

Biopolymer-Based Blends

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Abstract

The indispensable nature of plastic-based materials in packaging processes and their widespread global dependency marks an era of a "plastic crisis" with toxicological and environmental consequences to all living entities in our ecosystem. The potential biohazards associated with plastic manufacturing industries resulting from the chemical breakdown to toxic components present a challenging technological issue. While the petroleum-based plastic market is predicted to shrink marked by a notable effort toward an emerging bioplastic market bearing a low environmental load, the shift is expected to abolish the dependency on plastic use in a plastic-free society. The bioplastic growth trajectory is discretely rising, but advancements have been dampened by price economics and the underperformance of biobased plastics due to material properties in comparison to their counterparts. Polymer bending is considered an important route in the

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design of new materials' properties to incorporate adhesive and interfacial features to impart biodegradable characteristics in the form of bioplastics. This chapter aims to present various approaches to blending strategies and to discuss the physical and chemical limitations of polymer blending, and structure-property relationships can yield bioplastics as viable materials.

Keywords

Bioplastics · Polymer blends · Compolymerization · Biodegradability · Biopolymers · Microbial degradation

Introduction

Polymers are the most abundant commercially used materials. Consumer-driven use of plastic use has exponentially increased. Alarming statistics reveal that one million plastic bottles reach consumers every minute and five trillion plastic bags are in circulatory use each year (United Nations, Environment Programme 2022) - a situation that promises to worsen with devastating consequences with the rise of industries (Mecking 2021). Plastic materials by their compositional nature are "single use products" and can show considerable resistance to degradation under ambient conditions making them heat, force (e.g., mechanical) and chemically, moisture, biologically, and weather resistant. This resistance can span decades of slow toxic release of plastic constituent materials into the environment. The consequential ripple effect of nondegradable plastics is driven by the dynamics of mother nature in the form of high velocity winds and ocean currents from local to global scales spreading to oceans (Jenna Jambeck et al. 2015) resulting in their accumulation (Lebreton et al. 2018) in ecosystems as far as the Artic polar regions on the planet (Bergmann et al. 2022). The disintegration of plastics into secondary products in the form of microplastics (Zhang et al. 2021) from their bulk counterparts which exist on the millimeter scale or smaller is environmentally catastrophic to marine, land, and human life and results from the lack of reliable methods to detect and remove small-scale contaminants particularly if embedded within animals that enter the human food chain. Consideration is now being given to the fate of nanoplastics that find their way into reproductive organs of organisms which can be inherited by their offspring (Zhao et al. 2017). Plastic waste has now reached catastrophic proportions threatening the existence of life incubated by an exponentially increasing microtoxic environment.

The purpose-built nature of plastics as long durable polymer chains is resistant to environmental stress and strain, chemical attack, and physical absorption which are variable features of different plastic compositions. Such characteristics define material toughness, stiffness, mechanical properties, moisture and gaseous absorption (vapor diffusion), hydrolysis, compressibility (mechanical load) and creep, and UV resistance. Questions that are universal to understanding the physical and chemical resistance of plastics and many pertinent issues related to plastic degradation remain



Fig. 1 Comparison of plastic degradation rates of Landfill (L), Soil (S), Marine (M), Biological (B), and Sunlight (S). (Reprinted from (Chamas et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

elusive (Chamas et al. 2020). The variability in degradation rates of commonly categorized plastics summarized in Fig. 1 provides insightful clues of the persistence of polymers in the environment, and their degradation profiles can be highly multiphasic as the disintegration of the materials depend on their dimensional occurrence, polymer type and complexity, filler content, and susceptibility to degradation and the surroundings. Such factors decidedly determine the fate of degradation that may be mediated by chemical, physical, or biological means.

Reducing plastic waste consumption through the utilization of alternative material packing and increasing efforts to recycle plastics can certainly slow down the impact of plastics and their derivatives. However, the huge global dependency on plastics from food containment to pharmaceutical packaging inevitably means that the demand for cheap plastics will continue to contribute to this growing crisis. Hence, there are growing concerns that recyclability which applies to only 10–25% of waste plastics will not be able to sustain and accelerate growth to a plastic-free environment. To overcome this limitation, it is essential to ensure that plastic utilization is aimed to be entirely recyclable or to undergo some process to reinvent waste plastic into a reusable form. Solutions to resolving the sustainability of environmentally friendly and degradable plastics have become an urgent matter of formulating polymer chemistry through engineering of molecular building blocks and bond accessibility for safe degradation using a multidisciplinary approach involving aspects of polymer chemistry, materials engineering, and biological science (Fig. 2). This reflects that the future of plastic formulation has evolved into a multifaceted cross-disciplinary area (Belontz et al. 2019). This will likely involve engineering new functionalities into plastics for the facile disassembly of persistently long-chain lengths into smaller components which are not toxic (Yun 2011).



Fig. 2 Multidisciplinary overlap to engineering plastics

Breaking of C-C and C-H bonds via oxidative bond cleavage resulting in the fragmentation of the carbon framework into removable or nontoxic components on a timescale that can process tonnes of quantities of plastic on a daily basis is currently unachievable. A key goal is to deliver a rational technology to modify the polymer skeleton of plastics by weakening bonded structures and making available new entities for transformations into precursors for manufacturing of industrially important constituents (Vollmer et al. 2020). Ceasing such opportunities for the conversion of degraded synthetic by-products into commercially useful avenues can visibly have a positive impact on the environment.

Mechanisms that involve bioremediated destruction of polymers by microorganisms are inspirational by design provided by nature itself. Bioplastics from a cost perspective are considered expensive, but their interest has slowly but steadily increased over the last decade. A hallmark of biodegradation is often signified by metabolic products – carbon dioxide, water, and methane – driven by electron transfer processes that utilize oxygen, hydrogen, and metals and thus facilitating bond cleavage for energetically demanding bond conversions.

A promising route that has steadily gained considerable interest over the last few decades is the concept of polymer blending. Principally, polymer blending is based on the rationale of tuning the physical and chemical characteristics of polymers which when combined into a single polymer, certain properties can be suppressed or enhanced, or more probable is the introduction of new characteristics acquired by the resulting blend. Polymer blending has the potential to deliver renewable plastics as new materials from existing sources through mixing and processability by overcoming barriers to their formation that may be chemically demanding. There is an unmet need that combines the economics of material production with selected engineered properties that falls within the periphery of stable plastics for the purpose they are

made but adequately unstable for less costly degradation strategies. These limitations can be overpowered by the design of blended polymers which can structure and shape materials for one of the most sought after functionality of materials today – controlled degradability of by-products.

This chapter brings a recent perspective on polymer blending strategies to introduce new material capabilities as viable solutions to ultimately reduce the environmental burden from the overload of plastic released into the far-reaching habitats of our ecosystem and beyond through ocean waste (Suaria et al. 2016; Jambeck et al. 2015). We also discuss the limitations of polymer blends with a view to explore some of the key reasons that must be addressed in order to secure the future from the growing threat of plastic intoxication.

Nonbiodegradable Degradation of Plastics (Abiotic)

The chemical degradation of polymers that do not involve the action of microbial components in their breakdown to liberate polymer fragments is termed as abiotic. Early investigations on biopolymers, namely, starch, show that they ordinarily degrade assisted by the presence of prooxidant (Koutny et al. 2006) which under abiotic conditions driven by thermal aging degenerates to monomer products released as ketones, aldehydes, alcohols, lactones, and carboxylic acids (Albertsson et al. 1994). Polymers receptive to photoxidation also represent important abiotic pathways (Fig. 3) through which common plastics can absorb external light energy to excited chemical states and photo-degenerate to smaller stable products (El-hiti et al. 2022). Under changing weathering conditions, synthetic plastic/polymer degradation is unfeasibly slow spanning decades with very limited depolymerized fragmented product evolution. Evidence has recently surfaced which points to the abiotic chemical destruction of potent chlorinated tetrachloroethene (PCE) and trichloroethene (TCE) using abiotic processes. An abiotic route for the accelerated breakdown of synthetic plastics was shown by the addition of oxo-additives to synthetic plastics PP, namely, oxo-degradable polypropylene (PP-oxo) and high



Fig. 3 Degradation products generated form abiotic products. (Reprinted from (Chamas et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

density polyethylene (HDPE-oxo) under weathering differing conditions (Ángeles-López et al. 2016). The study reveals that it is possible to reduce plastic resistance to disassemble under ambient conditions. Further, the use of Fe(II) at concentrations of 20 mM were effective in the structural degradation of chlorinated polymers resulting in the release of detectable PCE and TCE reduction products (Entwistle et al. 2019).

A recent study attempted to decipher some of the complexities associated with plastic degradation by probing abiotic and biotic activities related to polymer degradability and structure-property data as predictors for screening underlying hierarchical patterns of variable polymer types. Using a key parameter defined by hydrophobicity (Log*P*) modeling, crystallinity, T_g , number-average molecular weight (M_n), and dispersity (M_w) were screened against 110 polymers exhibiting a wide range of hydrophobicites (Fig. 4b) using a computational predictor tool, modeling (Fig. 4a), and machine learning. The findings provide significant insight of functional group chemistry of carbonates, esters, and amides with low hydrophobicity that assists abiotic hydrolysis and biotic mechanisms. This is in contrast to higher Log*P* values correlating to C-H bond the breakdown of which is perturbed by additives. Polyester hydrolysis is largely influenced by positive changes in values of Log*P* and crystallinity affecting degradability. Further, the study concludes that biotic mechanisms operate more rapidly compared to abiotic routes (Min et al. 2020).

The Problem with Plastic and the "One-Way" Transition from Recycling to Polymer Blends

The long-chain composition of polymers and the resulting complexity in terms of shape and structure are usually a result of strong bonded networks intricately defined by assembly patterns of repeated units locked into a predetermined configuration. Thus, molecular bond chemistry is at the heart of the "plastic" industry. Decades on, polymer chemists are now working to undo what their predecessors have worked tirelessly to achieve – strong polymer plastics. However, reversing tough polymer bond synthesis is no easy task. While some plastics are easily reversible, others pose a huge environmental burden. The variability in polymeric bond strength, the toxicity of breakdown products, and the recovery of starting materials coupled to the cost and severity of processes pose workable barriers to manage plastic disposal. While it is chemically feasible to drive polymerization reactions form monomeric units, it is energetically demanding to depolymerize some of the more common plastics. For instance, polyolefins composed of polymerized alkenes are an example of some of the most difficult plastics to degrade and are estimated to decompose only up to 0.5% of their original structures over a period of 100 years. Polyolefins such as polypropylene and polyethylene are ubiquitous industrialized plastics used for their high density, low density, and linear low-density characteristics with wide-scale properties highly resistant to oxidation in their hydrophobic states (Koteswara Reddy and Kiran 2019).



Fig. 4 Functional group chemistry of abiotic and biotic activities revealed by (a) predictor tools used in machine learning for (b) profiling polymer hydrophobocity and water solubility. Reprinted from (Min et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0)

Due to bond strength, pyrolysis continues to be a commonly chosen method for breaking polymers into smaller units. With temperature, time, and pressure being key parameters for steering the molecular assembly of polymers, the same parameters are being used to control the release of monomers from their polymeric counterparts as a pyrolysis-based renewable technology for recycling complex plastics on a commercial scale. The technology drives the process to deliver useable monomers from a high carbon feed to a low carbon output by minimizing the oxygen availability of the environment. Mundane degradation caused by weathering conditions in the natural environment typified by low susceptibility to polymer oxidation and hydrolysis' subsequent breakdown is both uncontrolled and impractical for managing plastic pollution. The initial conversion of hard-to-degrade plastics from a state of low-to-high susceptibility for bond cleavage to occur requires (1) processes which can match or exceed the current and future rate of plastic utilization; (2) the conversion or incorporation of bond types that are accessible to bond fission; and the (3) controlled release and containment of degradation products for safe disposal, particularly microparticles that often find their way into the digestive tracks of animals.

While toughness has been a key attribute to polymer performance, environmental policies are reshaping a new trend in polymer design, and time and cost are an added advantage of bond making and bond breaking. Although high-temperature recycling and polymer blending approaches are conceptually different, both methods border on the same on delivering low-carbon products as precursors for further recycling and commercialization (Fig. 4). However, the primary advantage of using polymer blending to pyrolysis or catalytic processes for disposing chemicals is the suppression of volatile toxic fume release such as chlorine from poly(vinyl chloride)which is often uncontrolled in the latter process. Gaseous by-products like hydrochloride render heat-driven processes unsuitable, and polymer blending using chemical approaches could be a more environmentally acceptable procedure to possibly reduce, divert, or even eliminate poisonous side products during the monomerization of polymer chains (Walker et al. 2020). Using the example of polyolefins as one of the most persistent man-made plastics that exist on our planet, processes which involve oxidative degradation usually via the absorption of thermal energy from natural sunlight result in excessively slow degradation (0.5%) of the polymer that spans decades. The O₂ activation from the suns energy can directly permit bond scission of the carbon chain and liberate free radical structures with variable energies, and the radicals formed hold the potential to introduce a new array of reactive mojeties such as carboxylate and hydroxide anions and hydrocarbon radicals which pacify other radicals to form stable shorter chains and molecules (Fig. 5). The introduction of localized hydrophilic regions within the hydrophobic polymer through high energy absorption of thermal energy from the surroundings forming smaller structures can be further used by microorganisms as a source for carbon. The utilization of carbon units in metabolic product assembly is coupled to CO₂ and H₂O release and underlines processes that essentially support life. This can only occur by the interaction of microbial cells with recognizable structures and their entry into cells. However, most plastics have almost negligible oxodegradation profiles and must be assisted by additional groups that are aligned to nature. Considerable efforts are being applied to engineer nonbiodegradable plastics derived from petrochemicals into biodegradable forms to enable their interaction and uptake by microorganisms for carbon recycling. Polymer blending is one such process to formulate new but more desirable properties by combining existing ones which is inherently different to the intrinsic nature of the separated polymer components. Hence, copolymerization of the blended components offers a cheaper alternative to modify polymer properties using a facile route compared to the polymerization of new monomers or their reformation prior to polymerization.

Polymer blending as an approach to tailor polymer properties as desired for taskspecific functions has gained superiority to using base materials for the assembly of different types of plastics with variable characteristics that traditionally depended primarily on synthetic conditions. The distinctive functional features of the new



Fig. 5 Thermocatalytic recycling of complex plastics and polymer blending of synthetic polymers leading to the introduction of engineered properties for facile degradation into useful recyclable precursor products

polymer blend take advantage of the most economical and most versatile approach to access the most diverse property range completely different from its constituent properties. In view of the current accumulation rates of plastic (Geyer et al. 2017) and its effect on the natural environment, the complete recovery of carbon from plastic for renewable use is a leading mandate of the twenty-first century. Degradation strategies are now geared toward biobased plastics composed of compostable and biodegradable polymer frameworks. A central concern to the design of biodegradable plastics is the degree of synergistic interaction and compatibility during coprocessing of the blended components to make the process and the product as feasible as possible. While the properties are different to the source, both the physical and chemical properties are dependent on individual elements that come together in a single phase rather than as a composite in which the components are separated by virtue of their own properties in a multiphase. Structural factors such as complexity, bond type, composition, polymer arrangement, and the degree of crystalline / amorphous morphology and physical properties like solubility, density, and molecular weight and toughness ultimately determine the polymer degradability (Zeenat et al. 2021).

Biodegradable Plastics: Understanding Microbial Interaction

To gain an appreciable understanding of the mechanisms microbes use in their interaction and degradation of plastic, it has become necessary to profile the inherent structural and functional characteristics microbes use to derive carbon from plastics

waste. Modeling microbes versed in polymer chain scission can provide a potential wealth of information in understanding the mechanistic aspects of biodegradation of polymers to useful precursor materials such as hydrocarbons (Pundhir and Gagneja 2016). In the same context, biostability of plastics that show resistance to degradation in biological environments is equally of interest to determine how material persistence is related to functional group chemistry (Padsalgikar 2017). Some earlier observations demonstrated the biodegradable activity of microbes toward synthetic plastics. The parametric of weight loss, polymer elongated shape change, and tensile strength were notable effects of the interaction of lignose microorganisms with heat and UV-treated oxidized polyethylenes under culture conditions (Lee et al. 1991). Microbial degradation of UV-irradiated samples showed superior performance indicating increased susceptibility to the UV-induced oxidized state of the polymer and hence better accessibility to bond cleavage and highlighting the importance of the pro-oxidized weakened state of the extensive carbon skeleton framework. This is suggestive of the notion that a thermo-or UV oxidative pathway is the preferred route by which oxygen can liberate shorter chain lengths from polymers that are elevated to structures of higher energetic order. This can initiate chain scission events along the length of the polymer resulting in radical formation (George Wypych 2015) (Fig. 6). The diverse range of detectable oxidative products that include a wide selection of functional organic structures including alkanes, esters, alcohols, carboxvlic acids, aldehydes, ketones, and keto acids, among others, brings into question the multiple mechanisms nature microorganisms employ to access (Hakkarainen and Albertsson 2005).



Fig. 6 Slow polyolefin bond degradation under natural weathering conditions can be accelerated by the introduction of engineered polymer blends

Barriers to Biodegradation

Some of the common commercially used plastics are shown in Fig. 7. Most of the polymers targeted for degradation by microbes are naturally occurring polycaprolactone (PCL) and polylactic acid (PLA) and have not evolved to efficiently dissemble unsaturated bonds of the C = O and C-O-C type which are often further stabilized by additives as plasticizers or fillers as supports (Björkner 2000). However, there is considerable debate surrounding the biodegradation of synthetic of plastics by microorganisms (Lear et al. 2022) and their standardization in general to degradation (Chamas et al. 2020). Modest efficiencies typically less than the 20% upper limit which falls far below the expected threshold required to diminish the plastic population to nontoxic levels. Currently, the high molecular weight of macroscale plastics and the addition of fillers, plasticizers, and antioxidants intensified to their general inertness make accessibility to these chemical functional groups extremely difficult as microbial substrates. Other barriers to biodegradation are shown in Fig. 8. Degradability of high resistant plastics notably low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene(PP), polyvinylchloride (PVC), polyethyleneterephthalate (PET), and polystyrene (PS) is largely attributed to high bond strengths which usually require temperatures



Fig. 7 Structures of some common plastics used in commercial products in a varying proportion



Fig. 8 A summary diagram of the barriers to biodegradation through natural processes

exceeding 100 °C and external mechanical stresses ranging from 10 to 15 MPa to break them. The alignment of the polymer bond is enhanced through the stacking of chains which contrasts the arrangement of branched polymer morphologies forming less densely packed structures which are more accessible to bond scission and enzyme degradation. Unrelated to the stacking or nonstacking nature of the polymer, the morphological state of plastics that reside between the fully crystalline and amorphous state impacts the extent to which it can be biologically degraded (Ronkvist et al. 2009) suggesting that microbial enzymes such as PETase may be better suited to depolymerize plastic materials of semicrystalline character and aromatic polyesters while showing little to no specificity for aliphatic structures. Also functional group chemistry exhibited by plastics becomes important not only for the potential for degradation but also for the utilization of degradation products as a carbon source for energy and metabolic product growth as demonstrated by the assimilated use of poly(ethylene terephthalate) (Yang et al. 2016). Perhaps the biggest barrier to biodegradation is functional group chemistry. Since nonpolar aliphatic C-C bonds are intrinsically inert, their uncreativeness renders them demanding to split enthalpically. The exceptional stability of the carbon bonds makes it difficult to excite bond opening to more stable complexes particularly those of the metal type via an insertion mechanism (Jun 2004). However, C-C bond cleavage is ubiquitous in nature, and the high bond inertness necessarily requires access to functionalized groups within the polymer structure that is integral to biological catalysis. As in enzymatic cleavage of C-C bonds, transformation to other forms requires redox reactions which is often not the case with C-N and C-O bonds in the case of cytochrome P450 reactions (Guengerich and Yoshimoto 2018). Hence, bacterial enzymes can target polymer degradation products such as aldehydes and ketones for conversion to alkenes, alcohols, and acids from aromatic hydrocarbons via carbocation and de-saturated intermediates, electrophilic, decarboxylation, nucleophilic, desaturation, and oxidative cleavage-driven reactions.

Hence, in the same context, it becomes crucial to understand the importance of functionalization of synthetic polymers in plastics in pursuit of their biodegradation. Plastics that use polyvinyl alcohol (PVC) and polyethylene succinate (PES) are able to accommodate more cleavable groups in their structure in the form of hydroxyl and ester moieties, respectively, which are recognizable by a large number of microbial strains. The incorporation of hydroxyl groups in highly resistant polymers can considerably aid polymer breakdown as modeled by polyethylene glycols (PEG) containing terminal hydroxyl groups (Rogers et al. 2019), and the conjugation of PEG-OH can provide added hetro-functionality to biopolymers like chitosan broadening their utility (Wu et al. 2008). Recently, Hadad et al. (2005) found carbonyl residues induced through photo-oxidation had a strong correlation with biodegradation activity of polyethylene via the thermophilic bacterium *Brevibaccillus borstelensis*.

Polystyrene, on the other hand, is strongly hydrophobic, variably thick, and a very durable plastic which makes the polystyrene composition hard to degrade in most landfill and soiled environments. The chemical modification of the polystyrene is required for microorganisms to adapt for the metabolic feed to occur usually oxidative enzymes to make available metabolically utilizable carbon-based substrates. This can occur readily under UV irradiation (Yousif and Haddad 2013) which initiates the production of mobile radicals that recombine following carboncarbon bond chain scission to form energy precursors (Fig. 8). In the absence of a high energy input, PS degrading bacteria isolated from the gut of superworms have been identified as a serine hydrolase where the enzyme activity is characterized by a shift from hydrophobicity to a hydrophilic environment, and this change is accompanied by an increase in unsaturated carbon-oxygen bonds. Hence, oxidation of the C-C bond to a C-O is the first step to the enzyme-directed depolymerization process (Kim et al. 2020). Depolymerized products obtained from sunlight-treated oxo-biodegradable bags were taken up as metabolic substrates reinforcing the importance of the prooxidant state of the original polymer (Da Luz et al. 2014).

The attachment and growth of microbial colonies leading to the formation of biofilms also has an important place in plastic degradation. Surface hydrophobicity in plastics tend to discourage the colonization of bioentities to microparticles by PVA (Hüsler et al. 2018) and also by resisting non-specific protein adsorption via surface water (Shengfu Chen et al. 2006) which forms both a formidable phyiscal and enthalpic barrier to invading microbes (Shenfu Chen et al. 2010). It has been reported, however, that certain synthetics support growth of bacterial colonies (Sivan et al. 2006). The lack of adhesion is overcome through the secretion of biosurfactants that take the form of lipopeptides and glycolipids from microbes that enable swarm mobility at the surface correlated to surfactant release (Be'er and Harshey 2011). The notion that plastics are not fully eliminated from the environment but persist as microplastics of the size order ~100 μ m in effluent waters (Wolff et al. 2019) adds another layer to the plastic problem. In an effort to ascertain how biofilm communities grow and effect polymer surfaces, microplastics derived



Fig. 9 Bond scission of polystyrene units forming carbon-free radicals as precursors to small metabolic products



Fig. 10 Effect on polymer surface chemistry of PE (Polyethylene), PP (Polypropylene), and PS (polystyrene) measured by changes in (a) crystallinity, (b) stiffness, (c) compression, (d) roughness, and (e) diameter. The asterisks denote major differences in sample treatment relative to the control. (Reprinted from (McGivney et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

from polyethylene [PE], polypropylene [PP], and polystyrene [PS] were incubated with sea water bacterioplanktons. Figure 9 shows that crystallinity, stiffness, and compressibility are affected significantly relative to control samples in water in the absence of microbes. The increased crystallinity of [PE] was notable in comparison to the control sample, and [PP] experienced the most significant loss in stiffness while the other polymers were similar to the control (McGivney et al. 2020). The loss in material property from the structural changes observed in this study and the irreversibility associated with this loss primarily from the breakdown of structure and mechanical properties suggest that degradation of smaller particles through the formation of biofilms is possible resulting in the variable accumulation of different bacterial colonies (Fig. 9). Specific effects are assigned to changes in surface chemistry and provide evidence for the attachment and degradability of polymers with strong dependency on the polymer structure. Hence, biofilm formation is polymer specific (Figs. 10 and 11).

These studies suggest that polymer biodegradation hinges on a number of factors, a single decisive factor rests on the structural and group composition, and the structural compatibility of the polymer-microbe is highly dependent on the nutritional source and energy requirements of microorganisms. Hence, the general limitation of polymer degradability might also be regulated by nutritional and energy requirements and the process may relate to a specific source type of plastic. This



Fig. 11 The genesis of biofilm formation and accumulation on Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH): (a) Untreated polymer; (b) biofilm after 2-week incubation; and (c) washed polymer exposing degraded regions. The RHS graph summaries the relative accumulation of bacterial strains on the PHBH polymer. (Reprinted from (Morohoshi et al. 2018). This work is licensed under a Creative Commons Attribution International (CC BY))

indicates that synthetic polymers are not optimal substrates for secreted enzymes but rather are optimized for biopolymers that undergo rapid biodegradation such as chitin, cellulose, corn, starch alginate, etc. This requires the implementation of strategies and technologies to accelerate polymers that are not biologically designed for depolymerization but synthetically resistant in their makeup. One of the biggest challenges faced in the current era is the mass availability of alternative polymers that can easily replace plastics with sustainable properties that rival the mechanical characteristics and durability of polymerizable "hardcore" plastics. While polymer blending can deliver eco-friendly replaceable plastics, much effort is being directed to fabricate favorable polymers blends formulated with new elements for easy waste disposal with the same utilizable quality of existing plastics. Polymer blending is perhaps the only sustainable alternative to reduce and minimize environmental toxicity while partnering with the mechanics of natural living ecosystems to recycle plastic waste.

Polymer Blends Composed of Synthetics Polymers

Mainstream materials used for "everyday" packaging applications still remain essentially nonbiodegradable, and their replacement or their compatibility through modification is necessary to deliver environmentally safe and sustainable degradable products. Polymerizable monomers that can be environmentally degraded such as biodegradable polymers are extremely attractive to overcome these challenges. While synthetic polymers possess very strong bonding associations across the polymer backbone in traditional material such as polystyrene, biodegradable polymers are generally characterized by weaker bonds that allow them to satisfy their natural role as functionally degradable biomaterials. The replacement of synthetics with existing biodegradable materials is often hindered by inadequate mechanical properties and cost limiting their long-term durability. In response to the plastic crises, interest has intensified in recent years to chemically rationalize polymer with phase properties that favor their breakdown without damaging the marine and soiled environments. The current approach is looking to overcome issues related to thermodynamic immiscibility which is often subject to thermodynamic aging in the face of nonstable interfaces that change physically with time (Vanhee et al. 2000).

Natural polymers fall into a number of functional group categories identified by their repeating chemical unit which are normally not programmable interconvertible with each other despite the adsorptive ability to interface with other chemicals, to show temperature and mechanical responsive behavior, and at the same time to resist change and retain their original structures which are strongly aligned to their chemical and physical properties. However, conditions are applied outside the stability range of the polymer by creating weak chemical links to liberate stable and reactive high energy radicals for creating new bonds in inert structures.

To address the process-cost factor relationship for achieving material sustainability for alternative polymers applicable in a broad commercial context, polymer blending finds considerable utility that makes use of a number strategies to enhance mechanical properties in particular (Paul 1992). Polymer composite technology is seeking to use base materials that are chemically different in tier properties and hold the potential to modulate both physical and chemical properties when strategically combined as a new biodegradable polymer blend. Man-made polymers that are not natural targets for biodegradation but can be chemically engineered to use biodegradable properties through compatible blending of functional are coming of age as the commercial is forced to move away from synthetics. While biodegradable polymers consist of many of the characteristics synthetic chemists aspire to incorporate into synthetic materials, the cost of making available natural biodegradable polymers is being challenged by tailoring chemistry itself to make synthetics susceptible to degradation via chemical routes using stimuli-responsive cleavable linkages - strategies that are becoming important for drug delivery (Zhang et al. 2012), cosmetics (Adli et al. 2020), and biomedical applications (Ju et al. 2009). Biobased polymers are poised to become the new bioplastics to replace petroleum of fossil-fuel plastics which have limited recyclability and utility after successive rounds of waste processing while decreasing the plastic grade quality. Selecting alternatives to "throw-away" plastics inevitably means choosing easily degradable components with limitless recyclability. To control the surge of petroleum-based plastics and their environmental impact, there has been a conscious shift to produce green plastics to replace their shift in product and food packaging and other sale products including toys and sports equipment. Such strategies open exceptional opportunities for overcoming these limitations with appropriate approaches to overcome barriers to their immiscibility, chemical compatibility, as it applies to performance-related behavior.

From an environmental point of view for the management of plastic degradation in soil, Varyan et al. (Varyan et al. 2021) proposed to use low-density polyethylene (LDPE) with natural rubber. With particular emphasis on low-strength synthetics, this approach makes use of low-strength polyethylene. The selection of the additive fits well with the rationale of weak bonds in LDPE in that the elasticity of the rubber additive reduces the elongation of break of the composite accompanied by increased water adsorption and caters for an efficient route for the biodegradability of PE in the soil environment. However, soil degradation of natural rubber composites by microbes was reported to be dependent on filler content, filler particle size, and chemical treatment. Figure 12 shows the different types of enzymes that degrade natural rubber. Particularly, lignocellulosic fillers at the microscale played a prominent role in degradation, but chemical treatment significantly delayed microbial degradation of composites. Microvoids (revealed by SEM) indicated that tensile strength and hardness were sharply reduced facilitated through the formation of microvoids which also resulted in weight loss determined over a period of days (Sareena et al. 2014). Figure 13 shows an image of microvoids by scanning electron microscopy (Muniandy et al. 2016).

Natural polymers are prime targets for replacing fossil-based plastics for mainstream applications. Some of the more common pursuits are poly (lactic acid) (PLA), among others, pertinent to industry including polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), polyhydroxy alkanoates (PHAs), and polybutylene adipate terephthalate (PBAT), silk wool, Nylon-2-nylon-6, Poly β -hydroxybutyrate–co- β -hydroxy valerate (PHBV), cellulose, cyclodextrin, chitin, alginate, polysaccharides, starch, and rubber. The most recent consensus is that materials like PLA are feasible as replacements for synthetics for artificial bioplastics balanced by a high biocontent exceeding 80% (van den Oever and Molenveld 2017). The performance profile of a substituted biopolymer benchmarked against PS is shown in Fig. 14. The modeling of additives or modifiers in the substituted polymer signifies retainment of a high biocontent between 72% and 85%. This might be indicative of the unchanged biodegradation characteristics between mineralized and nonmineralized polymers, namely, PBS, PHBH, PBSA, and PBAT but marked an increase in the moduli state of the polymer (Ángeles-López et al. 2016).

There has been considerable interest for formulating novel biodegradable materials with the capability of enhancing mechanical properties of biodegradable blends which currently are limited by their fragile mechanical and thermal properties. In this respect, cellulose and chitosan (Nasalapure et al. 2020), their derivatives at the micro/nanoscale, exhibit water properties which may be coupled to their mechanical resistance. Polymer blends with short-life properties are of particular interest for tuning their biodegradability as an intrinsic property of the blend. However, some of the most efficient biodegradability rates are associated with biodegradable polymer blends (PCL-Starch) compared to the individual components (PCL and Starch) (Cho et al. 2011), and the inclusion of synthetics tends to drastically slow down depolymerization. Another ongoing concern with acidic biopolymers is the highly acidic nature of biodegradable products into the environment. While the chemistry of biosynthetic degradable polymers can potentially curb the release of acidity products through strategic polymer design, a congruent structure mimicking the blend lactic acid and glycolic was synthesized to lower the acidity of released products relative to both the natural polymer acids. The requirement for neutralization of biodegradable products of polyphosphazene/poly(alpha-hydroxyester) blend were reported to be significantly lower than those associated with the natural polymer acids (Ambrosio et al. 2002).



Fig. 12 Enzymes involved in microbial degradation of natural rubber. (Reproduced with permission from (Soares and Steinbüchel 2022))



Fig. 13 (a) Scanning electron microscope image of natural rubber biocomposites. (Reproduced with permission from (Muniandy et al. 2016))



Fig. 14 Comparison of biobased content mechanical, thermal, and flammability of PLA performance against a synthetic reference PS. (Reproduced with permission from (van den Oever and Molenveld 2017))

Ideally, aligning the plastic properties of the polymer blend to suit its degradability under both biotic and abiotic conditions might be envisaged to broaden its applicability. This serves as an important goal to minimize the persistence of the synthetic component of the blend in diverse aquatic and soil environments that have variable effects on its degradability. For example, natural polymers may degrade differently under the same physical conditions (e.g., temperature) with varying degradation rates and accumulate differently in the environment. Biobased polymers are poised to become the new bioplastics to replace petroleum of fossil-fuel plastics which have limited recyclability and utility after successive rounds of waste processing while decreasing the plastic grade quality. Selecting alternatives to "throw-away" plastics inevitably means choosing easily degradable components with limitless recyclability. To control the surge of petroleum-based plastics and their environmental impact, there has been a conscious shift to produce green plastics to replace their shift in product and food packaging and other sale products including toys and sports equipment.

Controlled biodegradation and the release of nonharmful products from disposal plastics require a better understanding of the chemical and physical factors across all scales. Current and future objectives rest on understanding numerous aspects of polymer blends that relate to the composition type and methods used for blending, influence of blending ratios, and morphology and properties of composite; biodegrading rates and blends could be made smarter using analytical tools. A lack of understanding in the blending of biopolymers with synthetics such as that of starch with LPPE/TPS subjected to multiple cycles of extrusion processes does not often result in significant enhancement of mechanical properties (Peres et al. 2016) as desired. For example, AFM and ToF-SIMS have been used to conclude the distribution of surface energies in PLC and PVC blends and the location of Cl and O ions along the ridges and valleys of the blend (Chan and Weng 2016) (Fig. 15). Also, a leading limitation is in extending the utilization of polymer blends for the biodegradation of synthetics in distinguishing between miscibility, immiscibility, and complex mixed blends in between the extreme phases. In this context, Positron Lifetime Spectroscopy (PLS) and a hydrodynamic approach have been used to determine the level of interfacial adhesion (Ranganathaiah 2015) and to assess the potential for degradability. Such new techniques build upon knowledge relating to the compatibility of polymer blends using more traditional methods (Venkatramanan and Arumugam 2010). The method has been useful in establishing the degree of friction, repulsion, and attraction between biodegradable PCL and PVC components of the blend. For blends comprising a volatile solvent component, information is derived from processing conditions specific to blend ratio and evaporation rates. Computational approach has been insightful in relating such parameters to internal morphological patterns and to characterize emerging morphological types. The method therefore has considerable value in deciphering the mechanics of multistage processing, and often this information remains hidden and unavailable for process optimization (Pokuri and Ganapathysubramanian 2016). Additional factors driving the use of polymer blend technologies as future plastics not only reduce the carbon footprint of nondegradable plastics but also encourage the derivatization of CO and



Fig. 15 The analytical application of atomic force microscopy (AFM) and time-of-flight secondary mass spectrometry (ToF-SIMS) in polymer assessing energy surface distribution in PCL and PVC blends. (Reprinted from (Chan and Weng 2016). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

CO₂ while lowering energy requirements and temperatures, better by-product utilization of waste-degraded products. Efforts in this direction have seen new patented technologies emerging that take these into consideration by making use of polyolefins such as polyethylene (PE) and polypropylene (PP) as ingredients for blends and films with aliphatic polycarbonates (APCs) (Scott and Sanjeev 2013). For polymer blends that require a noninvasive route to their characterization, phasesensitive acoustic microscopy can uniquely probe elastic subsurface material properties revealing a detailed contour with water as a coupling fluid (Ngwa et al. 2005), imaging difference between atomic force microscopy (AFM) and phase-sensitive acoustic microscopy (PSAM) (Fig. 16).

The advantage of using polymer blends composed of both a synthetic and a biosynthetic component is that the degradation of the biosynthetic counterpart which proceeds more readily necessarily assists in the fragmentation of the synthetic part allowing it to be more easily metabolized and thereby reducing the polymers bioresistivity. Polycarbonate (PC) is an example of one such biodegradable – a semicrystalline polymer that exhibits strong rigidity and mechanical toughness. However, the PC has long been recognized for its industrial importance especially as a modified polymer using polyester to generate compositions for molding with increased modulus and tensile strength, but transesterification between PC and polyester was considered undesirable (Bassett 1991). To improve its physicochemical properties and cleavable properties under γ -radiation, PC-ethylene-vinyl acetate (EVA) blends, copolymer blends supplemented with abietic acid(Rosin) (20% Rosin/ 80% PC-EVA), were fabricated. Degradation of the copolymer under γ -radiation and the overall degradative properties of the copolymer are attributed to the photoreactive abietic acid moiety as demonstrated by the crosslinking activity of poly(glycidyl methacrylate) (Kim et al. 2005). The resulting photoactive



copolymer, comprising a thermally stable low-modulus flexible EVA moiety, can potentially function as a biodegradable plastic modulated by the Rosin content (Nouh et al. 2016). An organic synthetic in the form of castor oil used as a plasticizer with starch derived from pumpkin was applied as a multicomponent composition to chitosan. Enhancement in the tensile strength of the composite was correlated to an increase in chitosan with an optimum starch-to-chitosan ratio of 50:50, respectively Here, the ease of microbial biodegradability of the composite in the culture medium was correlated to be a function of the glucosidic bond content of the amylose and amylopectin units of starch and was counterbalanced by the Young's modulus which was strongly influenced by the presence of chitosan (Hasan, Rahmayani, and Munandar 2018). The role of starch degradability was supported by the bioplastic performance of a starch / chitosan composite reinforced by polypropylene as the synthetic component. The optimal ratio of starch/chitosan was established as 65/35 and displayed mechanical properties that were well-suited for material degradation under soil burial demonstrating a high percentage (>80%) after 28 days (Fig. 17).



Fig. 17 (a) Biodegradation rate and (b) composition of polypropylene reinforced starch / chitosan composite. (Reprinted from (Jangong et al. 2019). This work is licensed under a Creative Commons Attribution 3.0 License (CC BY 3.0))

Potential for Smarter Polymer Blends for Controlled Depolymerization

A novel route to degradability of polymers reportedly supports the existence of mechanically gated degradable polymers. The concept relies on combining a stimulated trigger degradation which is further enhanced by a site-specific mechanical force applied on the polymer backbone. In this specific example, cyclobutane (CB) serves as the mechanopore which acts as a "mechanical gate" that modulates an acid-responsive ketal group integrated into the polymer backbone. It has been evidenced that the acid component alone does not elicit the optimum breakup of the polymer in the absence of an ultrasonication step delivering the mechanical trigger (Fig. 18) (Lin et al. 2020b).

The observation also raised a pertinent question whether mechano-triggered bond scission leading to polymer fragmentation was confined to only to single site degradation or whether multiple site depolymerization was also a phenomenon. To shed further light on this area, in a follow-up study, a [4.2.0] bicyclooctene (BCOE) was investigated for properties as a mechanophore. In an exquisite study, Lin et al. (2020a) performed mechanical degradation on the solvent-treated polymer by ultrasonication and reasoned the effect of supplying a mechanical-based trigger for the type of polymer chosen should (a) result in the reduction of the MW, (b) fragmentation will lead to their respective mehanophore products, and finally (c) result in a ring opening of cyclobutane core of BCOE. The increase in sonication expectedly caused an increase in the rate of events (a), (b), and (c) followed by a decrease in rate as result of polymer fragmentation. In fact, it was revealed that the liberation of smaller molecular weight oligomers from stress-induced fragmentation via ultrasonication was operational giving credibility to the existence of mechanophores. The mechanism that was originally thought to be restricted to single-site scission is in fact driven by collective forces over a timescale of 221 h that when delayed, polymer degradation occurs very slowly resulting in multiple scissions across the length of the polymer. Mechanical degradation via this



Fig. 18 Schematic mechanism describing polymer backbone fragmentation by a mechanically gated mechanism. (Reprinted from (Lin et al. 2020b). This work is licensed under a Creative Commons Attribution License (CC BY))



Fig. 19 A schematic description of comparing (a) mechanical induced chain scission and the (b) mechanistic enhancement of polymer fragmentation via a multisite bond scission process. (Reprinted from (Lin et al. 2020b). This work is licensed under a Creative Commons Attribution License (CC BY)).

mechanism allows the degradation of polymers, and in this case multiple fragments were identified tenfold smaller than the original polymer. The mechanism is summarized in Fig. 19.

Concluding Comments

Depolluting the earth begins with drastically diminishing nondegradable plastic accumulation. The chemical merger of synthetic and biobased polymers materials in the form of biosynthetic blends to induce artificial and tuneable properties is just being understood. The quality and performance of the resulting polymer depends on selection of the blend, and the shift to biodegradable polymers to replace plasticbased materials derived from fossil derivatives is currently in development. There is tremendous interest in the application of polymer blends particularly toward the biodegradable plastics. The strategic blending of synthetic and biodegradable polymers continues to evolve but at a slower pace solely to their biodegradable counterparts. Material capability depends on deciphering complex factors to develop highly degradable plastics that also have synthetic value that provide the necessary mechanical support and rigidity that biodegradable plastics lack. To make progress, the evolution of analytical tool is also important to understand complex interfaces to optimize both the structural and functional performance of highly degradable blends. In the advancement of this technological pursuit to implement functionally competent eco-friendly biodegradables, engineering the design of smarter polymer blends should be a prime objective while exploring common and cost-effective synthetic materials.

Cross-References

- ▶ Biopolymer Waste Management: Reuse, Recycling and Disposal
- Engineering Biopolymers

References

- S.A. Adli, F. Ali, A.S. Azmi, H. Anuar, N.A.M. Nasir, R. Hasham, M.K.H. Idris, Development of biodegradable cosmetic patch using a polylactic acid/phycocyanin-alginate composite. Polymers 12(8), 1669 (2020)
- A.-C. Albertsson, C. Barenstedt, S. Karlsson, Abiotic degradation products from enhanced environmentally degradable polyethylene. Acta Polymerica 45(2), 97–103 (1994)
- A.M.A. Ambrosio, H.R. Allcock, D.S. Katti, C.T. Laurencin, Degradable polyphosphazene/poly (α-hydroxyester) blends: degradation studies. Biomaterials **23**(7), 1667–1672 (2002)
- Y.G. Ángeles-López, A. Gutiérrez-Mayen, M. Velasco-Pérez, M. Villavicencio Beltrán, M. Cano-Blanco, Preface: international conference on recent trends in physics (ICRTP 2016). J. Phys. Conf. Ser. 755(1), 011001 (2016)
- W.H. Bassett, Polycarbonate-Polyester Blends. US4981898A (1991)
- A. Be'er, R.M. Harshey, Collective motion of surfactant-producing bacteria imparts superdiffusivity to their upper surface. Biophys. J. 101(5), 1017–1024 (2011)
- S.L. Belontz, P.L. Corcoran, H. Davis, K.A. Hill, K. Jazvac, K. Robertson, K. Wood, Embracing an interdisciplinary approach to plastics pollution awareness and action. Ambio 48, 855–866 (2019)
- M. Bergmann et al., Plastic pollution in the Arctic. Nat. Rev. Earth Environ. 3, 323-337 (2022)
- B. Björkner, Plasticizers and other additives in synthetic polymers, in *Handbook of Occupational Dermatology*, ed. by L. Kanerva, J. E. Wahlberg, P. Elsner, H. I. Maibach, (Springer, Berlin/Heidelberg, 2000)
- A. Chamas et al., Degradation rates of plastics in the environment. ACS Sustain. Chem. Eng. 8, 3494–3511 (2020)
- C.M. Chan, L.T. Weng, Surface characterization of polymer blends by XPS and ToF-SIMS. Materials 9(8), 655 (2016)
- S. Chen, Y. Fuchen, Y. Qiuming, Y. He, S. Jiang, Strong resistance of a thin crystalline layer of balanced charged groups to protein adsorption. Langmuir 22(19), 8186–8191 (2006)
- S. Chen, L. Li, C. Zhao, J. Zheng, Surface hydration: principles and applications toward low-fouling/nonfouling biomaterials. Polymer 51(23), 5283–5293 (2010)
- H.S. Cho, H.S. Moon, M. Kim, K. Nam, J.Y. Kim, Biodegradability and biodegradation rate of poly (Caprolactone)-starch blend and poly(butylene succinate) biodegradable polymer under aerobic and anaerobic environment. Waste Manag. 31(3), 475–480 (2011)
- G.A. El-Hiti, D.S. Ahmed, E. Yousif, O.S.A. Al-Khazrajy, M. Abdallh, S.A. Alanazi, Modifications of polymers through the addition of ultraviolet absorbers to reduce the aging effect of accelerated and natural irradiation. Polymers 14(20), (2022)
- J. Entwistle, D.E. Latta, M.M. Scherer, A. Neumann, Abiotic degradation of chlorinated solvents by clay minerals and Fe(II): evidence for reactive mineral intermediates. Environ. Sci. Technol. 53(24), 14308–14318 (2019)
- R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made. Sci. Adv. **3**(7), 25–29 (2017)

- F.P. Guengerich, F.K. Yoshimoto, Formation and cleavage of C-C bonds by enzymatic oxidationreduction reactions. Chem. Rev. **118**, 6573 (2018)
- D. Hadad, S. Geresh, A. Sivan, Biodegradation of polyethylene by the thermophilic bacterium *Brevibacillus borstelensis*. J. Appl. Microbiol. **98**(5), 1093–1100 (2005)
- M. Hakkarainen, A.C. Albertsson, Environmental degradation of polyethylene, in *Long-Term Properties of Polyolefins. Advances in Polymer Science*, ed. by A.C. Albertsson, vol. 169. (Springer, Berlin, Heidelberg, 2005)
- M. Hasan, et al., IOP Conf. Ser. Mater. Sci. Eng. 333, 012087 (2018)
- A. Hüsler, S. Haas, L. Parry, M. Romero, T. Nisisako, P. Williams, R.D. Wildman, M.R. Alexander, Effect of surfactant on: *Pseudomonas aeruginosa* colonization of polymer microparticles and flat films. RSC Adv. 8(28), 15352–15357 (2018)
- J. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, Marine pollution. Plastic waste inputs from land into the ocean. Science 347(6223), 768–771 (2015)
- X.J. Ju, R. Xie, L. Lang, L.Y. Chu, Biodegradable 'intelligent' materials in response to chemical stimuli for biomedical application. Expert Opin. Ther. Pat. **19**(5), 683–696 (2009)
- C.-h. Jun, Transition metal-catalyzed carbon carbon bond activation. Chem. Soc. Rev. **33**(Scheme 2), 610–618 (2004)
- T.H. Kim, J.Y. Chang, J.U. Choi, W.S. Kim, Synthesis and characterization of a polymethacrylate containing photoreactive abietic acid moiety. Macromol. Res. **13**, 545 (2005)
- H.R. Kim, H.M. Lee, H.C. Yu, E. Jeon, S. Lee, J. Li, D.H. Kim, Biodegradation of polystyrene by *Pseudomonas* sp. isolated from the gut of superworms (larvae of Zophobas atratus). Environ. Sci. Technol. **54**(11), 6987–6996 (2020)
- G. Koteswara Reddy, Y. Kiran, A theoretical mechanism in the degradation of polyolefin plastic waste using phytochemical oxidation process. J. Solid Waste Technol. Manag. 45(4), 468–477 (2019)
- M. Koutny, J. Lemaire, A.M. Delort, Biodegradation of polyethylene films with pro-oxidant additives. Chemosphere 64, 1243–1252 (2006)
- G. Lear, S.D.M. Maday, V. Gambarini, G. Northcott, R. Abbel, J.M. Kingsbury, L. Weaver, J.A. Wallbank, O. Pantos, Microbial abilities to degrade global environmental plastic polymer waste are overstated. Environ. Res. Lett. 17(4), 043002 (2022)
- L. Lebreton, B. Slat, F. Ferrari, B. Sainte-Rose, J. Aitken, R. Marthouse, S. Hajbane, et al., Evidence that the great Pacific garbage patch is rapidly accumulating plastic. Sci. Rep. 8(1), 1–15 (2018)
- B. Lee, A.L. Pometto III, B.B. Theore Jr., Biodegradation of degradable plastic polyethylene by phanerochaete and streptomyces species. App. Environ. Biol. **57**(3), 678–685 (1991)
- Y. Lin, T.B. Kouznetsova, S.L. Craig, Mechanically gated degradable polymers. J. Am. Chem. Soc. 142(5), 2105–2109 (2020a)
- Y. Lin, T.B. Kouznetsova, C.C. Chang, S.L. Craig, Enhanced polymer mechanical degradation through mechanochemically unveiled lactonization. Nat. Commun. **11**(1), 1–9 (2020b)
- J.M. Luz, R. Da, S.A. Paes, D.M.S. Bazzolli, M.R. Tótola, A.J. Demuner, M.C.M. Kasuya, Abiotic and biotic degradation of oxo-biodegradable plastic bags by *Pleurotus ostreatus*. PLoS One 9(11), e107438 (2014)
- E. McGivney, L. Cederholm, A. Barth, M. Hakkarainen, E. Hamacher-Barth, M. Ogonowski, E. Gorokhova, Rapid physicochemical changes in microplastic induced by biofilm formation. Front. Bioeng. Biotechnol. 8, 20200301 (2020)
- S. Mecking, Chemistry can help make plastics sustainable but it isn't the whole solution. Nature **590**(7846), 363–364 (2021)
- K. Min, J.D. Cuiffi, R.T. Mathers, Ranking environmental degradation trends of plastic marine debris based on physical properties and molecular structure. Nat. Commun. 11, 727 (2020)
- T. Morohoshi, T. Oi, H. Aiso, T. Suzuki, T. Okura, S. Sato, Biofilm formation and degradation of commercially available biodegradable plastic films by bacterial consortiums in freshwater environments. Microbes Environ. 33(3), 332–335 (2018)

- K. Muniandy, N. Othman, H. Ismail, Characterization and properties of rattan fibre/natural rubber biocomposites, in *Green Biocomposites*, ed. by M. Jawaid, S. Sapuan, O. Alothman, (Springer, Cham, 2016)
- A.V. Nasalapure, R.K. Chalannavar, B.M. Ravindra, Preparation of poly (vinyl alcohol)/chitosan/ starch blends and studies on thermal and surface properties. AIP Conf. Proc. 1953, 8–11 (2020)
- W. Ngwa, W. Luo, A. Kamanyi, K.W. Fomba, W. Grill, Characterization of polymer thin films by phase-sensitive acoustic microscopy and atomic force microscopy: a comparative review. J. Microsc. 218(3), 208–218 (2005)
- S.A. Nouh, M.M. Magida, L.S. Al-Shekify, I.I. Bashter, Effect of polymer blend types and gamma radiation on the physico-chemical properties of polycarbonate. Radiat. Eff. Defects Solids 171(11–12), 879–889 (2016)
- A.D. Padsalgikar, Biological properties of plastic, in *Plastics in Medical Devices for Cardiovascular Applications*, (William Andrew Publishing, Oxford, UK, 2017), pp. 83–102
- D.R. Paul, in *Mechanical Behaviour of Materials VI*, ed. by M. Jono, T. Inoue, (Pergamon Press, Oxford, 1992), pp. 841–846
- A.M. Peres, R.R. Pires, R.L. Oréfice, Evaluation of the effect of reprocessing on the structure and properties of low density polyethylene/thermoplastic starch blends. Carbohydr. Polym. 136, 210–215 (2016)
- B.S.S. Pokuri, B. Ganapathysubramanian, Morphology control in polymer blend fibers a high throughput computing approach. Model. Simul. Mater. Sci. Eng. **24**(6), 0063 (2016)
- S. Pundhir, A. Gagneja, Conversion of plastic to hydrocarbon. Int. J. Adv. Chem. Eng. Biol. Sci. 3(1), 121–124 (2016)
- C. Ranganathaiah, Characterization of interfaces in binary and ternary polymer blends by positron lifetime spectroscopy. J. Phys. Conf. Ser. **618**(1), 012022 (2015)
- J.D. Rogers, E. Michael Thurman, I. Ferrer, J.S. Rosenblum, M.V. Evans, P.J. Mouser, J.N. Ryan, Degradation of polyethylene glycols and polypropylene glycols in microcosms simulating a spill of produced water in shallow groundwater. Environ. Sci. Processes. Impacts. 21(2), 256–268 (2019)
- A.M. Ronkvist, W. Xie, W. Lu, R.A. Gross, Cutinase-catalyzed hydrolysis of poly (ethylene terephthalate). Macromolecules. 42(14), 5128–5138 (2009)
- C. Sareena, M.P. Sreejith, M.T. Ramesan, E. Purushothaman, Biodegradation behaviour of natural rubber composites reinforced with natural resource fillers – monitoring by soil burial test. J. Reinf. Plast. Compos. 33(5), 412–429 (2014)
- A.D. Scott, N. Sanjeev, Polymer Blends. US 2013020 (2013)
- A. Sivan, M. Szanto, V. Pavlov, Biofilm development of the polyethylene-degrading bacterium Rhodococcus Ruber. Appl. Microbiol. Biotechnol. 72(2), 346–352 (2006)
- F.A. Soares, A. Steinbüchel, Natural rubber degradation products: fine chemicals and reuse of rubber waste. Eur. Polym. J. 165, 111001 (2022)
- G. Suaria, C.G. Avio, A. Mineo, G.L. Lattin, M.G. Magaldi, G. Belmonte, C.J. Moore, F. Regoli, S. Aliani, The Mediterranean plastic soup: synthetic polymers in Mediterranean surface waters. Sci. Rep. 6, 37551 (2016)
- UN Environment Programme, Our planet is choking. 2022. https://www.unep.org/interactives/beatplastic-pollution/
- M. van den Oever, K. Molenveld, Replacing fossil based plastic performance products by bio-based plastic products–technical feasibility. New Biotechnol. 37, 48–59 (2017)
- S. Vanhee, R. Koningsveld, H. Berghmans, K. Šolc, W.H. Stockmayer, Thermodynamic stability of immiscible polymer blends. Macromolecules 33(10), 3924–3931 (2000)
- I.A. Varyan, A.L. Bobkov, I.A. Mikhailov, N.N. Kolesnikova, Ensuring environmental safety and economic benefits from the use of biodegradable materials based on low-density polyethylene with natural rubber additives as products with a short service life. Macromol. Symp. **395**(1), 1–4 (2021)
- K. Venkatramanan, V. Arumugam, Compatibility studies of blends of PPG 4000 and PEG 4000 using viscosity technique. AIP Conf. Proc. **1249**, 59–62 (2010)

- I. Vollmer, M.J.F. Jenks, M.C.P. Roelands, R.J. White, T. van Harmelen, P. de Wild, G.P. van der Laan, F. Meirer, J.T.F. Keurentjes, B.M. Weckhuysen, Beyond mechanical recycling: giving new life to plastic waste. Angew. Chem. Int. Ed. 59, 15402 (2020)
- T.W. Walker, N. Frelka, Z. Shen, A.K. Chew, J. Banick, S. Grey, M.S. Kim, J.A. Dumesic, R.C. Van Lehn, G.W. Huber, Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation. Sci. Adv. 6(47), 1–10 (2020)
- S. Wolff, J. Kerpen, J. Prediger, L. Barkmann, L. Müller, Determination of the microplastics emission in the effluent of a municipal waste water treatment plant using Raman microspectroscopy. Water Res. X. 2, 100014 (2019)
- Y. Wu, C. Liu, X. Zhao, J. Xiang, A new biodegradable polymer: PEGylated chitosan-g-PEI possessing a hydroxyl group at the PEG end. J. Polym. Res. 15(3), 181–185 (2008)
- G. Wypych, UV degradation and stabilisation of polymers and rubbers, in *Handbook of UV Degradation and Stabilization*, 2nd edn., (ChemTec Publishing, Toronto, 2015), pp. 177–292
- Y. Yang, J. Yang, L. Jiang, Comment on "a bacterium that degrades and assimilates poly(ethylene terephthalate)". Science 353(6301), 759 (2016)
- E. Yousif, R. Haddad, No title photodegradation and photostabilization of polymers, especially polystyrene: review. Springerplus 23(2), 398 (2013)
- B.I. Yun, New higher order methods for solving nonlinear equations with multiple roots. J. Comput. Appl. Math. **235**(5), 1553–1555 (2011)
- A.E. Zeenat, D.A. Bukhari, S. Shamim, A. Rehman, Plastics degradation by microbes: a sustainable approach. J. King Saud Univ. Sci. 33(6), 101538 (2021). https://doi.org/10.1016/j.jksus.2021. 101538
- Q. Zhang, N.R. Ko, O. Jung Kwon, Recent advances in stimuli-responsive degradable block copolymer micelles: synthesis and controlled drug delivery applications. Chem. Commun. 48(61), 7542–7552 (2012)
- K. Zhang et al., Understanding plastic degradation and microplastic formation in the environment: a review. Environ. Pollut. **274**, 116554 (2021)
- L. Zhao, M. Qu, G. Wong, D. Wang, Transgenerational toxicity of nanopolystyrene particles in the range of µg L-1 in the nematode: *Caenorhabditis elegans*. Environ. Sci. Nano 4, 2356–2366 (2017)