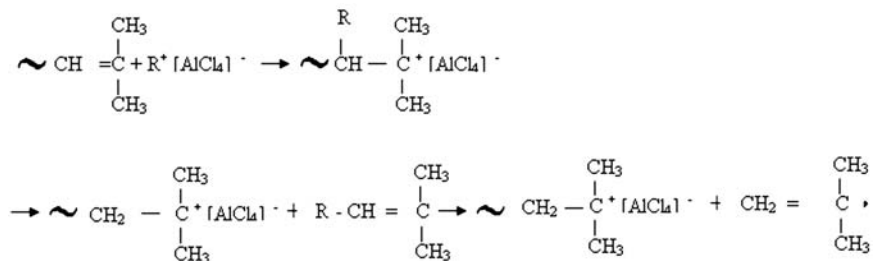
Figure 4.14 Chain transfer to polymer with further depolymerization of the macroions starting from end groups.

   In catalysis by the hydrates of $MAlCl_4$ salts the polyolefin degradation process is initiated at the active site $H + [MAlCl_4 \cdot OH]$—having the structure as shown in Fig. 4.15.

   The hydrate can initiate the degradation randomly along the chain and preferentially at end groups. The interaction of the catalyst with the weak bonds of the polymer chain is determined by the structure of the polyolefin. In PE the degradation process is initiated mainly at the vinylidene and trans-vinylene internal double bonds. The main initiation sites along the chain in butyl rubber are the coupling points of the isobutylene fragments with the isoprene units. End group initiation proceeds through the end double bonds [146]. It can be completely stated that the processes of initiation of electrophilically catalyzed polyolefin degradation may be expressed by the following structures:

1. End group processes, where R denotes CH_3 and H for (polyisobutylene, butyl rubber), and PE, respectively (Fig. 4.16).
2. Random hydride abstraction followed by chain cleavage (Fig. 4.17):
3. Or proton addition followed by chain cleavage (which is more probable for isobutylene—isoprene copolymer and PE) (Fig. 4.18):

   It can be concluded that the electrophilic degradation of different polyolefins is initiated by a few common pathways. Degradation may start either at double bond end groups or at weak bonds along the chain. The path of the chain degradation reaction is determined by the structure of the polyolefin.
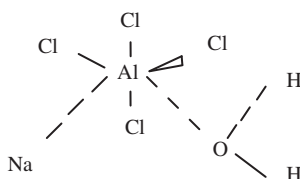
Figure 4.15 Structure of polyolefin degradation process is initiated at the active site $H + [MAlCl_4 \cdot OH]$.
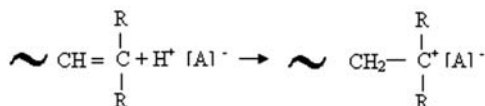
Figure 4.16 End group processes.
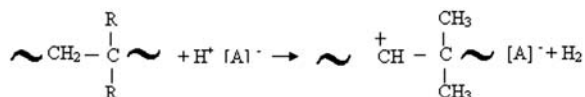
Figure 4.17 Random hydride abstraction.

$$\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}CH_2 - C = CH - CH_2 \sim + H^+[A]^- \longrightarrow \sim \overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}} - CH_2 - \overset{+}{\underset{R}{\overset{|}{C}}} - CH_2 \sim [A]^- \longrightarrow$$

$$\longrightarrow \sim CH_2 - \overset{R}{\underset{|}{\underset{R}{\overset{|}{C}}}}{}^{\bullet}[A]^- + CH_2 = \overset{}{\underset{R}{\overset{|}{C}}} - CH_2 \sim \bullet$$
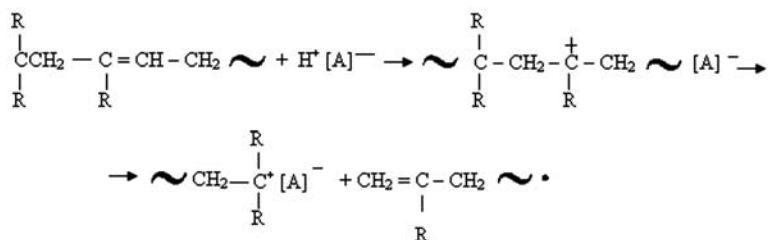
Figure 4.18 Proton addition followed by chain cleavage.

Initiation

(1) R_1-R_2 $\longrightarrow$ $R_1\cdot + R_2\cdot$

Chain reaction

(2) $R_1\cdot$ $\longrightarrow$ $R_3\cdot$ + C2 or C3

(3) $R_2\cdot + R_4$ $\longrightarrow$ $R_2 + R_4\cdot$

Termination

(4) $R_5\cdot + R_6\cdot$ $\longrightarrow$ $R_5 + R_6^=$

(5) $R_7\cdot + R_8\cdot$ $\longrightarrow$ R_7-R_8

Fe/A.C. + H_2

(6) $R_9\cdot + H\cdot$ $\longrightarrow$ R_9

(7) R_{10}-H $\longrightarrow$ $R_{10}\cdot + H\cdot$

(8) $R_{11}\cdot$ $\longrightarrow$ $R_{11}^= + H\cdot$
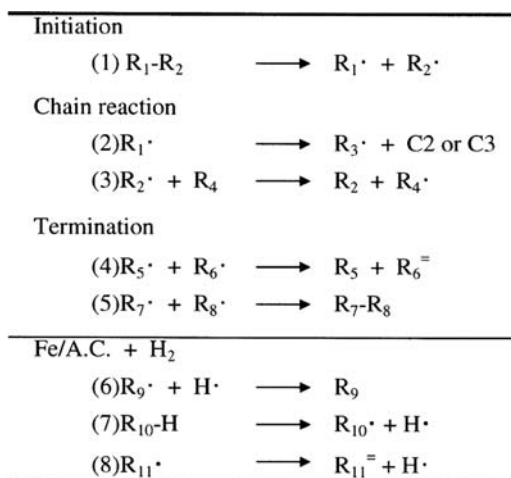
Figure 4.19 The sequence of radical chain reactions [148].

Sekine and Fujimoto [148] investigated the function of Fe and activated carbon (AC) as a catalyst by comparing Fe/AC with Fe/SiO$_2$ or AC. Furthermore, the effect of H$_2$ as a reaction gas on the product distribution in the catalytic degradation of PP was investigated. The reaction mechanism shown in Fig. 4.19, explains the reactions since Fe/AC is neither an acidic nor a basic catalyst, but a neutral catalyst. Initially (1) the random scission of the C−C bond of the main chain occurs with heat, to produce hydrocarbon radicals (HCRs). This process initiates the reaction. Then, (2) the HCR decomposes to produce small hydrocarbons such as propylene, followed by β-scission or (3) pulls out H radicals from other hydrocarbons to produce a new HCR. The former is called intramolecular radical transfer, and the latter is called intermolecular radical transfer. The three processes stated above are chain reactions. The termination reactions are (4) disproportionation or (5) recombination of two HCRs. In these mechanisms, (1) and (2) are the reactions in which the MWs decrease, (3) and (4) show no change, and (5) is the reaction in which, no MWs increase. In the case of catalytic degradation with Fe/AC in a H$_2$ atmosphere, (6) is

the hydrogenation of HCR (and olefin) and the pulling out of the H radical from hydrocarbon (7) or HCR (8) by AC. They concluded that supported Fe promotes H_2 consumption to decompose solid residues, and AC support degrades heavy oil to produce light oil. As a result, using Fe/AC as a catalyst gives the maximum yield of the liquid product.

Methods of catalytic degradation

The Taguchi technique is a method used for the designing of experiments to investigate how different parameters affect the mean and variance of a process performance characteristic that defines how well the process is functioning. The Taguchi method involves reducing the variation in a process through robust design of experiments (DOEs). The overall objective of the method is to produce high quality product at low cost to the manufacturer [149]. In literature, parameters such as temperature, catalyst concentration, and catalyst type have been identified. These parameters influence the decomposition of waste PP in a batch process and the Taguchi method was used to optimize the process parameters for the production of liquid fuel from waste PP. With the help of regression modeling an equation was developed for the yield of liquid fuel as a function of temperature, catalyst concentration, and catalyst type [149]. Researchers have further used the Taguchi experimental design to obtain optimum condition on catalytic degradation of the polymers [150]. The purpose of their research was to determine the maximum quantity of gasoline production from the degradation of mixed PE and PP using the Taguchi technique as a DOE method. Their findings suggested that the Taguchi is the most promising DOE method in order to investigate the optimum condition to produce a maximized factor such as gasoline. Their second major finding was that $\sim 51\%$ of the polymers can be degraded to gasoline components which can be used as automobile fuel. Finally, Taguchi suggested that 420°C and 50% catalyst is the most promising condition for maximum production of the gasoline from 40%, 20%, and 40% HDPE, PP, and LDPE as mixed polymers, respectively [150].

Catalytic degradation of plastic sample can also be performed in a batch autoclave. In order to determine the effect of temperature and a new catalyst on converting the polyolefins in present of PVC into liquid fuel, the semibatch reactor with ambient atmospheric conditions was designed. Also factorial design was employed as the DOE's method. The analysis of variance for the liquid and the gas showed that the main effects of temperature, catalyst percentage and PVC composition are significant. Also there is a significant interaction between temperature and catalyst percentage to liquid and gas production. Similarly, survey of interaction among the other factors indicated that there is not a significant interaction [151]. The effects of catalysts on the catalytic degradation of polymer have also been investigated by contacting melted polymers with catalyst in fixed bed reactors [152,153], heating mixtures of polymer, and catalyst powders in reaction vessels [154,155], and passing the products of polymer pyrolysis through fixed bed reactors containing cracking catalysts [156].

4.1.3   Factors affecting polyolefins degradation

4.1.3.1   Chemical composition

Chemical composition of polyolefins or polyolefins-based products play a very relevant role in their degradation. The presence of complete long carbon chains in the thermoplastic polyolefins makes these polymers nonsusceptible to degradation by microorganisms. Despite this the inclusion of hetero-groups such as oxygen in the polymer chains, polymeric substances are made labile to thermal degradation and biodegradation [38]. This is because many unsaturated polymers can undergo degradation from a range of sources, such as oxygen absorption, which leads to the release of organic peroxides. Linear saturated polyolefins are resistant to oxidative degradation. The presence of unsaturation in the polymer chain makes them susceptible to oxidation, for example natural rubber is more susceptible to degradation than PE [157].

4.1.3.2   Size of molecules/molecular structure

Literatures have shown that degradation rate is dependent on the size of the polyolefin being studied. Hydrogen has been used as a chain-transfer agent to control the molecular mass of the polymer for the commercial production of polyolefins such as PP and PE [158,159]. The particle size distribution of polymer particles was shifted to lower sizes by increasing the hydrogen concentration [159]. The size of the molecules in the polymers affects their mechanical degradation, thermal degradation, and biodegradation. These degradations increase as the size of the molecule decreases [38]. Paik and Kar [160,161] discovered that the particle size of PP and PE influences the thermal stability of these polymers, but they did not consider the molecular mass of the samples. Abbas-Abadi et al. [162] investigated the molecular mass of particle size on the thermal degradation of a commercial HDPE powder and they found that the biggest particles (>200 nm) with highest molecular mass maintained superior thermal stability of these particles. Their results showed that molecular mass is not the only key factor and in smaller sizes, bulk density, and heat transfer can affect the thermal stability.

Structure has a strong influence on the other properties of polyolefins. Thermal oxidation is complex process, including chain oxidation of HCRs, destruction of macrochains and structure formation (crosslinking, crystallization). Thermal oxidation is accompanied by structural−physical processes, leading to structure change (structural reconstruction) under the action of high temperature. The mechanism of these processes will depend on the polymer's morphology and in it turn, will influence the oxidation kinetics. The effect of a polymer crystallites in vacuum and on air: the effect of high temperature may lead to perfection of crystallites structure, rise of temperature and melting heat, at the same time at long high temperature effect the destruction of chains occurs and crystallites are decomposed [163].

4.1.3.3   Molecular weight

The MW is also important for biodegradability because it determines many physical properties of the polymer. Increasing the MW of the polymer decreased its degradability [164]. It has been reported in the literature that some microorganisms, for their growth, attack and utilize faster, polyolefins with low MW when compared to high MW polyolefins [165]. Linear polyolefins with MW lower than ∼620 support microbial growth [166]. Degradation of plastic polymers can further lead to low MW polymer fragments, such as monomers and oligomers can lead to the formation of new end groups, especially carboxylic acids [167]. As the MW of the polymers is reduced, the material becomes brittle [168] and it is more susceptible to fragmentation which makes a higher surface area available for further reactions. Owing to the high MW and the lack of functional groups biodegradation of long polyolefin chains is limited. [169,170]. Therefore high MW PE, PP, and PS polymers must be broken down by abiotic degradation to smaller pieces before biodegradation at a measurable rate takes place. If the polymers are too large, they cannot pass through the microbial cellular membranes [171].

4.1.3.4   Functionality

Polymers bearing polar functionalized side groups are highly desired materials, due to their unique and rapidly expanding range of material properties. When compared to their nonfunctionalized analogues they exhibit beneficial properties with respect to adhesion, toughness, print/paintability, miscibility, and rheological properties [172].

Nonfunctionalized polyolefins (i.e., polyethene and polypropene) have found their way in many (commodity) applications due to their outstanding properties, such as solvent resistance and thermal stability. Nowadays, these materials can easily be obtained in large scales and at low cost with very high precision of the polymer microstructures. However, due to the lack of functional groups in these polymers, they perform badly when surface chemistry is involved [173]. Thus functional polyolefins such as polyethene or polypropene that bear functional groups are highly desired materials, due to their beneficial surface properties. The incorporation of only a small amount of functionalized monomers, randomly placed in the polymer backbone, has a large effect on the surface properties of the resulting polymers, while the beneficial properties of the original nonfunctionalized polyolefins are retained [174,175]. The properties of the resulting materials can be further tuned by varying the structure of the functional groups, the amount of incorporation and the distribution of the polar functionalities along the polymer chain [173].

The choice of materials that will be incorporated onto PO is very important. Introduction of carbonyl groups in PO makes these polymers susceptible to photodegradation. As the number of chromophores increases the rate of photodegradation increases due to the extra sites, which are available to absorb more photons and to initiate the reaction for degradation. PO undergo slow sulfonation and oxidative degradation by reagents based on concentrated sulfuric acid. In chromic acid,

sulfonation results, in the more rapid oxidative degradation of PP with a slower attack on PE [35]. Obtaining functionalized polymers via direct copolymerization of nonfunctionalized olefins and polar vinyl monomers is of particular interest, since the control over the amount of polar monomers and their distribution along the chain could in principle be achieved by exploiting the reactivity differences of both monomers [175−177].

4.1.4 Controlling polyolefins degradation rate

4.1.4.1 Effect of pigments and dyes

Organic pigments and dyes are widely used in the coloration of polymer materials for many commercial applications. However, the presence of dyes and pigments can dramatically influence the chemistry of oxidation, degradation, and stabilization processes involved in a polymer and will quite often dominate the stability of the end-product. For example, by absorbing and/or scattering of UV light, pigments can induce a marked protective effect. The absorption of light by organic dyes and pigments is followed by various chemical and physical interactions which result from the dye or pigment molecules being promoted to an excited state which is more reactive than the ground state [77].

Pigments are colored, white or black materials, which are practically insoluble in the medium in which they are applied. Pigment is incorporated into the polymer by a dispersion process and forms in the material, a separate phase. They are conveniently classified as either inorganic or organic types. The properties of a pigment are primarily dependent on its chemical structure, i.e., the way in which the molecules pack in their crystal lattice [178]. Certain pigments, e.g., copper phthalocyanine, exist in different polymorphic forms with significantly different optical and stability properties. Other important factors, especially in influencing the strength or intensity of color of pigments, are particle shape and size.

The patent US 4360606 discussed organic dyes being used as photosensitizers [179]. Examples, such as acridine orange and yellow, congo red, crystal violet, brilliant green, bromothymol blue, alizarin, azure B, *N,N*-dimethyl-p-phenylazoaniline, and methylene blue, were given. The chemical structures of some of these dyes show some comparability to some of the structures listed as prodegradants, for example, alizarin is based on an anthraquinone type structure. Most other dyes contain highly conjugated unsaturated ethylene double bond groups [104]. In addition to organic dyes, inorganic pigments such as TiO_2 and ZnO that are often added to whiten the polymer can influence the degradation rate. As mentioned in the earlier section of this report, the photo activity of these additives is dependent on particle size, surface treatment, and crystalline form as well as any metal ion dopants that may be used [104].

Investigations on pigment−polymer stability interactions have been carried out with polyolefins, but there are limited studies which actually indicate that the pigments can have effect on the light stability of other polymers too [77]. Black, brown, and red pigments were recommended to improve color and physical

properties of Acrylonitrile-Butadiene-styrene rubber under weather aging. In rigid PVC, most pigments contributed to improved light stability on outdoor exposure. It was found that the surfaces degraded a lot faster than the bulk of the polymer with only minor differences in surface protection by the various organic and inorganic pigments (phthalocyanine blue, iron oxide red, channel black, P. Red 48, P. Yellow 83) [180−182].

4.1.5   Controlling environmental degradation of polyolefins

PO are known to degrade by an oxo-biodegradation mechanism and there is a single standard test method developed and published, namely, ASTM D6954-04, is a standard guide for exposing and testing plastics that degrade into the environment by a combination of oxidation and biodegradation. This guide provides a framework to compare and rank controlled laboratory rates of degradation and the degree of physical property changes of polymers by thermal and photo-oxidation processes and the biodegradation and ecological impacts in defined applications and the disposal environments after degradation. There are conditions selected for oxidation (UV or thermal at $20−70^{\circ}$C) in order to speed up the degradation likely to occur in a chosen application and disposal environment. The resulting residues from abiotic oxidation are then exposed to appropriate disposal or use environments in standard biometric test methods in order to measure the rate and degree of biodegradation. Lastly, the end-residues must be submitted to aquatic and terrestrial toxicity tests (E 1440, OCED guideline 207, and OCED guideline 208) in order to ensure that they are environmentally benign and not persistent [77]. Each degradation stage during polyolefins processes should be independently evaluated in order to allow a combined evaluation of polyolefins environmental performance under controlled laboratory settings. According to the standard of the control of environmental degradation of polyolefins the results of laboratory exposure cannot be directly extrapolated to estimate absolute rate of deterioration by the environment because the acceleration factor is material dependent and can be significantly different for each material and for different formulations of the same material. However, the exposure of a similar material of known outdoor performance (as a control) at the same time as the test specimens, allows comparison of the durability relative to that of the control under the test conditions [77].

In a growing number of cases the controlled degradation of a polymer in the environment is the desired result in the polymer processing industries. Electron irradiation technique is a well-known technique for crosslinking, graft-linking, and polymerization in the polymer industry [183]. Controlling the degree of degradation in the environment, with a consistent MWD of polymers, savings achieved in the use of chemicals (in conventional methods), reduced costs and environmentally friendly processes are the beneficial effects of using radiation technology in the polymer industries. Efforts should thus, be expanded to reducing the cost of irradiation required in such technologies. For example, advantages of employing high energy radiation to crosslink PE are that: (1) it can be performed at room temperature, (2) it offers increased flexibility in product processing, (3) varying degrees of

cure can be obtained without changing the product formulation, and (4) no impurities in the form of catalyst fragments are introduced into the material. In addition the production rate is higher and not subject to as many potential equipment problems as the thermal process [184].

Future progress in the capability to control the radiation-induced degradation of polymers is dependent on the understanding of the fundamental processes underlying degradation phenomena. Radiation degradation mechanisms are exceedingly complex, and constitute numerous chemical reaction sequences that result in changes to molecular structure. Significant changes in material morphology can also occur. The economics of controlled degradation process depends strongly on the doses involved to achieve a certain degree of MW change. The anticipated level of degradation should therefore be achieved at the lowest possible doses. The use of some oxidizing agents in small amounts has proven to help in reducing the required doses to economically acceptable lower levels [185].

4.1.6 Challenges for new generation of polyolefins

New generation of polyolefins plays a major role in the environmental issue and every progress achieved for them is a substantial progress for the whole issue. The modern approach to environmental issues deeply involves a wide sector of materials. Beside the several aspects that common to other parts of the processing industry, such as the use of friendly chemicals, clean and safe processes, and very low or zero emissions, other questions must be taken into consideration. It is highly desirable that the material does not have any negative effect on the environment during processing and during its transformation into articles or components. Again, it is very important to avoid similar negative effects on polyolefins at the end of their life [186].

Polyolefin-based materials are widely used in almost every aspect of processing industries due to their excellent properties, the ease of processing, recyclability, and of course a good performance cost. Compounding ingredients, such as mineral fillers, glass fibres, elastomers, flame retardants, pigments, or carbon black, are incorporated into the polymer according to its future application. With regards to this composition the analysis of polymeric materials turns out to be a challenging analytical task. Stabilizers are used at various stages of a polymer life cycle. It starts with controlling reaction rates or avoiding early polymerization in the actual polymer formation. Thus the analysis of stabilizers is very significant on multiple levels. Firstly, it is evident that the quantity of stabilizers is a matter of analytical concern because the concentration of these stabilizers determines how long a polymer will be stabilized sufficiently; thus formulating these stabilizers can be challenging. Secondly, stabilizers might be degraded by reactions unrelated to any stabilization. This decreases the concentration of intact stabilizer in the polymer and is hence undesirable. A knowledge on the formation of the degradation products helps to identify these degradation pathways of the stabilizers and to avoid them [187]. Lastly, degradation products of stabilizers generated when protecting the polymer

should be identified in order to have a better insight into involved reactions. If they are quantified, it is possible to determine the original level of stabilization.

4.1.7   Long-term performance of polyolefins in different environments

In the aspect of polyolefins processing; material performance has evolved significantly. This has enabled the demonstration and the validation of long-term performance of these new materials. Understanding the mechanisms of aging for any material and the key factors influencing the performance of polyolefins in their end use, is very important in knowing the capacity of how the material will be best applied and in the development of the methodologies that will be used in projecting the long-term performance of the product in service.

Antioxidants, UV stabilizers, and other protective additives have been developed in the past in order to improve the long-term durability of polyolefins, particularly in the outdoor environment. It is important for polyolefins to retain its useful properties through one or more fabrication procedures, e.g., extrusion, blending, injection molding, and palletizing and the final product must have a reasonable storage life. It is the end of the product service life that the controlled lifetime of polyolefins must degrade in whatever environment it is discarded [188]. The long-term performance of stabilized polyolefins in different environments has been studied with a focus on antioxidant consumption and migration [189]. The study was divided into two parts: In the first part, the migration behavior of three similar bifunctional phenolic antioxidants in two types of PE, in different media, was studied. Focus was then set on the antioxidants migration behavior due to factors such as media, antioxidant structure, morphology, and surface properties of the PE. The author [189] found that the structure of the antioxidants was similar; still the surrounding media had to be taken into account as a factor to influence the migration behavior. The more polar antioxidant showed a fast loss to the surrounding medium in the shape of water, both water saturated with air and water saturated with nitrogen. The chemical consumption of antioxidant was observed and the direct presence of oxygen as in air was the opposite of inert atmosphere, this was not playing a significant role in the migration behavior of antioxidant. The presence of oxygen however, as in water saturated with air, when compared to water saturated with nitrogen gas, had an impact on the migration behavior with an increase of loss of antioxidant due a high loss rate from the polymer boundary. The linear polyethylene samples showed in all cases, the fast loss of antioxidant when compared with the branched (BPE) samples. The large molecular size of the phenolic antioxidants was suggested as a reason. The amorphous area next to the crystal lamellae, interfacial component, was suggested to be more difficult to penetrate for the diffusant due to its large size and rigidity.

In the second part, polyolefin, pressurized pipes were exposed to chlorinated water at elevated temperatures. The author found that the PE pipes were stabilized with hindered phenols and phosphates. Measurement of the oxidation induction

time, using the DSC showed that the stabilizing system was rapidly consumed, chemically by the action of chlorinated water. Extensive polymer degradation was confined strictly to the surface and to the amorphous phase of the semicrystalline polymer. The growth of the highly degradated layer was constant in time. For the poly butene-1 (PB-1) pipes the chlorinated water caused an early depletion of the antioxidant system, with polymer degradation at the inner wall material, resulting to an early pipe failure. The reduction in the antioxidant concentration was essentially independent of the chlorine concentration in the range 0.5−1.5 ppm of Cl. The lifetime shortening in the isotactic poly(butene-1) pipes exposed to chlorinated water (0.5−3 ppm) was approximately by a factor of 10 with respect to that obtained with pure water. The lifetime shortening was significant even at low chlorine concentrations (0.5 ppm) and a further increase in chlorine content led only to a moderate additional decrease of lifetime [189].

4.1.8 Conclusion

Plastic wastes are of universal concern because of their long-term environmental and economic impacts and waste management problem. Degradation of plastic waste by various means and further assimilation into the environment is one of the ways that can be employed to curtail waste management problems. The degradation of polyolefins materials is caused by exposure to various factors such as heat, irradiation ozone, UV light, mechanical stress, and microbes. Degradation is further promoted by oxygen, humidity, and strain and led to such negative effects as brittleness, cracking, and fading. The mechanism of polymer degradation is highly complicated, involving simultaneous formation and decomposition of hydroperoxides. Understanding the mechanism of polymer degradation can go a long way in assisting researchers and the technologists to induce the different types of degradation in polyolefins. The addition of additives in polymers and the capacity to know the various factors responsible for these degradations could help to intensify these degradations.

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