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A short review on polymeric materials concerning degradable polymers

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Abstract. The demand for cutting-edge functional materials has been increasing since the decade. Polymeric materials usage in the past decade contributes to its commercial accomplishment, thus encouraging more groundbreaking research-based activities. Although this news is promising for polymer-related industries, the fast consumption rate of these materials throughout the world will seriously harm the environment through the accumulation of waste materials sourced primarily from by-products, faulty products or municipal from various agricultural farms and industries with disposal difficulties. Wide usage of polymeric materials is due to their ease of processing, light weight and relatively low manufacturing cost. Various advancements were made over the years in developing polymeric materials of high performance. Structure and ionic bonds of polymeric and biomaterials are the reason behind their physical and chemical properties. However, their usage is limited due to expensive manufacturing cost and difficulty in shaping and processing them.

Keywords. Polymeric materials; Degradable polymer; Thermal degradation; Biodegradable materials; Renewable resources.

1. Introduction

Sustainable society development is crucial in this age of exhausting fossil fuel reserves and increasing global temperatures resulted by the overdependence on fossil fuel and greenhouse gas emissions. Usage of renewable resources as feedstocks in producing essential products such as polymers is critical in order to achieve this goal. Thus, increasing interest in the development of green plastics using natural renewable sources is anticipated [1]. There are two categories of green polymers; the first category refers



to natural polymers, for example, chitin, lignin, cellulose, et cetera [2], where a number of these polymers exhibit excellent biocompatibility and biodegradability. Meanwhile, green plastics or materials produced from biomass-derived monomers such as plant oil are grouped under the second category. The second category is the industry's favorite due to its characteristics of having excellent thermal stability in synthesizing green polymers, indicating it as a good substitute to polymers available commercially [3]. The origin of the polymers can either be synthetic or natural. Biodegradability of the polymers can be affected by tiny distinctions in the polymers' chemical structures. Typical process of degradation starts with the conversion of polymers into their smaller units before going through the mineralization process [4]. Most polymers are consisting of exceptionally large-chain molecules and need to undergo depolymerization to reduce the large-chain molecules to monomers that consist of smaller units. Then, the microbial cells will absorb the monomers before being biodegraded, whereby the biodegradability is affected by the molecular form and weight, and crystallinity [5]. Figure 1 shows the classification of polymers based on their degradability influenced by the different factors.

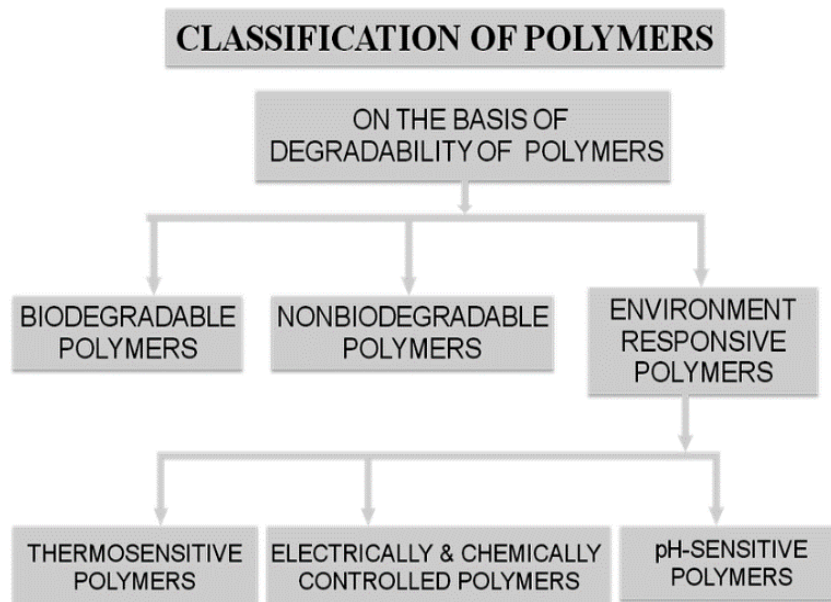


Figure 1. Classification of polymers based on their degradability influenced by the different factors.

There are two main dashes of polymeric biomaterials referring to necessary lifetimes, which are named as bio-stable and biodegradable [1]. Since years ago, bio-stable material is used for both long-lasting and finite applications [6]. Nonetheless, it appeared that the biodegradable system has emerged as an interesting choice for momentary therapeutic applications in surgery, pharmacology and tissue engineering. The first to emerge as a biodegradable synthetic polymer was the poly (glycolic acid). Unfortunately, this polymer, invented in 1954, was banned on use due to its poor thermal and hydrolytic stabilities, which are deemed unfit for regular plastic material [7]. However, 20 years later, it was found to be the first biodegradable suture material, but not akin to natural polymers [8]. After all those times, various other synthetic polymers had been studied and nowadays, they are known as biodegradable, bioabsorbable, bioresorbable, and biodegradable in research study. They are re-sorted to signify the differences in their degradation properties or mechanisms. Researchers have aimed to employ those terms competitively, forming much confusion that went against their increasing interest in the environmental biodegradation. Being established since sixty years ago, synthetic polymers had been recognized by medical people for its best application in therapeutic area. Previously, during World War

II, PVP or isotonic aqueous solutions of polyvinylpyrrolidone were utilized as plasma expander, even though there was deviation of the particular compound from ideal; but ever since, it was still employed for a long time before an alternative had appeared [7]. Due to this issue, numerous polymers had been nominated as candidate biomaterials. However, only a small number of those candidates had passed the clinical applications stage and were made available commercially.

Nowadays, it is important for synthetic polymers to be able to break down in a controlled manner, along with long-term stability properties. Either unaided or by enzyme-assisted mechanisms, both can be used to tailor biodegradable macromolecules for degradation control under inherent environmental stress. Compelling development in medical applications of these materials had grown, such as controlled drugs release, fertilizers and pesticides, absorbable surgical implants, skin grafts, and bone plates. Recognized by these developments, numerous studies on the biodegradation of synthetic polymers were inspired [6,8,9]. Later on, the issue on polymer waste management of packaging materials that has caught attention as an incentive to the research will be discussed. At present, biodegradable materials are available to finite function that undesired long-lasting strength retention [5]. Health professionals have a congruent opinion that in osteoporosis treatment (i.e., bone fracture fixation), it can be harmful as a consequence of stress shielding and the need for a second operation in the removal of device after the healing of the bone. Alternatively, lactic and glycolic acids were explored to solve these problems, as they had shown potential utility of being biocompatible, fully resorbable implant devices. It had been known for quite some time that the biocompatibility of poly (α -hydroxy acids) in vivo acute and subacute tissue reaction and in vitro cytotoxicity response. For years, sutures of these materials had been used and a number of variables that could affect the degradability had been exposed. According to Huang et al. (2015), the essential factors were the mobility, surface area, morphology, molecular weight, hydrophilic/hydrophobic interactions, and the availability of hydrolysable links [10]. Total understanding of behaviour was crucial, since the biomaterial requirements were severe. This group had successfully integrated paths that can imitate biopolymer degradation by incorporating amino acids into the synthetic polymer backbones from earlier on. It was acknowledged that the degradability could be enhanced through functional group recognition by specific enzymes.

In the previous century, amazing development in material technologies and science has improved our daily life, resulting in a more comfortable life with increasing self-confidence. Development of various synthetic polymeric materials was done for rubbers, plastics and synthetic fibers usage, substituting the traditional natural ones. Currently, synthetic polymers are crucial in the construction of controlled delivery devices for various implementations associated with food-related bioactive ingredients, genes and drugs [11]. Synthetic polymers are widely implemented in the daily necessities of the current society, such as in simple packaging, electronic devices, medical appliances, and construction among others due to their extensive mechanical properties, as well as for their cost effectiveness, performance and durability. Plastics play a crucial role in improving the quality of life ever since they were invented. About 280 million tons of plastics were manufactured globally in 2011, which is a 4% increment from the previous year [12]. Petroleum is the origin of most of these plastics and as the production of plastic materials increases, the oil consumption also increases. In addition, polymeric materials also contribute to serious environmental issue due to their persistence in the environment [13]. The global increase of plastic waste sparks various strategies with aims to minimize the negative effect of growing polymeric materials production and consumption [14-16]. Exhaustion of fossil resources as well as waste build-up issues stimulate a rising awareness in biodegradable polymers.

2. Polymeric materials

Polymer science is in the oldest area of science (i.e., exists ever since the appearance of living cells) and was formulated as separate, well-defined science by a German chemist named H. Staudinger less than 100 years ago—between 1920 and 1930 [17]. The use of polymer materials by human beings was done without any knowledge on the difference of these materials with the others. Their variety and numbers continue to increase due to the huge opportunities presented by the new synthetic paths and the

macromolecules property, which are their chain character. This enables the preparation of entirely new materials with preferred features, or the drastic improvement of a property in a designated path of material that is already known [18]. In addition to the various benefits of synthetic polymer materials, which indicate them as an attractive and crucial material, these materials also possess serious shortcomings, causing an adverse effect on the environment. The microscopic structure of polymer molecules affects the various properties of a polymeric material. As such, polymers can be classified either as amorphous or semi-crystalline (partially crystalline) (figure 2). Amorphous polymers have improper structural arrangement and are randomized, while semi-crystalline polymers are somewhat coordinated in an orderly crystalline structure.

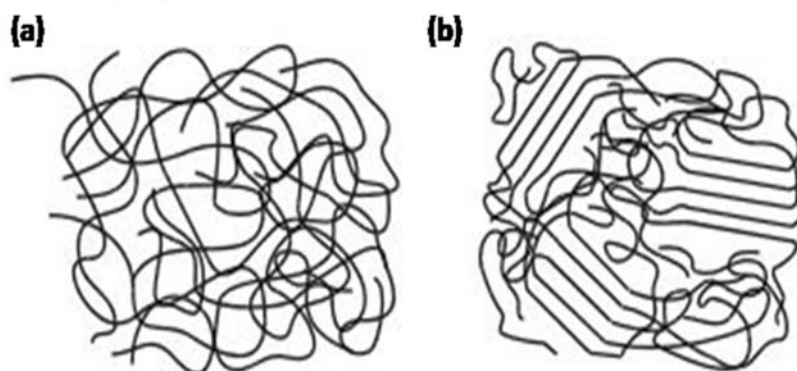


Figure 2. (a) Amorphous polymer (observe the entanglements among the polymer chains) and (b) Semi-crystalline polymer [19].

From basic knowledge, it is learned that the synthesis of polymers can be done based on two chemical reactions, which are the polymerization and polycondensation [20-22]. The first reaction works by opening the double or triple bonds, or cycles, with separated hollow molecular weight product, while the second reaction works via the reaction of the monomers' functional groups (e.g., -COOH, -OH, -NH₂, and others) with separated low molecular weight product (usually H₂O). The end of the macromolecules formed in the case of polycondensation stayed as functional groups, indicating another difference of both processes [21]. High chemical and physical stabilities cause polymer membranes with synthetic organic macromolecules to have a steady increment in terms of technical applications importance. Nevertheless, scientists in the last 30 years have concluded that the main synthetic polymers such as poly(alkylene oxide), poly(vinyl alcohol), poly(acrylic acid), and polyacrylamide can be replaced by natural and biodegradable polymers, for example, starch and cellulosic, in which they have less negative effects to the environment [9].

Practically, materials made of organic polymer have several advantages compared to materials made of metal and inorganic substances, for example, having the quality traits of ease of processing, anti-rust, high strength and light weight [23,24]. Polymer materials such as metal have a relatively high specific strength with no formation of colored rust. Nevertheless, high and/or low temperature, sunlight and/or rain exposure and being underwater and/or under the soil could cause polymer materials to degrade [23]. There are a variety of polymer material applications, for example, the vibration isolating and damping, reduction of weight, heat insulation and coating, and covering. Some can be implemented in the exterior and interior parts of the automobile, airplane, railway vehicle, and ship, while others can be used in houses, buildings, construction, housewares, commodities, toys, and electrical appliances. Degradation such as hydrolysis, oxidation, ultraviolet (UV) radiation, aging, chemicals influence, swelling, fatigue, the complex condition of respective degradation, as well as the wet and dry cycles, all of which can change various polymer material properties through respective life service. Various changes in mechanical strength are caused by the degradation of polymer materials, depending on the polymer material type, condition, production, as well as its additive package [25-27]. Thus, it is important to do

an investigation on the degradation factor through a reproduction test and an artificial aging test under practical conditions. Based on these backgrounds, various researches on polymer degradation were done according to its various aspects.

2.1. Thermal degradation of polymers

The cause of the degradation process is due to the involvement of bond scission, which is correlated to the energies of the bond. Thus, types of non-covalent or covalent bonds, elemental constituents of the polymer, and degree of unsaturation are the issues with direct connection to the bond energies in the structure of macromolecular [28]. As an example, polytetrafluoroethylene (PTFE) with higher thermal stability, $-(CF_2-CF_2)_n-$ consists of CaF bond, while polyethylene (PE), $-(CH_2-CH_2)_n-$, consists of CaH bond, which can be described by the bond energy difference of CaH and CaF (97 and 116 kcal/mol, respectively). Meanwhile, the thermal stability of polyvinyl fluoride, $-(CH_2-CHF)_n-$ had dropped as the three fluorine atoms in PTFE were substituted with hydrogen atoms due to the hydrogens being more effortlessly extractable from the carbons. The impact of intermolecular forces caused by secondary valence bonds due to induction, hydrogen bonding and dipole-dipole interaction is crucial for ordinary macromolecules, mainly, the functional polymers. Thermal stability of polyamides is enhanced by the existence of hydrogen bonding. High thermal stability is also caused by the high-resonance energy, as shown by the aromatic polymers. Meanwhile, the existence of CaH bonds or unsaturation of polymer chain stimulates peroxy radical's formation, as shown in the case of thermo-oxidative degradation. Thus, unsaturated polymers such as natural rubber (NR) are less impervious to thermo-oxidative degradation compared to saturated and structured polymers (PE). Similarly, resistance to oxidation can be observed for polymers with no hydrogen at all, those with unreactive phenyl and methyl groups.

Degradation is also affected by the molecular weight and size, functional group(s), MWD, cross-linking, the degree of branching, amorphousness, and crystallinity. As an example, carbonyl group insertion in polyolefins leads to the vulnerability of the polymers towards thermo-oxidative degradation. Polymers degradation starts with the process of industrial production. Figure 3 shows various techniques available for following/monitoring the degradation as well as for the stabilization. As an example, utilization of adipic acid in order to produce Nylon 66 is susceptible to cyclize. In Nylon polymerization reactors, cyclize is the main root of thermal degradation. A prediction model was developed by Karimi et al. (2012) [29], aiming to forecast the undesirable reactions rates in the Nylon 66 production end stage, which is in low-moisture and high-temperature conditions in an attempt to design upgraded operating strategies and equipment for the last stages of the polymer production. Increment of macromolecules size as well as molecular weight can also lead to enhanced thermal stability.

According to Cheng et al. (2016), decreasing in particle size decreases the thermal decomposition stability of polystyrene (PS) particles and micron-sized PMMA [31]. The polymers' amorphous regions have high permeability to molecular oxygen, resulting in the ease of being broken down due to thermal oxidation than in the crystalline areas [32]. The intra- and intermolecular forces are reduced due to the branching that is present in the polymer, thus affecting the crystallinity. Therefore, in many cases, branching tends to oxidize easier than linear structures, thus reducing the thermal stability of the polymers. The oxidation rate also increases with increasing branching degree. Cross-linked structure polymers need many bonds to be broken down simultaneously for molecular weight reduction, hence, offering higher thermal stability. Thermal stability is also affected by the structural order of the polymers. Therefore, ordered (tactic) polymers provide increased thermal and oxidative stability. Higher thermal stability can be found in head-to-tail arrangements, compared to head-to-head type structures. Hence, in PMMA, the thermal degradation is enhanced by the head-to-head linkage [33]. Copolymerization can increase the intermolecular forces, thus enhancing the thermal stability.

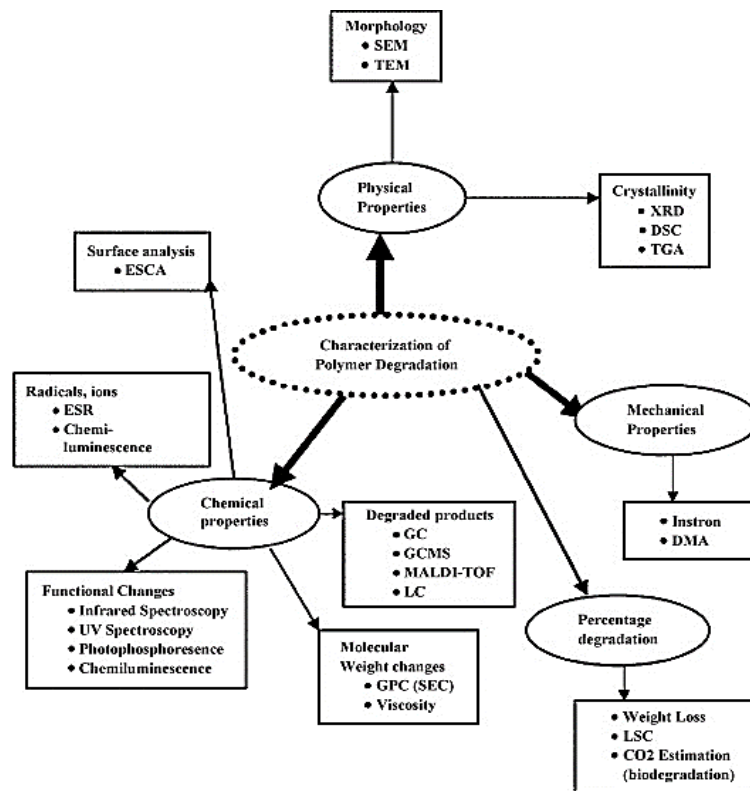


Figure 3. General techniques for characterizing polymer degradation [30].

Inconclusive experimental results can be found in many cases with unspecified involvement of exact chemistry in the process. Hence, consideration of a more fundamental approach is needed in order to explain the degradation kinetics of polymers. Polymer composites thermal degradation is a more complicated issue, as the stability of polymers is often seriously influenced by the fillers. Unexpectedly, with the exclusion of the relatively new nanocomposites field, only limited amount of data can be found on commercially used composite systems due to the lack of thorough study, unlike in the case of unfilled polymers stability. In terms of waste-to-energy technology, extensive research needs to be done in order to construct pyrolysis liquids with less residue content and higher octane value in obtaining a material with high practical suitability when producing gasoline range fuels with less refining required. The increment in the disposed of rubber quantity in which the majority is from waste tires dumped in landfill sites is also the contributor to fire and environmental hazards. Waste rubber pyrolysis is deemed as one of the most encouraging methods in retrieving valuable products. Currently, the commonly used waste polymers in landfilling have environmental consequences with no recovery of the materials' value allowed. Therefore, the end-of-life and recyclability issues of polymers need to be solved with a more sustainable solution, thus establishing an economy focused on circular materials [8]. In consideration of the importance of recyclability, environmental and stability issues, more attention needs to be given to this matter.

Achilias et al. (2007) conducted a survey, which concluded that 78 wt% of total plastic waste is comprised of commodity polymers such as PP, PE, PVC, and PS with epoxy resins and polyurethanes as the residual plastic wastes [34]. Landfilling and recycling can be implemented in disposing of these materials due to the characteristic of these polymers, which are not biodegradable. Thermal degradation is undesirable during the fabrication and application stages; however, the increment of the degradation process caused by polymers with inherent thermal sensitivities is advantageous for waste management of polymer as well as for energy recovery. Therefore, polymer waste pyrolysis is an encouraging method

in solving the disposal problems due to the limitations of landfilling as well as some difficulties in the recycling processes [35]. Polymeric materials in this process are heated under controlled conditions with no oxygen at all, resulting in a collapse of the macromolecular structure, thus producing valued oligomeric goods as well as monomers subjected to the type of polymer. For example, the thermal degradation of the PS results to the recovery of the trimer, dimer, and a monomer of styrene as the primary yields. However, it is important for these primary volatiles to be quickly reduced and collected with minimized secondary reactions in order to obstruct the relations between the evolving volatiles and pyrolyzing sample [36].

The yield of the valuable products can be increased by controlling the polymers' degradation pathway in the catalytic decomposition process [37]. In the recent waste-to-energy technology research trend, catalytic fast pyrolysis (CFP) is found to be an agreeable method in converting biomass directly to high-quality biofuel. The inclusion of waste plastics in CFP can notably enhance the production of aromatics and decrease the development of coke [38]. In addition, the yield of pyrolysis oil can be substantially improved by copyrolysis of different biomasses with different plastics. As an instance, Dixit et al. (2016) discovered that the yield of pyrolysis oil in the pyrolysis of HDPE and LDPE can be improved from less than 5% up to 56% with the inclusion of jute fiber [39]. The acid value, saponification value, glycerol percentage, free fatty acids percentage, and ester value of this pyrolysis oil was similar to that of the coconut oil. In order to break down PS to obtain utilizable by-products, Savoldelli et al. (2017) [40] had proposed a two-step bacterial and thermal degradation method. The work had proven the effectiveness of *Pseudomonas putida* in producing naphthalene and benzene from PS waste. The technique is potentially advantageous in recycling the PS waste, with extremely fast degradation kinetics and low operating temperatures, resulting in minimized energy cost.

Structural defects and impurities cannot be exempted from polymer samples even though both are the most susceptible in the thermal degradation process initiation. These could happen throughout the melt-processing stage, as well as the polymerization process. In the first case, mechanical shear and high temperature experienced by the polymeric materials aid in the production of peroxy radicals through its reaction with the atmospheric oxygen. Thus, polymers with the ability to easily develop radicals that are reactive free such as PVC and PP need preventing measures to evade unwanted degradation. Usually, these are managed through the incorporation of stabilizers, a naturally procured or synthetically manufactured special class additives. The natural stabilizer is similar to a hindered phenol, which is effective in polyamides, polyolefins, polyesters, and polycarbonates, and is also effective in high temperature, as well as long-term usage under ambient process conditions. Polymers with unsaturation such as SBR and NR subjected to oxidation reaction will result in the use of antioxidants in formulating the product [41].

The thermal stability of PVC/EVA blends was investigated by Monteiro et al. (1997) [42]. In this study, EVA samples were used with various vinyl acetate contents. The results indicated that all blends have had the autocatalytic effects, which increased the degradability, while degradability reduction can be observed in blends with EVA containing higher vinyl acetate compared to EVAs with a lower content of VA. Khurma and co-workers (2005) [43] explored the thermal degradation characteristics of PVC-poly(vinyl butyral) (PVB) blends. Preparation of the blends was done by blending the solution and thermogravimetric method was used in investigating their degradation behaviour. The investigated thermal stability increased as the PVB percentage increased. Zulfiqar et al. (1999) [44] investigated the thermal degradation of PVC with polydimethyldiphenylsiloxane (PDMDPS) and polydiphenylsiloxane (PDPS) blends through the adaptation of thermogravimetric method, which also allowed the calculation of order reactions and activation energy for the blends, as well as for the component polymers. The results showed that small amounts of two polysiloxanes had caused a slight destabilizing effect. Meanwhile, a stabilizing effect was detected with contents of higher than 50% and raised upon larger content of siloxane, which was particularly accurate for the PDMDPS blends. This result was explained with several considerations: a) polysiloxanes has higher stability than PVC with an obvious increase in the stability that can be observed by increasing their percentage, b) increasing amount of siloxane also results in the Cl or HCl radical's buildup, thus decreasing the effect of catalyzing, as well as the

dehydrochlorination rate. Investigation of the PVC/PMMA blends thermal degradation was done by Ahmad et al. (2008) [45]; they stated that the thermal decomposition temperatures of the neat PVC were lower than the PVC in the presence of PMMA; in particular, the stabilizing effect was identified to be more significant at PMMA content of 10 wt%. This interpretation was done through the consideration of reaction mechanism between the degradation products from both polymers, resulting in the stabilization of PVC. The thermal degradation of electrically conductive poly(vinyl chloride)/polyaniline (PVC/PAni) blends was studied by Pielichowski and co-workers [46].

According to this work, HCl, which was the main product of decomposition from the degradation of PVC, had a crucial role in encouraging the blends' second component decomposition through the reaction with PAni structures, categorized by the various degrees of protonation. Polyamide/rubber blends are the focus in only a few studies. In the study of thermal degradation behavior of acrylate rubber (ACM) and nylon-6 blends using thermogravimetric method by Jha and Bhowmick [47], it was found that the blend has lower thermal stability than nylon 6, with interchange reaction of ester-amide at high temperatures, as well as preferential degradation of the polyamide phase that was suggested in order to clarify this behaviour. Meanwhile, investigation of the thermal degradation behaviour of ethylene propylene rubber (EPR-g-MA) grafted with nylon 66/maleic anhydride blends at various contents of EPR-g-MA was done by Choudhury et al. (2008) [48]. According to this work, the activation energy and the thermal degradation reaction order were decreasing, as the rubber content increased, which is in correlation with the decrement in the disseminated phase particle size caused by the in situ compatibilization of nylon 66 and EPR-g-MA.

2.2. Mechanism of thermal degradation of polymers

Degradable polymers compose a significant ground in polymer science due to its incredible development in the past three decades through its many uses in the applications of medicine, biotechnology and microelectronics industries, as well as in the preservation of environment from plastic wastes. Degradable polymers are specially used as erodible matrices for controlled drug delivery [25,49-51], erodible tissue for engineering scaffolds [52,53], as positive or negative resists in microlithography in the construction of integrated circuits [54,55], and as degradable packing material [56-58]. The monomer, cross-linker or initiator fragment can be used to host degradability into the polymer. Most degradable polymers are created from degradable monomer repeating units, with glycolic and lactic acids as their main representatives. Apart from that, degradable, branched polymers that carry degradable cross-linkers vary upon the different cleavable groups. These groups are categorized into two major classes: those that can be chemically cleaved in solution, and the enzymatically degradable ones. Peptide and azoaromatic groups are exploited in the enzymatically degradable cross-linkers. Meanwhile, tertiary ester or Diels–Alder adduct groups are applied in the case of thermolyzable cross-linkers. The use of many other various labile groups are seen in the class of chemically cleavable cross-linkers; this includes acetal groups, anhydrides, amide esters, disulfides, esters, and carbonates. The prepared polymer architectures from the use of degradable initiators are shown in figure 4.

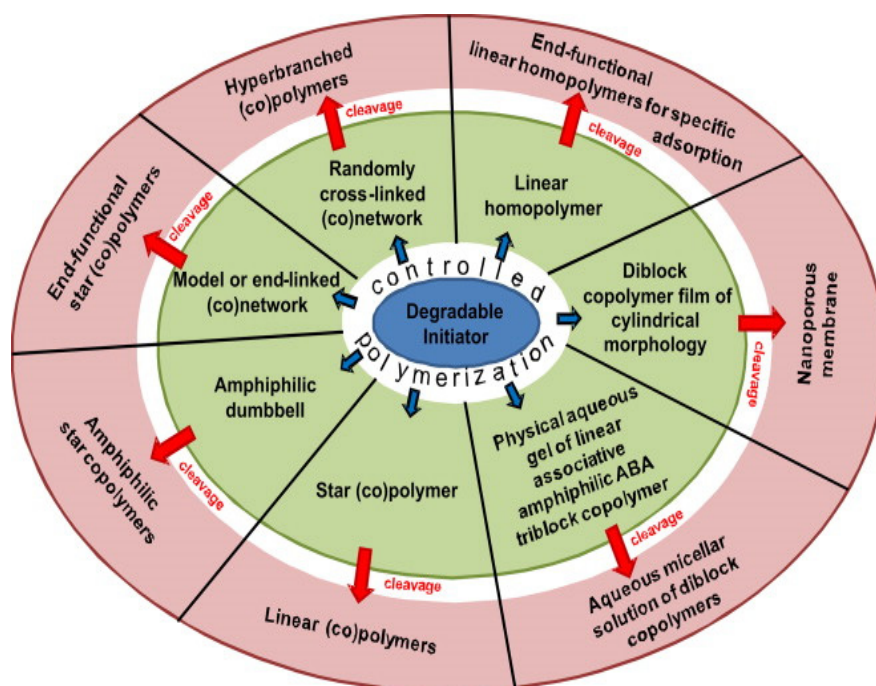


Figure 4. Polymer architectures prepared using degradable initiators [55].

Generally, alteration related to polymers thermal degradation is in accordance with a sequence of chemical reactions through macromolecules chain scission. There are several factors involved in the actual chemistry of the reaction mechanism as recounted earlier. Chain-scission reaction is consisting of a multistep free-radical route that is comprised of: (i) initiation, (ii) propagation, and (iii) termination steps. In the initiation step of the common thermoplastic polymers, the major backbone chain breaks down into smaller molecules forming free radicals, which could occur randomly at the weak macromolecule sites or the chain end. Degradation of chain-end type results in a process known as unzipping, in which the monomers are formed in high yield. Unzipping process usually happens as the backbone bonds are more delicate compared to the side groups bonds with only polymer molecules, taking active chain ends with a free radical, anion, cation, et cetera, such as α -substituted vinyl polymers, for example, PMMA, PTFE and poly α -methyl styrene [59]. Degradation of random-type such as in the cases of PET, PS and PE can cause the formation of main oligomers and a small portion of monomers. In the presence of air, free radicals formed throughout the initiation step react with oxygen, forming hydroperoxide or highly reactive peroxide intermediates. Throughout the propagation step, various decomposition reaction types may occur simultaneously, leading to the main-chain unsaturation, intermolecular or intramolecular hydrogen transfer, and cross-linking together with additional main chain degradation through chain-end or random pathways. Nearby degraded chains may interact forming cross-links during this process, resulting in the production of char. The volatile product, main-chain unsaturation, and cross-linking formation are caused by the removal of substituents and pendant chains from the main chain. Side-chain cyclization may also occur through the reaction of two nearby side groups, forming a bond between them that would eventually lead to the production of char such as PVC and polyvinyl chloride. Termination reaction may occur either through the radical coupling or radical disproportionation through hydrogen atoms transportation from one radical to another. Meanwhile, in thermo-oxidative degradation, the formation of various by-products during the termination step may consist of oxygen-containing groups such as carbonyl and ether. In some cases, oxygen regeneration may also occur, thus further speeding up the degradation process.

The study of kinetics for polymers thermal degradation is important in thoroughly understanding the degradation process and is also very convenient in forecasting the thermal stability, which is very beneficial in evading unwanted thermal degradation of polymeric products [60]. In addition, information gained from the kinetic studies can be implemented in the development of pyrolysis reactors to thermally treat the solid polymer wastes. The thermogravimetric analysis (TGA) is a commonly utilized analytical method, especially in the investigation of polymer degradations kinetics. This method assesses the activation energy of the polymer's thermal degradation. Kinetics data are fitted to various reaction models in order to obtain the activation energy, thus providing the Arrhenius parameters [61]. Experimental data acquired from various temperatures (isothermal) or heating rates (non-isothermal) should be used in the computations. In studying the decomposition of the polymer, various thermal kinetic models with the inclusion of global reactions, which transform virgin material to volatiles as well as char, is frequently utilized [62]. Snegirev et al. (2017) [63] stated that different polymer behaviors can be observed throughout pyrolysis in nitrogen. As an example, throughout pyrolysis, PS, PC and PE undergo an autocatalytic type of reaction, while PMMA follows the monotonic reaction model of the n -th order. The model-fitting technique that utilizes a single heating rate needs to be avoided due to the production of unclear kinetics descriptions. Multi-thermal history model-fitting techniques are unable to precisely forecast the thermal stability of a polymer due to restrictions such as the incapability to differentiate the formation of volatile and non-volatile fragments throughout the degradation reactions even though these techniques can be more effective.

Different apparent activation energy values can be obtained by various model-fitting methods. Model-free isoconversional technique used to calculate the activation energies was developed, aiming to define the polymer degradation processes, which are beneficial in curbing issues due to the uncertainty of the reaction model, as well as allowing the determination of the activation energy dependence on the conversion. Multiple heating rate data are also required in the isoconversional method [61]. DSC experiments that follow the isothermal measurements of dynamic thermal analysis methods can be used to determine the kinetic parameters. Measurements based on isothermal techniques may unable to entirely follow the reactions occurred throughout the degradation process even though the techniques have the ability to separate the time and temperature variables. The advantages of dynamic thermal analysis method over the isothermal method are its ability to apprehend the kinetics data better at the beginning, as well as the end of a reaction and its complex reaction mechanisms, which can be translated easier by comparing the measurements at various rates of heating. Additional crucial variables that need to be considered in the kinetics studies are the thermal conductivity change, specific heat, material density throughout the degradation process, as well as the temperature gradient present in the layer of heat penetration for in-depth and surface absorption [64].

2.3. Degradable polymeric materials analysis

While numerous methods have been established to study the thermal properties of polymeric materials, the thermogravimetric (TG) analysis prevails as the most commonly used [61]. In essence, this method constantly observes for any fluctuation in the sample weight or mass function of temperature and/or time. The gathered data can then be employed in the evaluation of thermal stability and for the prediction of conceivable lifetime data of the polymeric materials [65]. Other than that, the information can also be helpful when studying the impacts of thermal stabilizer and additives on the thermal degradation process of the composite materials. As such, the thermal degrading profile of the material establishes the polymer composite formulation by adopting this method in the calculation of the different quantities of ingredients present in the formulation said. Another frequently used analytical technique is the differential scanning calorimetry (DSC). This technique measures the amount of heat energy adsorbed or released by a sample during thermal treatment in order to study the changes in enthalpy and to understand the phase transition and reaction involved. Even though both approaches could provide important information regarding a decomposition process, they are still insufficient to understand the chemistry of the process. Therefore, it is important to investigate the evolvment of gasses and degraded products from the decomposition reactions. Apart from that, in the attempt of understanding the process

of degradation and development of reaction kinetics, analytical techniques such as the gas chromatography (GC), mass spectrometry (MS), matrix-assisted laser desorption/ionization (MALDI) MS, Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, electron spin resonance spectroscopy, methods based on chemiluminescence and positron annihilation lifetime mass spectrometry, microscopy, and multivariable curve resolution techniques [66] have provided further aid the TG and DSC analyses.

Conclusion

The breakthrough of polymeric materials in commercial market in the past decade has given an inspiration for research-based activities to blooms. Currently available conventional polymers are assumed to possess various benefits, for example, excellent properties of the barrier, hydrophobicity and good process ability; yet, these materials are categorized by high biological agents' resistance as well as the widespread use for packaging, indicating these materials as the cause of several environmental issues. Total understanding of polymeric material behavior was crucial, since the biomaterial requirements were severe. Though this increment of interest in polymer-related industries, the environment can easily have affected as the high production rate of these materials in worldwide will seriously harm the environment through waste accumulation of its by-products, faulty products or urban various agricultural farms with disposal difficulties of industrial disposal. An example of a strategy that can be implemented in order to solve this growing issue is through the introduction and promotion of consistent usage of biodegradable or natural polymers packaging in the market. The commonly used waste polymers in landfilling have environmental consequences with no recovery of the materials' value allowed. Therefore, the end-of-life and recyclability issues of polymers need to be solved with a more sustainable solution, thus establishing an economy focused on circular materials. In consideration of the importance of recyclability, environmental and stability issues, more attention needs to be given to this matter. Synthetic polymers look different from nature's wastes and many man-made products, particularly those manufactured from non-renewable resources are not considered to be bio assimilable into the natural cycle. The latter view, there are very few man-made carbon-based polymers that are not ultimately bio assimilated; resulting in no environmental hazard.

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