Biodegradable Polymers: Types, Mechanism of Degradation, Analysis and Emerging Approach in the Field of Pharmaceuticals

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Abstract: Since the flip of the century, there was a boom within the demand for modern-day purposeful substances. Polymeric materials' use over the past decade has contributed to their industrial success, driving further floor-breaking research-primarily based initiatives. Although this is right information for polymer-associated industries, the rapid consumption of these materials round the arena will significantly damage the environment by accumulating waste materials derived in general from by means of-merchandise, defective products, or municipal waste from diverse agricultural farms and industries with disposal troubles. Polymeric substances are broadly used because of their simplicity of processing, mild weight, and occasional manufacturing fee. Various advances in the development of high-overall performance polymeric substances were accomplished over time. The physical and chemical houses of polymeric and biomaterials are determined through their structure and ionic bonding. However, their use is constrained because of the excessive value of manufacture and the problems in shaping and processing them. The cutting-edge article emphasizes various sorts of biomaterials, their degradation, analysis, and diverse futuristic applications of biodegradable polymers.

Keywords: Degradable polymer; Thermal degradation; Renewable resources

INTRODUCTION

In this age of dwindling fossil fuel supplies and growing world temperature generated by overreliance on fossil fuels & greenhouse gases, sustainable society development is vital. For accomplish this goal, conventional resources must be used as fuel in the production of valuable products including polymers. As a result, there is increased intent in the evolvement of eco-friendly plastics made from natural resources, and the usage of renewable sources is expected [1]. Sustainable polymers are classified into two types. Natural polymers such as chitin, lignin, cellulose, and others [2] are included in the first group, and many of them have great biocompatibility and biodegradability. Sustainable plastics, on either hand, or materials created from agricultural residues monomers including plant oil, fall into the secondary category. Industry's choice is the second group, which has great thermal stability for manufacturing green polymers, implying that it is a viable alternative to currently available polymers [3]. Polymers can be made synthetically or naturally. Polymers' biodegradability can be influenced by minor changes in their chemical structures. The normal degradation process begins in the breakdown of polymers to small components prior to moving on to the mineralization phase [4]. The majority of polymers are made up of very long-chain molecules that must be depolymerized to be turned into monomers made up of small unit. Microbial cells will then consume the monomers before biodegrading them, with biodegradability influenced by molecular structure and weight, as well as crystallinity [5].

Bio-stable and biodegradable polymeric biomaterials are divided into two categories depending on their required lifetimes [1]. Bio-stable materials have been employed for both long-term and short-term purposes for many years [6]. Regardless, the disposable approach has emerged as a viable option for transient therapeutic applications in surgery, pharmacology, and tissue-engineering. Polymer was the first biodegradable synthetic polymer [glycolic acid]. Consequently, because towards its low thermal and water loving stabilities, which make it inappropriate for regular plastic goods, this polymer, developed in 1954, has been barred from use [7]. Decade later, they were determined to have been the first disposable suturing material; however, it was unequal to natural polymers [8]. Various synthetic polymers have subsequently been examined, & these are now referred in research studies as compostable, bioabsorbable, bioresorbable, and biodegradable. They've been reformed to suit fading characteristics or practices. Researchers have sought to employ such statements in a competitive manner, which has resulted in a significant deal of uncertainty, stifling their rising interest in environmental biodegradation. Non -natural polymers have been recognised by medical experts for their outstanding use in the therapeutic field since their inception sixty years ago. PVP or isotonic liquid polyvinylpyrrolidone solutions was employed as plasma expanders for a long period before an alternative developed during World War II, even if the compound departed from optimal [7]. Several polymers have been proposed as possible biomaterials as a consequence of this problem. Just a small percentage of candidates advanced to the clinical application process but were ultimately commercialized. Synthetic polymers must now be able to degrade in a regulated manner while remaining stable over time. Biodegradable macromolecules can be tailored for breakdown control under intrinsic environmental stress using either unaided or enzyme-assisted processes.

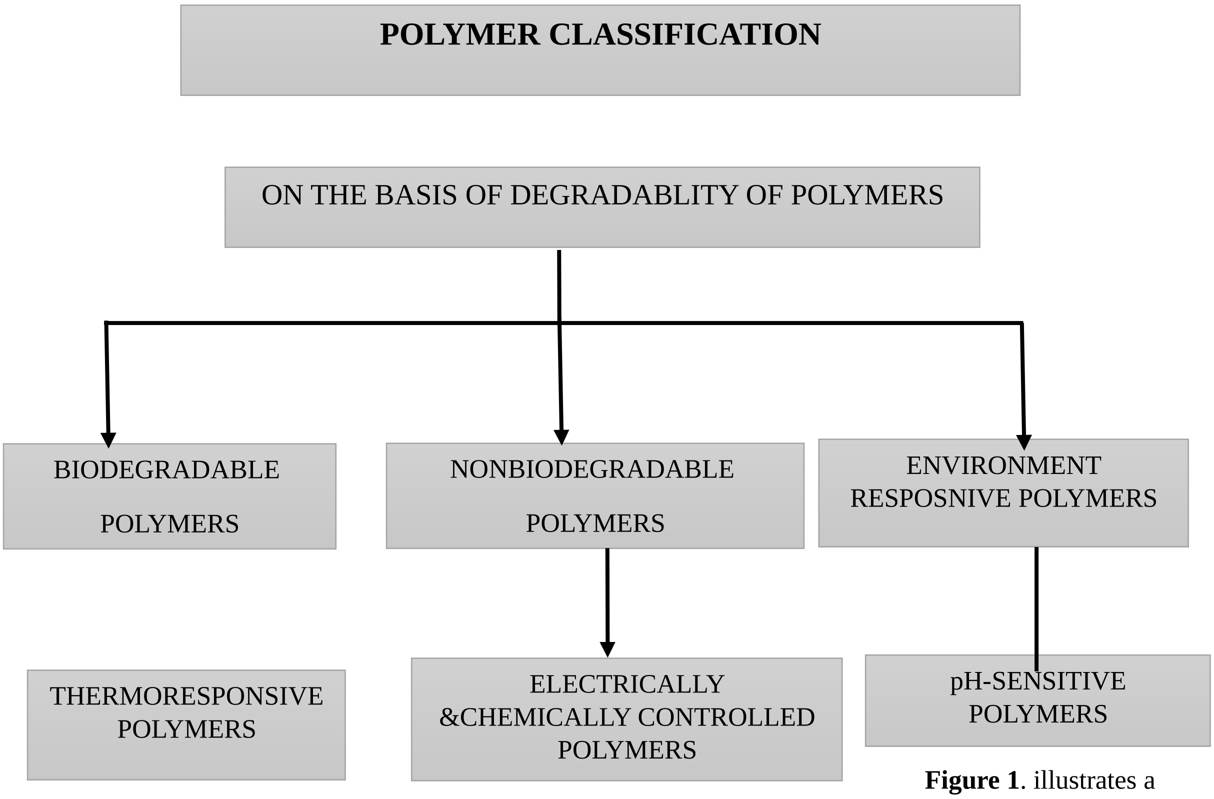


Figure 1. illustrates a categorization of polymers according to their degradability, which is influenced by a variety of factors.

Controlled drug release, biodegradable surgery implant, skin and bone grafts, fertilizers & pesticides are just a few of the medical uses that have exploded in popularity. As a result of these results, several studies on biodegradation of synthetically modified polymers have begun [6-10]. Following that, the researchers will look at the subject of polymer waste disposal in packaging, which has sparked their interest. Biodegradable materials can now overcome the problem of long-term strength retention [5]. According to experts, stress guarding and need for a second treatment to remove an implant after the bone heals can be dangerous in treatment of osteoporosis bone fracture fixing. Synthetic polymers play an important role in the development of controlled delivery strategies for a wide range of applications, including food-related bioactive compounds, genes, and pharmaceuticals [11]. Because of their comprehensive mechanical properties and low cost, chemically modified polymers are widely used in modern society's necessities like simple packaging, electrical equipment, medical instruments, & building, among others. Efficacy, performance, and long-term durability are all critical factors to consider. Plastics have an important part in enhancing people's health. They have existed since the development of the wheel. In 2011, around 280 million tons of plastics were produced globally. This is a 4% increase over the previous year [12]. The bulk of these polymers are sourced from petroleum, and as the production of plastic items grows, so does the demand for oil. Furthermore, because of their permanence in the environment, synthetic polymers contribute to serious environmental concerns [13]. The global growth in plastic trash has spurred a variety of solutions aimed at reducing the negative impact of rising polymeric material production and consumption [14-16]. Concerns over the loss of natural resource, as well as waste build-up, are driving interest in biopolymers.

POLYMERIC MATERIALS

Polymer’s science seems to be the oldest scientific discipline (it predates the birth of living things) and was established as a distinct, well-defined discipline about 1920 and 1930 by a Scientist named H. Staudinger [17]. Humans uses polymer materials with little understanding of how they varied from others. Their variety and number continue to grow because of the enormous prospects given by new synthetic routes and the attribute of macromolecules is their chain character. This permits the development of entirely new materials with desired qualities, as well as the significant improvement of a quality in an existing material route. [18]. In addition to the various advantages that make synthetic polymer materials appealing and vital, these materials have significant downsides that have a harmful influence on the environment. Polymer microscopic structure a polymeric material's different properties are influenced by molecules. As a result, materials can be classified as such an amorphous or semi-crystalline substance (partially crystalline) (Figure 2). Amorphous materials have an unsuitable structural organisation and so are randomly dispersed, whereas quasi polymers have a slightly correlated crystalline structure.

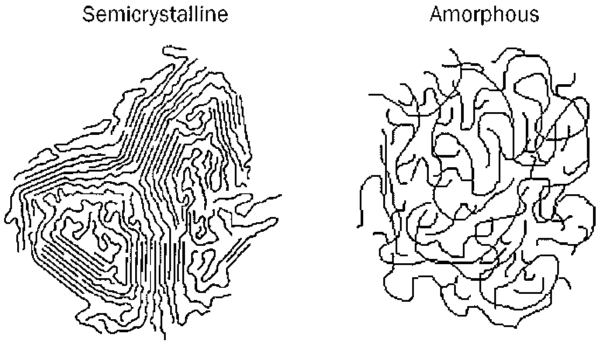


Figure2. [Semi-Crystalline polymer and Amorphous polymer (Take note of the entanglements between the polymer chains) [19]

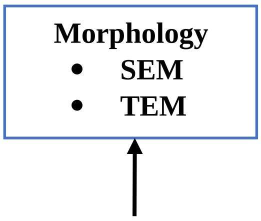
Polymerization & polycondensation are two chemical processes that may be used to synthesise polymers [20-22]. The first reaction involves the reaction of a monomer's functional groups (e.g., -COOH, -OH, -NH2, and others) to divided hollow molecular weight item, whereas the 2nd reaction involves a reaction of a monomer's functional groups (e.g., -COOH, -OH, -NH2, and others) to divided low - molecular - weight product. In case of polycondensation, ends of the produced macromolecules retained functional groups, showing still another distinction between the two processes [21]. Polymerization and polycondensation are two chemical processes that may be used to synthesise polymers [20-22]. In first reaction, a functional group of the monomers (e.g., -COOH, -OH, -NH2, and others) interact to separated hollow molecular weight product, while being in the second reaction, the functional groups of the monomers (e.g., -COOH, -OH, -NH2, and others) react with a low molecular weight product that has been isolated (usually H2O). In case of polycondensation, ends of the generated macromolecules preserved functional groups, demonstrating still another difference between the two processes Polymer material uses include vibration isolation and damping, weight reduction, thermal insulation, and coating, and covering. A few are appropriate to be used on the exterior and interior of a car, plane, train, or ship, and others are appropriate for use in dwellings, buildings, construction, housewares, consumables, toy, and electronic devices. Decay During in the course of each service”, polymeric characteristics can be affected by hydrolysis, oxidation, ultraviolet (UV) radiation, ageing, chemical impact, expansion each degradation's complicated condition, as well as the wet and dry cycles cellulose and starch, both of which are less harmful to the environment [9].

In practice, organic polymer materials have several advantages over metals and inorganic substances, including ease of preparation, anti-rust properties, high strength, and low weight [23,24]. Metal, for example, has a reasonably high specific strength and no coloured rust development. However, exposure to hot and/or cold temperatures, sunshine and/or rain, as well as being underwater and/or beneath the earth, may cause polymer materials to breakdown [23]. Mechanical strength changes when polymer materials degrade, depending on the polymer material type, condition, manufacture, and additive package [25-27]. As a result, conducting a practical inquiry on the deterioration factor utilising a reproduction test and an artificial ageing test is crucial. Various investigations on polymer degradation in various areas have been undertaken based on these foundations.

Polymer thermal deterioration

A participation of bond scission, that's associated with the energies of the bond, reasons the degradation technique. Thus, the bond energies in macromolecular systems are proportional to the type of non-covalent or covalent bond, polymer additives, and diploma of unsaturation [28]. A difference of bond strength throughout CaH and CaF (97 and 116 kcal/mol, respectively) explains why polytetrafluoroethylene (PTFE) has advanced thermal stability, –(CF2-CF2)n–, while polyethylene (PE), –(CH2-CH2)n–, has CaH bond. However, while the three fluorine atoms in PTFE are changed by hydrogen atoms, the thermal stability of polyvinyl fluoride, –(CH2-CHF)n– was diminished due to the fact hydrogens are extra eliminated without problems from carbons. For usual macromolecules, particularly purposeful polymers, their position of molecular interactions resulting from secondary valence bonds because of induction, hydrogen bonding, and dipole-dipole interplay is vital. The presence of hydrogen bonding improves the thermal balance of polyamide. As fragrant polymers have proven, excessive-resonance electricity is also associated with excellent thermal balance. However, as demonstrated via thermo-oxidative degradation, the presence of CaH bonds or polymer chain unsaturation will increase the formation of peroxy radicals. Karimi et al. (2012) [29] evolved a prediction version to count on unwanted reaction fees in the Nylon 66 manufacturing cease degree, that's under low-moisture and high-temperature conditions, so as to construct up to date working strategies and gadget for the polymer production's final levels. Thermal balance can be progressed by means of increasing the size and molecular weight of macromolecules.

According to Cheng et al. [2016] [30-31], the thermal breakdown stability of polystyrene (PS) particles and micron-sized PMMA decreases with particle size. Polymer amorphous portions have a high permeability to molecular oxygen, which allows them to be broken down more quickly by heat oxidation than crystalline parts [32]. The polymer's branching diminishes intra- and intermolecular forces, causing crystallinity to change. As a result, branching oxidises quicker than linear structures in many circumstances, lowering polymer thermal stability. As the degree of branching rises, so does the rate of oxidation. Cross-linked structural polymers require numerous links to be broken down at the same time to reduce molecular weight and hence give greater thermal stability. The structural order of the polymers influences thermal stability as well. As a result, ordered (tactic) polymers have greater thermal and oxidative stability. When compared to head-to-head constructions, head-to-tail configurations have higher thermal stability. As a result, the thermal deterioration of PMMA is accelerated by the head-to-head coupling [33]. Copolymerization can enhance intermolecular forces, which improves heat stability.



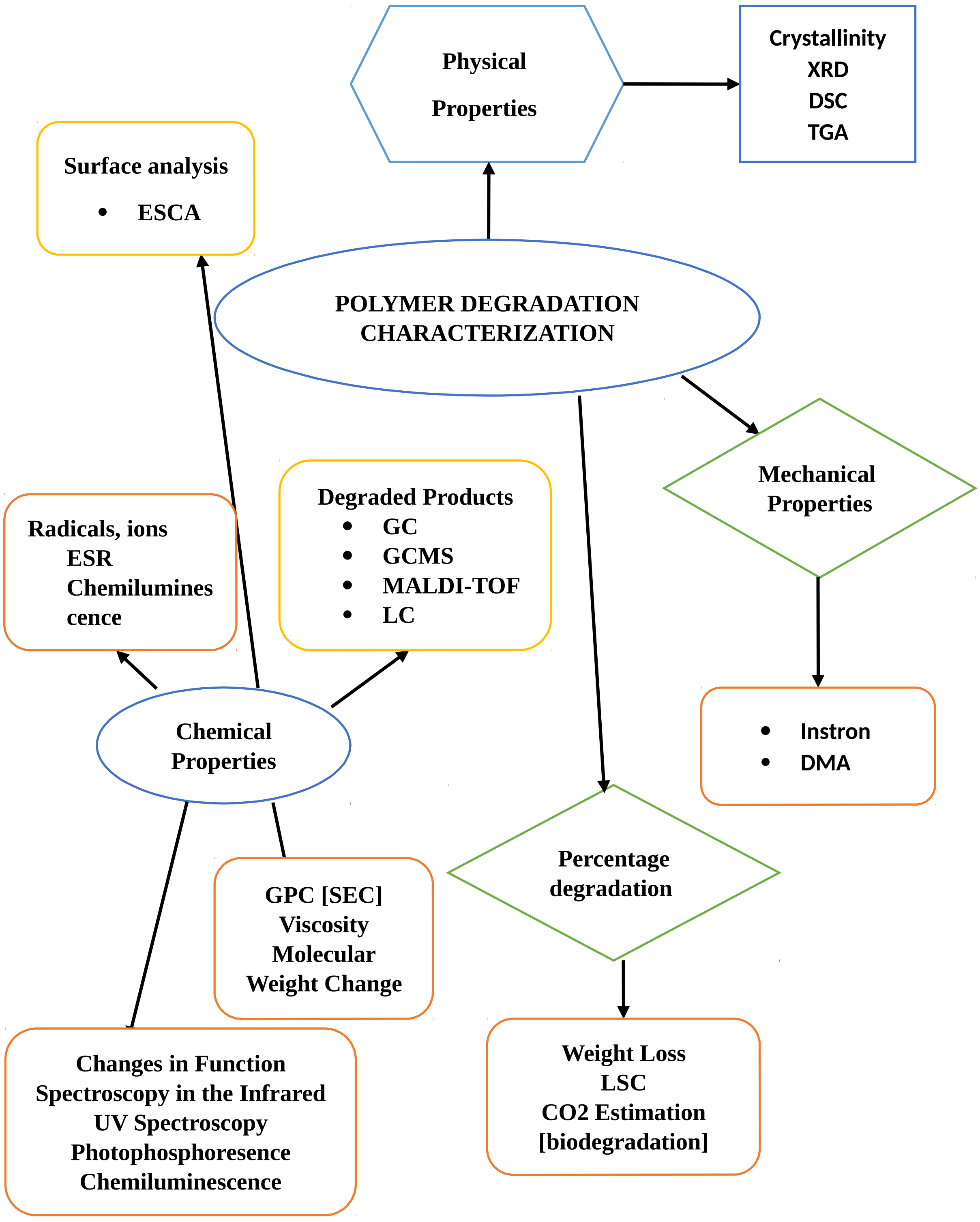


Figure 9: Techniques for characterising polymer degradation in general [30].

In many circumstances, with an unknown amount of precise chemistry involved in the process, inconclusive experimental findings might be obtained. As a result, a more fundamental understanding of polymer degradation dynamics is necessary. Heat degradation of polymer composites is a more problematic topic since additives frequently impact polymer stability. Surprisingly, aside from the relatively new nanocomposites business, there is only a limited quantity of data on commonly used composite systems available due to a lack of rigorous study, as contrasted to unfilled polymer stability. Further research in waste-to-energy technology is required to create pyrolysis liquids with lower residue content and higher-octane value to offer a material with high practical appropriateness for manufacturing gasoline range fuels with less refining required. The rise in waste rubber, the bulk of which comes from discarded tyres deposited in landfills, is also increasing fire and environmental dangers. Waste rubber pyrolysis is one of the most promising processes for recovering valuable materials. Currently, waste polymers routinely utilised in landfilling have significant environmental repercussions, with no authorised recovery of the materials' value. As a result, concerns such as polymer end-of-life and recyclability must be addressed more sustainably, culminating in the establishment of a circular economy [8]. Given the significance of recyclability, environmental, and structural issues, this issue warrants more examination.

Albeit primary imperfections and pollutions are the most delicate toward the beginning of the thermal process, they can't be forestalled in polymer tests. These can happen both during the liquefy handling stage and the polymerization stage. The mechanical shear and high temperature of the polymeric materials in the primary case prompted the age of peroxy radicals because of their reactivity with surrounding oxygen. Subsequently, polymers that quickly create receptive free extremists, like PVC and PP, require careful steps to stay away from undesired debasement. While underlying deficiencies and pollutions are generally delicate toward the start of the thermal decay processes, they are unavoidable in polymer tests. These can happen both during the melt-processing and polymerization stages. In the main case, the mechanical shear and high temperature of the polymeric materials create peroxy revolutionaries because of their reactivity with encompassing oxygen. Subsequently, polymers that make responsive free revolutionaries rapidly, like PVC and PP, need safeguard steps to limit undesirable degradation [34].

Stabilisers, which are either naturally occurring or synthesised special class additives, are frequently utilised to treat them. A natural stabiliser works in a similar way to a hindered phenol in that it works in polyamides, polyolefins, polyesters, and polycarbonates, and at high temperatures and for long periods of time under ambient processing conditions. When unsaturated polymers, such as SBR and NR, are oxidised, antioxidants must be included in the final formulation. As the proportion of PVB grew, so did the thermal stability under consideration. To research the warm debasement of PVC utilizing polydimethyldiphenylsiloxane (PDMDPS) and polydiphenylsiloxane [PDPS] mixes, Zulfiqar et al. [1999] [35] utilized a thermogravimetric procedure to decide request cycles and enactment energy for the mixes just as the part polymers. Small dosages of two polysiloxanes had a minor destabilising effect, according to the findings. Meanwhile, a stabilising impact was seen at concentrations more than 50% and increased with higher siloxane content, particularly in the PDMDPS mixes. Several factors were considered to explain this result: a] Polysiloxanes are more stable than PVC, with a noticeable improvement in stability found when the percentage of siloxane is raised; b] increasing the quantity of siloxane results in the creation of Cl or HCl radicals, which lessens the effect of catalysis and the rate of dehydrochlorination. Ahmad et al. (2008) [36] looked at the thermal degradation of PVC/PMMA blends. The thermal breakdown temperatures of neat PVC were found to be lower than those of PVC with PMMA; the stabilising effect was found to be more significant at a PMMA dosage of 10% wt. This was accomplished by accounting for the reaction mechanism between the breakdown products of both polymers, resulting in PVC stabilisation. Pielichowski and colleagues [37] investigated the heat degradation of electrically conductive PVC/PAni mixes. According to this study, HCl, a key byproduct of PVC degradation, was critical in accelerating the disintegration of the blend's second component via interactions with PAni structures classified according to their degree of proportion.

Several studies on polyamide/elastic combinations have been conducted. Jha and Bhowmick [38] used the thermogravimetric technique to investigate the warm corruption behaviour of acrylate elastic (ACM) and nylon-6 mixtures. They discovered that the mixture has lower warm strength than nylon 6, with ester-amide trade response at high temperatures, as well as a special debasement of the polyamide stage, which was proposed to explain this behaviour. Choudhury et al. (2008) [39] focused on the thermal debasement conduct of EPR-g-MA mixed with nylon 66/maleic anhydride at various EPR-g-MA concentrations. According to this evaluation, when the elastic material developed, so did the enactment energy and warm debasement response request, which compares to the decrease in scattering stage molecule size triggered by in vivo crosslinking of nylon 66 and EPR-g-MA.

Polymer thermal degradation mechanism

Degradable polymers have set up a generous balance in polymer research during the most recent thirty years, inferable from their assorted uses in medication, biotechnology, and microelectronics, just as in natural security against plastic waste. Degradable polymers have a variety of applications, including erodible lattices for controlled medication conveyance [25,40-43], erodible tissue for designing platforms [43,44], pro or con opposes in microlithography in the development of coordinated circuits [45,46], & compostable pressing material [47-49]. The monomer, cross-linker, or activator fragments can all be used to promote degradability in the polymer. Most biodegradable polymers are composed of repeating units of biodegradable monomers, the most frequent of which are glycolic and lactic acids. Furthermore, the cleavable groups of degradable, branching polymers with degradable cross-linkers vary. These are divided into two categories: one that can be chemically split in solution and those which can be removed by enzymes. Peptide and haloaromatic groups are used in enzyme-biodegradable cross-linkers. Chemically cleavable crosslinkers include acetal groups, anhydrides, amide esters, disulfides, esters, and carbonates. Figure 4 depicts the polymer structures generated by degradable initiators. Chemically cleavable crosslinkers include acetal group, anhydrides, amide esters, disulfides, esters & carbonates. Figure 4 displays the polymer structures produced by degradable initiators.

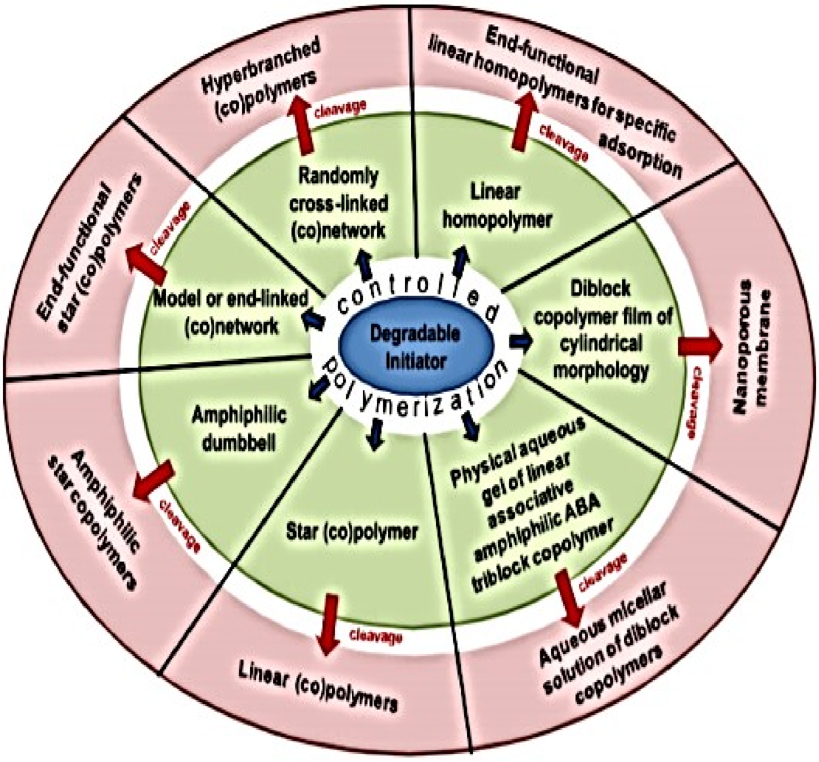


Figure 4. polymers architecture prepared using degradable initiators [46].

Polymer thermal corruption changes are frequently produced by a succession of compound cycles including macromolecule chain scission. As recently noted, different factors bewilder the genuine science of the response cycle. The chain-scission response comprises three stages:

(i) initiation
(ii) propagation,
(iii) termination.

These are for the most part steps in a multistep free-extremist pathway. During the inception stage, the primary spine chain of run of the mill thermoplastic polymers breaks. At the point when greater atoms separate into more modest ones, which can occur whenever at the most fragile point, free revolutionaries are made. Destinations of macromolecules or the end of a chain. At the point when the chain-end type diminishes, a cycle known as unfastening happens, bringing about high monomer yields. The unfastening system is predominant because spine linkages are considerably more delicate than side gathering bonds with just polymer particles, for example, - subbed vinyl polymers as PMMA, PTFE, and poly-methyl styrene [50]. Unconstrained corruption, as found in PET, PS, and PE, can create countless oligomers just as a set number of monomers. Within the sight of oxygen, free extremists framed during the commencement stage respond with oxygen to shape hydroperoxide or exceptionally receptive peroxide intermediate.

During the proliferation stage, numerous breakdown response types might happen simultaneously, bringing about fundamental intermolecular or intramolecular hydrogen move, & cross-connecting, just as additional principal chain corruption through chain-end or arbitrary pathways. Close by corrupted chains might cooperate and produce cross-joins during this interaction, bringing about the making of burn. When substituents and pendant chains are eliminated from the primary chain, an unstable item is framed, just as fundamental chain unsaturation and cross-connecting. Side-chain cyclization can likewise happen because of the response between two neighbouring side gatherings, which brings about the making of a bond and the combination of roasts like PVC and polyvinyl chloride. An end response can rise out of extremist coupling or revolutionary disproportionation occasions in which hydrogen iotas are moved to start with one revolutionary then onto the next. In the meantime, at the last phase of thermo-oxidative breakdown, oxygen-containing gatherings, for example, carbonyl and ether might create an assortment of side effects. In uncommon conditions, oxygen recovery might happen, rushing the decay cycle significantly more. The investigation of polymer thermal debasement energy is basic for totally understanding the corruption cycle just as expecting thermal solidness, which is fundamental in staying away from undesirable polymeric item thermal crumbling [51]. Moreover, the discoveries of the active investigations might be used to support the plan of pyrolysis reactors for thermally handling strong polymer squanders. Thermogravimetric analysis (TGA) is a famous scientific technique, outstandingly for looking at the elements of polymer debasement. Utilizing this methodology, the initiation energy of the polymer's hotness corruption is figured. Fitting dynamic information to different response models yields the Arrhenius boundaries [52], which are then used to figure the actuation energy. Exploratory information from various temperatures [isothermal] or warming rates [non-isothermal] ought to be utilized in the calculations. In the investigation of polymer debasement, a few warm motor models with the expansion of worldwide cycles that convert virgin material to volatiles just as scorch are as often as possible used [53]. As indicated by Snegirev et al. [2017], a few polymer practices can be seen during nitrogen pyrolysis. PS, PC, and PE, for instance, play out an oxidative response during pyrolysis, however PMMA follows the n-the request monotonic reactivity model. Due to the presence of obfuscated energy portrayals, the model-fitting procedure that uses a solitary warming rate ought to be stayed away from. Regardless of multi-warm history model procedures are more fruitful, they can't as expected foresee a polymer's warm strength because of impediments like the failure to recognize the arrangement of unpredictable and non-unstable sections during debasement occasions. The evident actuation energy levels may differ contingent upon the model-fitting methodology utilized.

A without model is conversional procedure for computing dynamic boundaries was created fully intent on characterizing polymer debasement processes. This strategy is useful in bringing down issues brought about by the reaction model's vulnerability just as empowering the assurance of enactment energy dependence on change. The social event of different warming rate information is needed for the is conversional approach [52]. To decide the active boundaries, DSC concentrates on that follow the isothermal perceptions of dynamic warm investigation strategies may be utilized. While isothermal methods can isolate time and temperature factors, estimations dependent on them will be unable to completely follow the responses that happen during the crumbling system. The powerful warm examination technique enjoys numerous upper hands over the isothermal strategy, including the capacity to even more likely grasp energy information toward the beginning and end of a response, just as its mind-boggling response processes, which can be deciphered all the more rapidly by looking at estimation’s paces of warming. Warm conductivity change, explicit hotness, material thickness during decay, and the temperature angle present in the hotness infiltration layer for inside and out and surface retention are exceptionally significant components to consider in energy study [55].

Analyses of biodegradable polymeric materials

Albeit various procedures for estimating the warm properties of polymeric materials have been created, thermogravimetric (TG)examination is regularly utilized [52]. Fundamentally, this strategy consistently screens any progressions for example weight or mass as a component of the temperature as well as time. Then data collected may be used to evaluate thermal stability and predict probable lifespan data for polymeric materials [5]. Aside from that, the data might be utilised to explore the influence of thermal stabilizing agents & additive in composite thermal deterioration. The polymer composite formulation is determined by the material's thermal degrading characteristic because of applying this approach to compute the various quantities of components present in the formulation. Another well-known analytical approach is DSC (differential scanning calorimetry). Quantity of heat energy emitted or absorbed during thermal treatment of sample is estimated to examine enthalpy changes and gain a better understanding of the phase transition and reaction involved. While these methods can provide useful information about a process of decomposition, they are insufficient for understanding the chemistry of the process as a result, it is vital to understand how gases and degradation products form during breakdown processes. Mass spectrometry [MS], Matrix Assisted Laser Desorption/Ionization (MALDI) MS, Fourier change infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, electron turn reverberation spectroscopy and quantum mechanics techniques were also used to try to understand the debasement rate and response energy improvement.

CONCLUSION

In the recent decade, the commercialization of polymeric materials has prompted a rise in research-based activities. Conventional polymers are thought to have several advantages, such as excellent barrier properties, hydrophobicity, and processability; however, these materials are classified by high biological agent resistance and widespread packaging use, implying that they are the source of a number of environmental issues. Because the biomaterial requirements were so demanding, a thorough polymeric cognition material behaviour was required. Regardless of the expanded revenue in polymer-related ventures, the climate might have been harmed because of the world's high pace of creation of these materials, which will truly harm the climate through the waste aggregation of results, broken items, or metropolitan different rural homesteads with modern removal troubles. One methodology that may be used to address this extending issue is the turn of events and promoting of biodegradable or regular polymer bundling available. The standard utilization of waste polymers in landfilling has ecological results since there is no strategy to recover the materials' worth. Therefore, concerns concerning polymer end-of-life and recyclability should be dealt with in a more economical way, coming full circle in the development of a roundabout economy Given the relevance of recyclability, environmental, and stability concerns, this topic warrants more investigation. Because manmade polymers do not, for all intents and purposes, take after typical squanders, most man-made goods, particularly ones come from non-renewable resources which are not assimilable into natural process. According to the last point of view, almost all man-made carbon-based polymers are eventually bio assimilated and pose no ecological risk.

REFERENCES

(1) R. Appiah-Ntiamoah, H. Kim, B. T. Gadisa, A. F. Baye, M. W. Abebe, and S. V. Kostjuk, Mater. Chem. Phys. **219**, 468-477 [2018]. https://doi.org/10.1016/j.matchemphys.2018.08.061.

(2) M. Rinaudo, Prog. Polym. Sci. **31**/7, 603-632 [2006]. https://doi.org/10.1016/j.progpolymsci.2006.06.001.

(3) D. Quinzler and S. Mecking, Angew. Chem. Int. Ed. Engl. **49**/25, 4306-4308 [2010]. https://doi.org/10.1002/anie.201001510.

(4) N. Kamaly, B. Yameen, J. Wu, and O. C. Farokhzad, Chem. Rev. **116**/4, 2602-2663 [2016]. https://doi.org/10.1021/acs.chemrev.5b00346.

(5) L. S. Nair and C. T. Laurencin, Prog. Polym. Sci. **32**/8-9, 762-798 [2007]. https://doi.org/10.1016/j.progpolymsci.2007.05.017.

(6) A. Sionkowska, Prog. Polym. Sci. **36**/9, 1254-1276 [2011]. https://doi.org/10.1016/j.progpolymsci.2011.05.003.

(7) B. Laycock, M. Nikolić, J. M. Colwell, E. Gauthier, P. Halley, S. Bottle, G. George, Prog. Polym. Sci. **71**, 144-189 [2017]. https://doi.org/10.1016/j.progpolymsci.2017.02.004.

(8) M. Hong and E. Y. -X. Chen, Green Chem. **19**/16, 3692-3706 [2017]. https://doi.org/10.1039/C7GC01496A.

(9) E. Jalalvandi and A. Shavandi (review), Eur. Polym. J. **109**, 43-54 [2018]. https://doi.org/10.1016/j.eurpolymj.2018.08.056.

(10) A. Shrivastav, H. Y. Kim, and Y.R. Kim, BioMed Res. Int. 2013, 212 [2013].

(11) M. E. Iñiguez, J. A. Conesa, A. Fullana, Waste Manag. **79**, 339-345 [2018]. https://doi.org/10.1016/j.wasman.2018.08.006.

(12) M. Sienkiewicz, H. Janik, K. Borzędowska-Labuda, and J. Kucińska-Lipka, J. Cleaner Prod. **147**, 560-571 [2017]. https://doi.org/10.1016/j.jclepro.2017.01.121.

(13) C. Ma, J. Yu, B. Wang, Z. Song, J. Xiang, S. Hu, et al, Renew. Sustain. Energy Rev. Fakirov S 2018 **61**, 433-450 [2016]. https://doi.org/10.1016/j.rser.2016.04.020

(14) S. Fakirov, Prog. Polym. Sci. 89, 1–18 [2019]. https://doi.org/10.1016/j.progpolymsci.2018.09.003.

(15) P. Samaddar, Y. S. Ok, K. H. Kim, E. E. Kwon, and D. C. W. Tsang, J. Cleaner Prod. **197**, 1190-1209 [2018]. https://doi.org/10.1016/j.jclepro.2018.06.262.
(16) S. Fakirov, Adv. Ind. Eng. Polym. Res. **1**/1, 40-47 [2018]. https://doi.org/10.1016/j.aiepr.2018.02.001.
(17) N. Goonoo, A. Bhaw-Luximon, D. Jhurry, Polym. Int. **64**/10, 1289-1302 [2015]. https://doi.org/10.1002/pi.4937.
(18) J. D. Badia, O. Gil-Castell, and A. Ribes-Greus, Polym. Degrad. Stab. **137**, 35-57 [2017]. https://doi.org/10.1016/j.polymdegradstab.2017.01.002.

(19) J. Garnier, P. E. Dufils, J. Vinas, Y. Vanderveken, A. van Herk, and P. Lacroix-Desmazes, Polym. Degrad. Stab. **97**/2, 170-177 [2012]. https://doi.org/10.1016/j.polymdegradstab.2011.10.019.
(20) J. P. Lutz, M. D. Hannigan, and A. J. McNeil, Coord. Chem. Rev. **376**, 225-247 [2018]. https://doi.org/10.1016/j.ccr.2018.07.015.
(21) M. Ito and K. Nagai, Polym. Degrad. Stab. **93**/10, 1723-1735 [2008]. https://doi.org/10.1016/j.polymdegradstab.2008.07.011.
(22) M. S. Selim, M. A. Shenashen, S. A. El-Safty, S. A. Higazy, M. M. Selim, H. Isago, A. Elmarakbi, Prog. Mater. Sci. **87**, 1-32 [2017]. https://doi.org/10.1016/j.pmatsci.2017.02.001.
(23) R. M. D. Soares, N. M. Siqueira, M. P. Prabhakaram, and S. Ramakrishna, Mater. Sci. Eng. C Mater. Biol. Appl. **92**, 969-982 [2018]. https://doi.org/10.1016/j.msec.2018.08.004.
(24) B. Notario, J. Pinto, and M. A. Rodriguez-Perez, Prog. Mater. Sci. 78-79, 93-139 93-139 [2016]. https://doi.org/10.1016/j.pmatsci.2016.02.002.
(25) K. Hamad, M. Kaseem, and F. Deri, Polym. Degrad. Stab. **98**/12, 2801-2812 [2013]. https://doi.org/10.1016/j.polymdegradstab.2013.09.025.
(26) S. S. Stivala and L. Reich, Polym. Eng. Sci. **20**/10, 654-661 [1980]. https://doi.org/10.1002/pen.760201003.
(27) H. Karimi, M. A. Schaffer, and K. B. McAuley, Macromol. React. Eng. **6**/2-3, 93-109 [2012]. https://doi.org/10.1002/mren.201100051.

(28) P. Kumar, D. Depan, N. Singh Tomer, and R. P. Singh, Prog. Polym. Sci. **34**/6, 479-515 [2009]. https://doi.org/10.1016/j.progpolymsci.2009.01.002.
(29) T. Chen, C. Dong, X. Li, and J. Gao, Polym. Degrad. Stab. **94**/10, 1788-1794 [2009]. https://doi.org/10.1016/j.polymdegradstab.2009.06.011.
(30) G. Y. Li and J. L. Koenig, Rubber Chem. Technol. **78**, 355-390 [2005].
(31) K. Holland and I. Rae, Aust. J. Chem. **40**/4, 687-692 [1987]. https://doi.org/10.1071/CH9870687.
(32) B. Kirschweng, D. Tátraaljai, E. Földes, and B. Pukánszky, Polym. Degrad. Stab. **145**, 25-40 [2017]. https://doi.org/10.1016/j.polymdegradstab.2017.07.012.
(33) S. Zulfiqar and S. Ahmad, Polym. Degrad. Stab. **65**/2, 243-247 [1999]. https://doi.org/10.1016/S0141-3910[99]00010-5.
(34) Z. Ahmad, N. A. Al-Awadi, and F. Al-Sagheer, Polym. Degrad. Stab. **93**/2, 456-465 [2008]. https://doi.org/10.1016/j.polymdegradstab.2007.11.019.
(35) K. Pielichowski, J. Therm. Anal. Calorim. **54**/1, 171-175 [1998]. https://doi.org/10.1023/A:1010129205138.

(36) Jha and A. K. Bhowmick, Polym. Degrad. Stab. **62**/3, 575-586 [1998]. https://doi.org/10.1016/S0141-3910[98]00044-5.
(37) Choudhury, A. Balmurulikrishnan, and G. Sarkhel, Polym. Adv. Technol. **19**/9, 1226-1235 [2008]. https://doi.org/10.1002/pat.1116.

(38) Y. Fu and W. J. Kao, Expert Opin. Drug Deliv. **7**/4, 429-444 [2010]. https://doi.org/10.1517/17425241003602259.
(39) J. Heller, Crit. Rev. Ther. Drug Carrier Syst. **1**/1, 39-90 [1984].

(40) K. S. Soppimath, T. M. Aminabhavi, A. R. Kulkarni, and W. E. Rudzinski, J. Control. Release **70**/1-2, 1-20 [2001]. https://doi.org/10.1016/s0168-3659[00]00339-4.

(41) E. Murray, B. C. Thompson, S. Sayyar, and G. G. Wallace, Polym. Degrad. Stab. **111**, 71-77 [2015]. https://doi.org/10.1016/j.polymdegradstab.2014.10.010.

(42) S. Wu, X. Liu, K. W. K. Yeung, C. Liu, and X. Yang, Mater. Sci. Eng. R Rep. **80**, 1-36 [2014]. https://doi.org/10.1016/j.mser.2014.04.001.

(43) H. Ban, A. Tanaka, Y. Kawai, and S. Imamura, *Synthesis of alkali-soluble silicone resin suitable for resist material in microlithography Polymer 31*, [1990], pp. 564-578.

(44) M. D. Rikkou and C. S. Patrickios, Prog. Polym. Sci. **36**/8, 1079-1097 [2011]. https://doi.org/10.1016/j.progpolymsci.2011.01.004.

(45) K. Ginjupalli, G. V. Shavi, R. K. Averineni, M. Bhat, N. Udupa, and P. Nagaraja Upadhya, Polym. Degrad. Stab. **144**, 520-535 [2017]. https://doi.org/10.1016/j.polymdegradstab.2017.08.024.

(46) M. Musioł, W. Sikorska, H. Janeczek, W. Wałach, A. Hercog, B. Johnston, J. Rydz, Waste Manag. **77**, 447-454 [2018]. https://doi.org/10.1016/j.wasman.2018.04.030.

(47) S. Yuan, F. Shen, C. K. Chua, and K. Zhou, Prog. Polym. Sci. 91, 141-168 [2019]. https://doi.org/10.1016/j.progpolymsci.2018.11.001.

(48) Singh and N. Sharma, Polym. Degrad. Stab. **93**/3, 561-584 [2008]. https://doi.org/10.1016/j.polymdegradstab.2007.11.008.

(49) N. Hayeemasae, H. Ismail, S. Matchawet, and A. Masa, *Kinetic of thermal degradation and thermal stability of natural rubber filled with titanium dioxide nanoparticles Polymer Composites*, [2018].

(50) J. D. Peterson, S. Vyazovkin, and C. A. Wight, Macromol. Chem. Phys. **202**/6, 775-784 [2001]. https://doi.org/10.1002/1521-3935[20010301]202:6<775::AID-MACP775>3.0.CO;2-G.

(51) J. Li and S. I. Stoliarov, Combust. Flame **160**/7, 1287-1297 [2013]. https://doi.org/10.1016/j.combustflame.2013.02.012.

(52) Y. Snegirev, V. A. Talalov, V. V. Stepanov, O. P. Korobeinichev, I. E. Gerasimov, and A. G. Shmakov, Polym. Degrad. Stab. **137**, 151-161 [2017]. https://doi.org/10.1016/j.polymdegradstab.2017.01.008.

(53) N. A. Sazelee, N. H. Idris, M. F. Md Din, N. S. Mustafa, N. A. Ali, M. S. Yahya et al, Int. J. Hydr. Energy 43/45, 20853-20860 [2018]. https://doi.org/10.1016/j.ijhydene.2018.09.125

(54) N. Sazali, W. N. W. Salleh, A. F. Ismail, K. Kadirgama, and F. E. C. Othman, Solid State Phenom. **280**, 308-311 [2018]. https://doi.org/10.4028/www.scientific.net/SSP.280.308.

(55) N. Sazali, W. N. W. Salleh, N. A. H. M. Nordin, and A. F. Ismail, J. Ind. Eng. Chem. **32**, 167-171 [2015]. https://doi.org/10.1016/j.jiec.2015.08.014.