REVIEW

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Mechanical Recycling of Packaging Plastics: A Review

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The current global plastics economy is highly linear, with the exceptional performance and low carbon footprint of polymeric materials at odds with dramatic increases in plastic waste. Transitioning to a circular economy that retains plastic in its highest value condition is essential to reduce environmental impacts, promoting reduction, reuse, and recycling. Mechanical recycling is an essential tool in an environmentally and economically sustainable economy of plastics, but current mechanical recycling processes are limited by cost, degradation of mechanical properties, and inconsistent quality products. This review covers the current methods and challenges for the mechanical recycling of the five main packaging plastics: poly(ethylene terephthalate), polyethylene, polypropylene, polystyrene, and poly(vinyl chloride) through the lens of a circular economy. Their reprocessing induced degradation mechanisms are introduced and strategies to improve their recycling are discussed. Additionally, this review briefly examines approaches to improve polymer blending in mixed plastic waste streams and applications of lower quality recyclate.

1. Introduction

The global demand for plastics continues to rise. The amount of plastics in circulation is projected to increase from 236 to 417 million ton per year by 2030.[1] Recycling or reuse of plastics in circulation is essential to prevent increased accidental or purposeful release of polymeric materials into the environment, and thus curb environmental pollution. In 2016, only 16% of polymers in flow were collected for recycling while 40% were sent to landfill and 25% were incinerated (**Figure 1**).[1] Recently, European countries have increased efforts to improve recycling rates. In 2018, 29.1 million tons of post-consumer plastic waste were collected in Europe. While less than a third of this was recycled, it represented a doubling of the quantity recycled and reduced plastic waste exports outside the European Union (EU) by 39% compared to 2006 levels. Much of this plastic flow (39.9%) was for packaging.[2]

Packaging recycling is often more economically feasible than other sectors of the plastic market due to high turnover rates of the collected post-consumer waste in Europe, 42% is recycled, 40% is sent for energy recovery and 19% is sent to landfill.[2] The stability of plastics, a key performance feature that has promoted their use, also reduces their ability to degrade. As a result landfill sites become saturated and excess waste is disposed of into the environment.[3] The ubiquity of the material and variability of its disposal has also led to physical fragmentation, introducing micro and nanoplastics into bodies of water, urban environments, conservation areas, and our food chain.[3] The EU Waste Directives imposed landfill taxes that have stemmed some of this tide, increasing recycling rates, although much of landfill avoidance is through questionable energy-from-waste strategies.[4,5] The severity of tax imposed depends on the country in question: 24 out of 27 EU countries have landfill taxes in place while 18 have landfill bans implemented.[2,4,5] In addition to this, the use of non-recyclable packaging will be taxted according to the European Council conclusion dated the 17–21 July 2020.[6] The UK currently charges £94.15 ton^{-1} for land-filling of plastic waste, a 1345% increase to the landfill tax in 1996.[7] According to a report published by The Waste and Resources Action Programme (WRAP) in 2018, the United Kingdom collects 47% of its plastic packaging waste for recycling, although only 43% is converted into valuable feedstock.[2,8]

Using the UK as an exemplar, 40% of the waste collected in 2015–16 was poly(ethylene terephthalate), (PET), followed by 22% polyethylene, (PE), 10.2% polypropylene, (PP), with poly(vinyl chloride), (PVC), and polystyrene, (PS), making up 2% (Figure 1).[9] These five polymers are those primarily used in packaging (**Table 1**). High-density polyethylene (HDPE) and PET are used to produce bottles to package toiletries, food and household cleaning products. Packaging films are primarily made out of linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), and PVC.[10] Plastic beverage bottles are made out of PET, HDPE, and PVC, although the latter is under legislative pressure to ban its use.[10] Single use plastic bags are usually made out of LDPE and LLDPE.[10] In its solid or expanded form, PS is primarily used for packaging purposes in the food and consumer goods industries.

The global plastics economy is largely linear. Plastics are produced, used and more than half of them are disposed with no recovery.[8] With this disposal necessitating more production,

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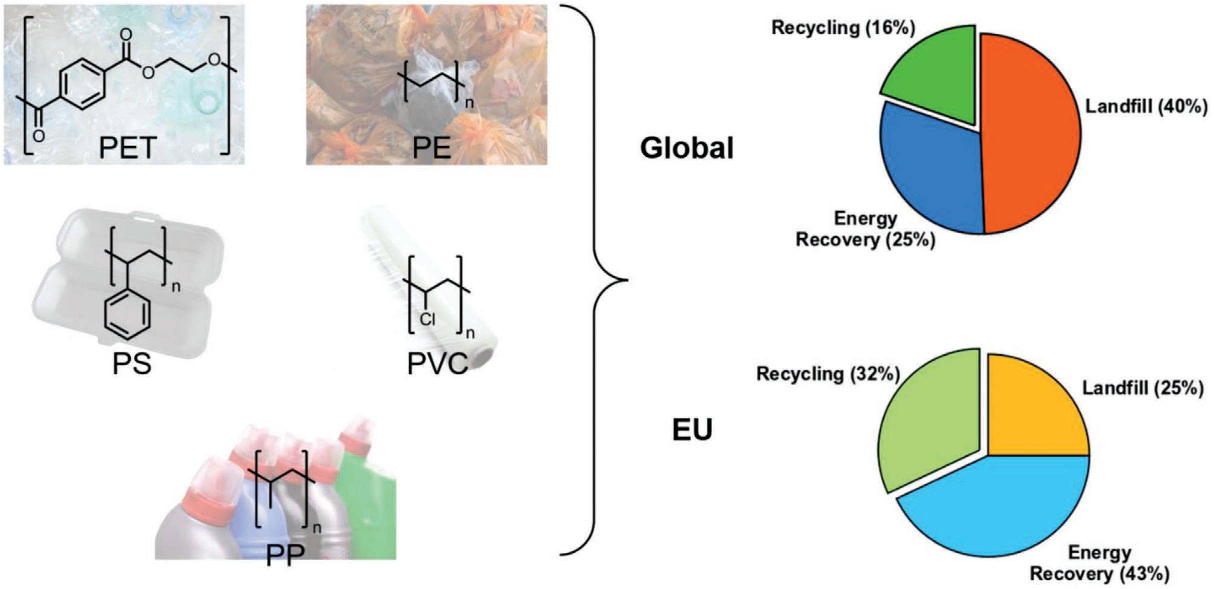


Figure 1. The main packaging polymers: poly(ethylene terephthalate) (PET), polystyrene (PS), polyethylene (PE), polypropylene (PP), and poly(vinyl chloride) (PVC) and current global and EU plastic waste management rates.[1,2]

the dependence on petroleum feedstock and resultant pollution of the planet grows. To preserve the environment while meeting consumption demands, a global effort to shift the linear economy into a circular model must be made.

Much of the focus on sustainable polymers has focused on the development of new feedstocks for the plastics industry, although many of these new polymers struggle to meet the challenging requirements of low cost, production at scale, and exceptional properties. A circular economy model suggests judicious use of the resources we have, including petroleum feedstocks, as it promotes re-valorizing plastics already in circulation. While reduction and reuse economies must be promoted, and biosourced feedstocks that avoid impacting our agricultural industry will continue to grow, the recycling of plastics is a lynchpin to reducing plastic waste.[11–13] With zero land-filling of collected waste as a target for full circularity, recycling must improve.[2]

Table 1. The five main packaging polymers by collection proportion and their main uses.[9]

Polymer	Proportion of total waste collected from kerbside [%]	Applications in packaging
PET	40	Beverage bottles, trays, jam jars
HDPE and LDPE	22	Bottles, bags, bin liners, food wrapping material, squeeze bottles
PP	10.2	Bottles, straws, bottle caps
PVC	<2	Films, trays
PS	<2	Fast-food packaging, food packaging, disposable cutlery, consumer goods

The COVID-19 pandemic has highlighted the need for single use plastics. Potential health risks and societal fears concerning virus-contaminated products increase plastic consumption, introduce consumer fears of reuse and decrease recycling rates.[14] Personal protective equipment (PPE), previously controlled through dedicated medical waste, is now appearing in municipal and institutional waste streams.[15,16] Increases in PPE waste are often unavoidable with mask use either promoted or enforced, creating new challenges for recycling and plastic production. The increased prevalence of PPE, paired with near record low crude oil prices, favors virgin plastic over more costly recyclate.[17] Uncertainties surrounding second spikes and long term behavior change complicates predictions on the lasting impact COVID-19 will have on our plastics economy. Nevertheless, these socio-material challenges necessitate a systems approach to plastic waste management. It is imperative to maintain the polymers in their highest value state, ensuring the materials we depend upon can stay in circulation. Thus, contamination of plastics, sorting and degradation remain the major barriers to efficient recycling.[2,18]

There are four main types of recycling process: primary recycling, secondary recycling, tertiary recycling and quaternary recycling (**Table 2**).[19] Primary recycling involves extruding pre-consumer polymer or pure polymer streams. Secondary recycling requires sorting of polymer waste streams, reduction of polymer waste size, followed by extrusion. With proper control over processing conditions, many polymers can undergo several cycles of primary and secondary mechanical recycling without concern for loss of performance (Sections 3 and 4.1.1). Tertiary recycling is used on polymers no longer suitable for these straightforward mechanical recycling methods. This chemical recycling is often complementary to traditional recycling methods, and can retain significant value if this process

Table 2. Common definitions of plastic recycling.

ASTM D7209 definitions (withdrawn 2015)[22]	ISO 15270:2008 standard definitions[23]	Example
Primary recycling	Mechanical recycling	Bottle to bottle closed loop recycling
Secondary recycling	Mechanical recycling	Recycling into lower value plastic
Tertiary recycling	Chemical recycling	Depolymerization of polyesters
Quaternary recycling	Energy recovery	Pyrolysis

is selective (by returning the polymer to its monomeric feedstocks) instead of non-selective (as in pyrolytic or hydrocracking strategies). Quaternary recycling is applied to plastics that are unsuitable for any other type of recycling and are used for energy recovery via pyrolysis.[20] Quaternary recycling, while retaining little value, may also have unintended consequences from societal consequences and greenhouse gas production.[21]

The need for improved plastic circularity is clear, and chemists, materials scientists and engineers have been responding to this challenge for several decades. The most concerted effort to improve the sustainability of plastics is evidenced by the growth of biodegradable and bio-based plastics.[24] Biodegradable plastics aim to degrade due to natural processes (enzymatic or hydrolytic degradation) while bio-based plastics are often drop-in replacements produced using renewable carbon sources.[24–26] Selective chemical recycling of polymers has more recently gained popularity in recent years, as depolymerisation to form the original monomers offers the potential, if not the reality, of infinite recyclability.[27,28] Biological recycling has also grown, using fermentation and enzymatic degradation to produce downcycle feedstocks.[29–32] Although both chemical and biological recycling are regarded as "green" recycling methods, full and objective life-cycle assessments are needed to evaluate their sustainability. Our rudiementary analysis suggests that mechanical recycling will remain the most effective method to recycle plastics – in terms of time, economic cost, carbon footprint and environmental impact.

Reprocessing of polymers has been further improved with innovation in extrusion technologies. Extruders can be built to include sections to degas, soften, dry and filter extrudate in order to improve polymer melt quality.[33,34] Degassing sections are vacuumed or open vents from the barrel which allow release of a number of volatile compounds within polymer melts. Removal of such volatiles minimizes hydrolysis, acidolysis, and improves polymer melt odor to increase the value of recyclate.[33,34,35] Polymer melts can also be filtered to remove larger, non-volatile, contaminants such as dust or gel particles and improve blend homogeneity, mechanical and optical properties.[33,36,37] Melt filters are chosen according to specific extrusion contamination and can include screen-changers such as slide plates, woven screens, or filter cartridges.[38,39] Lengthening extruders must be balanced against the increase in system dwell times that can exacerbate chain scission. Recycling systems must be designed with consideration to specific degradation mechanisms.[39]

As a foundation for future efforts, this review explores common mechanical recycling challenges and solutions for the main packaging polymers. Their degradation mechanisms will be discussed alongside details of current and past research efforts to improve their recycling, both from a process perspective and through compatibilising polymer blends and incorporating fillers. Efforts to understand the reprocessability of individual packaging polymers explores these themes with more specificity. This review will demonstrate that mechanical recycling is key in improving our plastics use by highlighting the incredible progress made in the last 30 years.

2. Plastic Waste Recycling

2.1. Melt Blending

Extrusion is the foremost method used in mechanical recycling industries to produce regranulated material from the common waste plastics. It is cheap, large-scale, solvent-free, and applicable to many polymers.[21] An extruder uses heat and rotating screws to induce thermal softening or plasticization,[40] after which it is fed through temperature-controlled barrel sections to produce fixed cross-section extrudate (**Figure 2**).[40–43]

The thermal conduction and viscous shearing applied to polymers within an extruder leads to thermo-oxidative and shear-induced chain scission, chain branching or crosslinking of the material.[44–46] This chain degradation reduces the polymer chain length and in turn lowers its mechanical properties and processability.[44] The impact of the extrusion process depends on the chemical characteristics of the polymer and the chosen extrusion conditions. The main degradation mechanism is the formation of radicals along the polymer chain due to oxygen-induced peroxy radical and thermally induced abstraction of hydrogen atoms (**Scheme 1**).[46] These radicals can cause β-scissions of chains, exacerbated by the shear forces applied, decreasing chain length, and as a result viscosity.

Degradation can be controlled to some degree by choice of extrusion conditions. Temperature and screw speed have direct impacts on the process stability as well as the product quality.[43] Extruding at excessive temperatures and screw speeds accelerates chain scission and forms unprocessable polymers.[44,47] Polymer chain lengths also impact

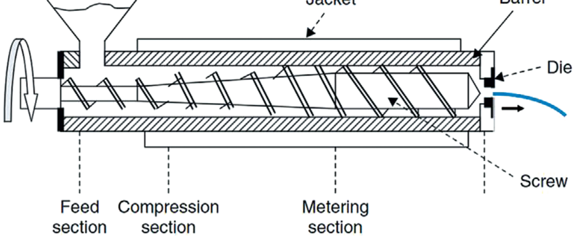
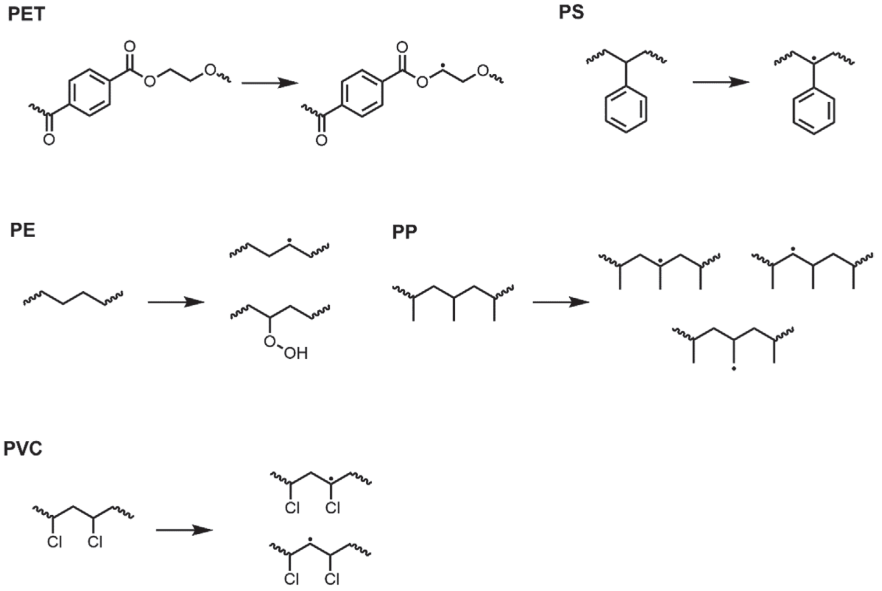


Figure 2. Schematic representation of a single screw extruder. Reproduced with permission.[43] Copyright 2009, Elsevier.



Scheme 1. Common radicals produced during extrusion-induced hydrogen abstraction in absence of oxygen.[46] Consequent reactions are detailed in Schemes 2,5,7,8

degradation behavior: Liu et al. investigated the processing of starch through an extruder to model typical polymer behavior inside the machine.[48] Starch exists in two forms: high branch density amylopectin and linear-style amylose, with the two used to model LDPE and HDPE respectively.[48,49] Starch is chemically inert during extrusion and undergoes simple shear scission, which allows the study of thermo-mechanical chain scission in isolation. The authors suggest that the susceptibility of a polymer to shear-induced degradation is directly proportional to its chain length and degree of chain branching, a phenomenon confirmed by Gooenie et al. and La Mantia et al. for PET.[47,48,50] Thus, the length of polymer chain controls degradation kinetics (suggesting that it can autoaccelerate through repeated extrusion) whereas thermo-oxidative processes are dictated by the both structure of and oxygen diffusion through the polymer matrix.[51] Environmental oxygen reacts with shear-induced radicals and subsequent reactions produce peroxy radicals which propagate radical decomposition.[46] Thus, high oxygen permeability leads to increased thermo-oxidation rates within the material.

Due to the chemical and physical forces at play during extrusion, mechanical recycling often decreases the tensile strength and elongation at break of rPP, tensile strength for rHDPE, elongation at break for rLLDPE, impact strength of rPP, and a multitude of issues for rPET.[46,52,53] To combat the degradation of material properties, many industrial recycling plants opt for an "open-loop or semi-closed-loop" recycling system where virgin polymer (v-polymer) is fed in during the recycling process. For example, in PET bottle recycling, the virgin to recyclate ratio is often 70/30 by weight.[52] While in-extruder degradation reactions can decrease recyclate quality, this is more acutely impacted by the lack of proper polymer sorting. Contamination of recycled material contributes to the decrease in quality and increase in variability of the regenerated polymer (Section 2.2).[52] While often thought of as being extraneous polymers, these contaminants are often associated with the polymers themselves. Pigments used to color plastics can accelerate degradation reactions within extruders. Printing inks and plastic or paper labels can introduce volatile ink components within the final recyclate pellet. Fatty-acid based plastic lubricants, often used to facilitate the easy opening of plastic bags in shops, can be oxidized to produce unwanted odors in the recyclate.[54,55,56] Extraneous plastics from incorrect sorting can exacerbate these issues or even lead to process failure. Trace amounts of PVC in PET streams induces hydrodechlorination at PET processing temperatures. The resultant release of HCl in turn accelerates PET degradation (**Figure 3**) and damages processing equipment.[57,55]

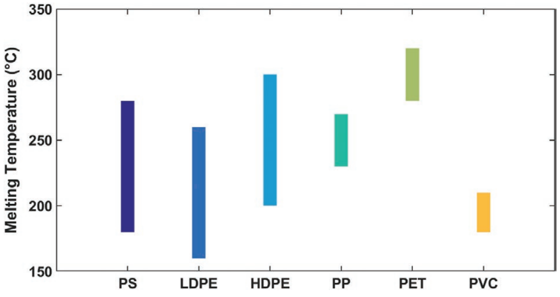


Figure 3. Processing ranges for the six most common packaging polymers.[60]

The presence of polyamides can also catalyze the aminolysis of PET which increases chain scission.[27] If a polymer blends is produced, due to accidental processing of mixed polymer waste streams, both the food-grade safety standards and mechanical properties are compromised., such as polyolefin and PET blends.[58] Effective plastic sorting is key to efficient recycling.[59]

2.2. Waste Sorting for Recycling

Plastics are currently sorted using a combination of automated and manual processes. Near infrared (NIR) technologies are used to determine the polymer type, with optical color recognition sorting plastics into clear and colored fractions.[19,60] There are numerous other complementary sorting technologies including X-rays, density, electrostatics, melting point, hydrocyclons, selective dissolution, and manual sorting.[19,60–62] Plastics may then be flaked by grinding. These flakes can then be further separated using sink/float methods, air elutriation and heat discoloration for further optical separation.[19,28]

Each of these methods depends upon the chemical nature of the bulk polymer. This has limitations on the value of mechanical recycling, as sorting methods are not yet available at scale to differentiate food-grade plastics, which command higher prices, from other recyclates.[63] Accurate polymer marking systems would allow waste sorting facilities to retain value in food versus non-food plastics and aid with sorting of multi-layered materials.[48] While potential general marking systems have been reported in patents,[64–66] they remain commercially elusive. Several patents describe the use of fluorescent dye systems containing rare-earth and organic dyes to separate classes of polymer using spectroscopic techniques.[64–66] Maris et al. and Bezati et al. report the use of other rare earth based compounds for marking uses.[67,68] The former report that their tracing methods function at low concentrations and allow detection in the presence of carbon black, a common filler preventing polymer detection by Fourier transform infrared spectroscopy (FT-IR).[67] Papers discussing the use of heavy metallic elements for fluorescent detection do not mention potential migration of markers from polymers into their surrounding environments nor their potential role as catalysts during extrusion. The use of perylene esters, perylene carboxylic bisimides, and terylene carboxylic bisimides as fluorescent tracers is reported by Langhals et al. but no mention of the method of tracer incorporation is made.[69] Using a multidisciplinary approach, Lussini et al.[70] and Micallef et al.[71] synthesized profluorescent nitroxides to monitor photodegradation in cyclic olefin copolymers and PP respectively during natural aging. The profluorescent nitroxides are composed of a stable nitroxide free radical linked to a fluorophore that fluoresces when radicals are released during the degradation process of the polymer and detected using fluorescence measurements and UV-vis spectroscopy (**Figure 4**).[70,71] Although research has not focused on using these reactive molecules in extrusion, these marking methods have the potential to act as molecular tags due to the susceptibility of polymers to radical attack during processing. While the incorporation of dyes is a key opportunity to improve sorting, questions surround the viability of these dyes in melt extrusion remain unanswered. While they hold the potential to improve sorting accuracy, and thus minimize contamination, a marking and tracing system with secondary anti-degradation (Section 2.3) effects would be most beneficial in realising a circular economy of plastics.

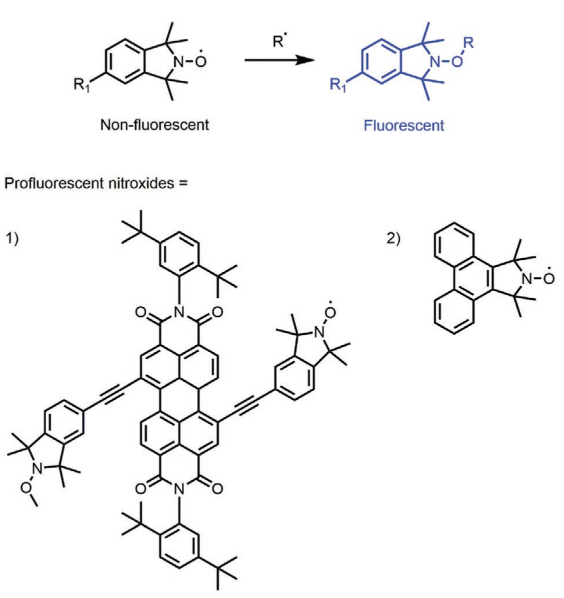


Figure 4. Profluorescent nitroxide compounds used by 1) Lussini et al. and 2) Micallef et al. to monitor radical based aging in polymeric materials.[70,71]

2.3. Stabilizer Use in Plastic Recycling

Free radical reactions, including those occurring during extrusion, can be inhibited through both thermal and light stabilizers.[72] For this reason, polymers are generally extruded with stabilizers, such as antioxidants, to prevent oxidation during both mechanical recycling and product use. Antioxidants can be classified as primary or secondary. Primary antioxidant stabilizers act as radical scavengers and form stable peroxy radicals with oxygen and protect chains during the polymers' lifetime, acting as "chain breaking" antioxidants.[73] Secondary antioxidants, usually sulfur- or phosphorus-based chemicals, protect chains during melt processing of polymers by decomposing hydroperoxide accelerants into alcohols, acting as "preventative" antioxidants.[74] Stabilizers may also absorb and dissipate energy from light to protect chains from UV based degradation.[73] Polymers are generally only stabilized for their first lifecycle as packaging is designed to be short lived, highlighting the need for polymer design to incorporate consideration of end-of-life recycling.[75,76] Some of the main antioxidant types and corresponding compounds are detailed in **Table 3** and **Figure 5**.

UV vulnerability can be triggered by both the chemical composition of the polymer or the additives incorporated during processing. For example, HDPE and PP are more affected by

Table 3. Common antioxidants and their corresponding stabilization mechanisms.

Antioxidant type	Chemical example	Stabilization mechanism
Hindered amines (HALS)	Tetramethylpiperidine, Tinuvin 770	Continuous cyclisation[50,51,77] (primary)
Phenol based compounds	Irganox 1010, Curcumin, Vitamin E	Hydrogen donors[78–80] (primary)
Phosphorous based compounds	Irgafos, PEP 36	Decomposing hydroperoxides[79,80] (secondary)
Carbon black	–	Decomposes hydroperoxides and acts as reinforcing filler[81]

UV exposure than LDPE and high impact polystyrene (HIPS) due to additives incorporated to promote polymer matrix stabilization.[51] PET is less susceptible to UV and thus is usually processed without these protective additives.[76]

While additives offer benefits by mitigating an immediate challenge in reprocessing, they further complicate the recycling process. Antioxidants cause issues in waste sorting, migration and aesthetics. Carbon black is widely used to color polymers, doubling as a reinforcing filler and a UV protector.[80] Again, the benefits for polymer use creates issues with waste sorting due to high absorption rates of IR radiation. Carbon black also poses aesthetic issues, discoloring, and devaluing recyclate. Recent developments in stabilizing systems for food products include the incorporation of active antioxidants in packaging. The active antioxidants stabilize the polymer matrix and have a secondary antioxidant function as they migrate into food. This

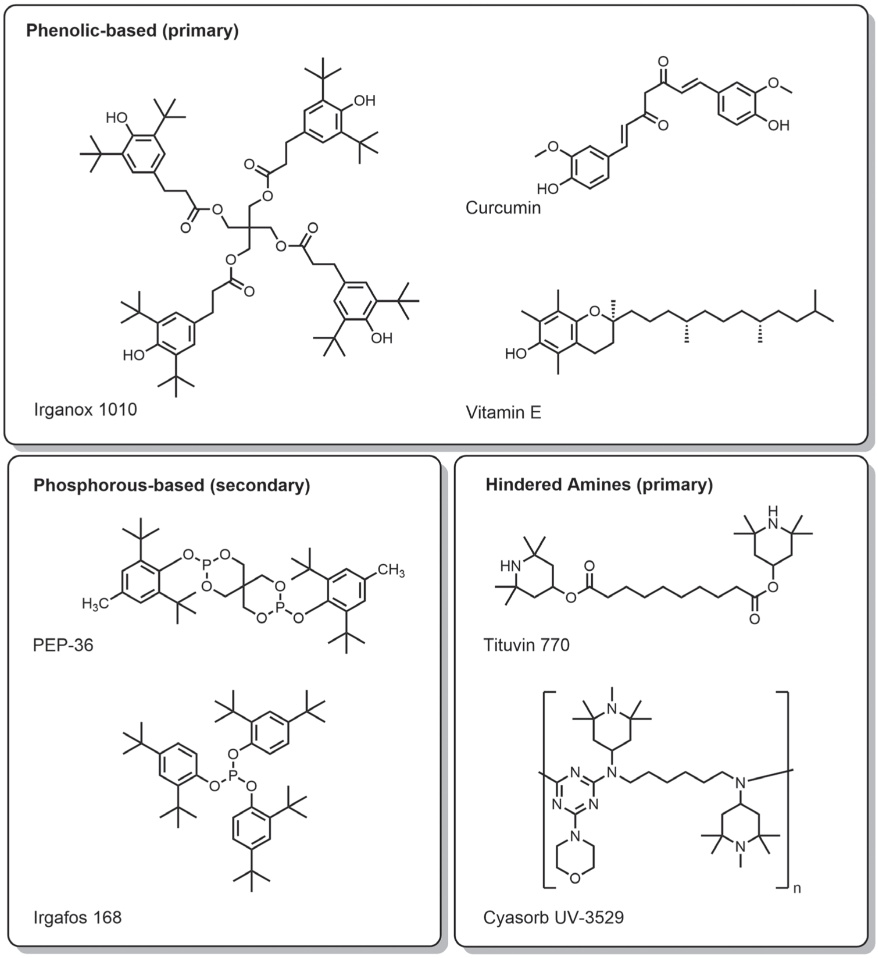


Figure 5. Structures of common polymer antioxidants including 1) phenolic-based compounds, 2) phosphate-based compounds, and 3) hindered amine systems.

eliminates the need for antioxidant incorporation inside food products.[81] Stabilizers can also migrate to phase boundaries present in contaminated polymeric materials and cause areas of degradation where the stabilizer is not properly dispersed.[81] Most, if not all, of these additive mitigations understand their response to continuous recycling, and the potential unintended consequences of thermal and oxidative degradation products. Antioxidants primarily protect polymers for their first processing cycle and research rarely explores antioxidant stability during repeated extrusion cycles.

2.4. Polymer Blends in Recycling

If sorting challenges are not overcome in the plastics industry, value must be found from this impure feedstock. Mixed polymer streams, though prevalent in mechanical recycling, usually form weakened materials due to the immiscibility of the polymer phases. These melt incompatibilities create fracture points in the extrudate.[82,83] Flory-Huggins theory predicts that, when large enough, the Gibbs free energy of mixing for two polymers will disfavor their blending and lead to phase separation.[81,84] Demixed polymers can form an array of phase separated morphologies, including, spheres, cylinder, lamellae and continuous segments.[84–86] Phase separation in blends results in poor mechanical properties due to ineffective stress and strain transfer across phase boundaries. Stress transfer across boundaries can be improved by increasing the number of interactions between phases.[87,88,21] Improved compatibilization of polymer blends would increase value of recyclate through better processability, plant flexibility, product tailoring, and upgraded mixed recyclate performance.[89] Compatibilizers prevent severe demixing of two polymer phases and promote stability of blends when the dispersed phase is larger than 10% through reducing the interfacial tension between the two phases to promote dispersion, stabilize the morphology of the two phases and enhance phase adhesion. Enhancing this adhesion enables proper stress and strain transfer within the blend.[89] Compatibilizers can also prevent damage from contaminants migrating to interphases during the extrusion process. This aids blending of household wastes which have higher levels of contamination.

Polymer blending usually requires very similar chemical polarities due to energetic compatibilities. Copolymer compatibilizers are used to aid in blending polymers of dissimilar chemical polarities.[90,91] These copolymers usually comprise a non-polar backbone with polar functionalities spaced along the chain to promote interactions between both polar and non-polar chains. Common stabilizers include styrenes grafted with maleic anhydride or different polyolefins grafted with maleic anhydride.[90,91] These common stabilizers are known to be expensive and so used in small proportions to minimize costs.[90] Copolymers used as compatibilizers show varying degrees of efficiency which are largely based on their structural features. Di-block copolymers are much more efficient at reducing the interfacial tension between polymers than their random counterparts. However, longer, random chains outperform shorter di-block polymers in terms of surfactant behavior.[21] Moreover, in multi-block compatibiliser systems, the number of entanglements between phases increases and can then interlock. Increased interlocks across the blend interphases improves toughness and adhesion within blends.[92]

Reactive extrusion processes, which combine chemical reactions such as polymer modifications with melt reprocessing, can also be used to improve the miscibility of immiscible polymer blends. There are four different reactive processes to produce copolymers or blends in extruders:[21,93] Redistribution reactions, in which the end group of one polymer attacks the chain of the other to produce graft or block copolymers; crosslinking polymers by reactions between pendant groups present in both polymer chains; ionic bond formation through ionic linking agents or by protonation of a basic polymer by an acidic polymer; dynamic vulcanization which occurs when one phase is immobilized in situ dispersed in a mobile thermoplastic phase.[21,93]

Examples of successful blends of recycled and virgin polymers will be discussed in further detail in subsequent sections of this review article and a more thorough discussion of polymer blending in recycling processes was published by Maris et al.[21] Present blending research and development predominantly focuses on the initial production of blends, without consideration for their applicability in continuous recycling. We suggest it is essential to consider the consequences of blending strategies on future reprocessing lifecycles. Incorporating an end-of-life recycling as a design principle for blends, where due consideration of the impact of further extrusion on polymer melt temperature, degradation and stabilization is key.

3. Mechanical Recycling of Poly(ethylene terephthalate)

Virgin PET (vPET) has excellent mechanical properties, processability and barrier properties.[42] PET is thus widely used for packaging, with a large proportion of this being food grade.[46] Virgin PET is ductile and boasts high elongation at break values of >80% which have been found to rapidly reduce by a factor of 4 when mechanically recycled (**Figure 6**).[28] The sharp reduction in the properties of the material is due to deterioration thermo-oxidative and thermo-mechanical degradation of the chains as well as hydrolytic scission.[47,53]

3.1. Degradation Mechanisms of Poly(ethylene terephthalate)

Chain scission lowers polymer molecular weights and forms potential side products including carbon dioxide, water and carboxylic acid or aldehyde end groups.[94] Shorter chain lengths reduce polymer elasticity, embrittle the polymer, and decrease viscosity. Melt viscosity reductions thus require recalibration of processing equipment. Moreover, contaminants introduced during the life-cycle of the PET promote chain scission reactions in post-consumer polymer melts. In particular, traces of poly(vinyl alcohol) (PVA), or poly(lactic acid) (PLA), and PVC can leach acids and promote acidolysis or hydrolysis of PET during extrusion (**Scheme 2**).[53] PET can also undergo

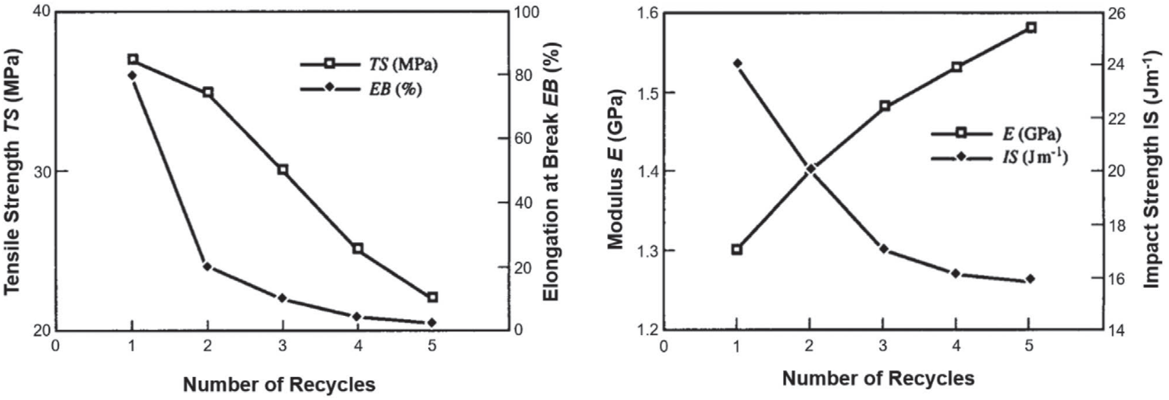
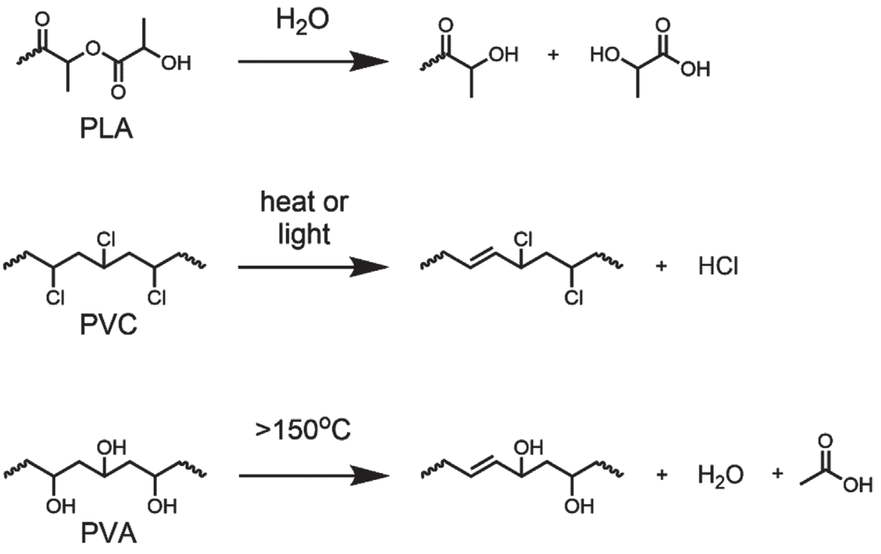


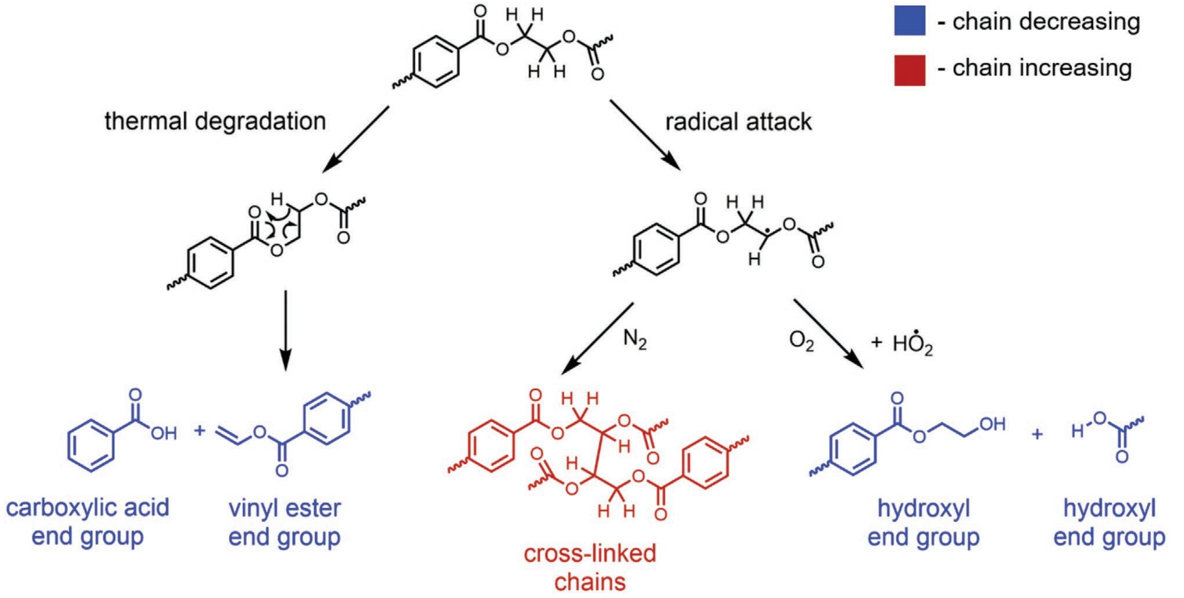
Figure 6. Left: Tensile strength and elongation at break versus number of recycles for PET. Right: Young's modulus and impact strength versus number of recycles for PET. Reproduced with permission.[47] Copyright 1994, Elsevier.

crosslinking of its chains that adversely impacts recyclate quality.[50] Large increases in viscosity due to crosslinking reactions pose a problem for large scale recycling, as increased torques can damage processing equipment. Once PET has been subjected to irreversible damage due to mechanical recycling, it is usually destined for landfill due to potential damage to reactors during pyrolysis.[95,96]

PET chains degrade by free radical attack or by carbon to hydrogen transfers (**Scheme 3**). The stress and heat of the extruder produce a macroradical to react with oxygen and form a peroxy-based radical. Radical hydrogen abstraction can reform the macroradical and produce hydroperoxide that decomposes to form two new radical species that can initiate more macroradical chains. High concentrations of carboxylic acid end groups promote thermo-oxidation.[90] Thus, increased cycles of mechanical recycling will cause faster rates of chain scission due to thermo-oxidation. As well as this free radical degradation, PET undergoes crosslinking, esterification, transesterification, and hydrolysis reactions (Scheme 3).[47,50,53] In the absence of oxygen, radical crosslinking can also occur.[50,53] These degradation reactions impact the polymer's microstructure. The microstructure of PET has three fractions: mobile amorphous, crystalline and rigid amorphous fractions.[97] The partially ordered rigid amorphous fraction lies between the ordered crystalline and mobile amorphous fractions.[98] The mobile amorphous phase is most readily attacked,[99] releasing of short chains which fold into intercrystalline domains and nucleate crystallization. Thickening and rearrangement of the crystalline domains is observed, with new crystalline domains with



Scheme 2. Reaction pathways PLA, PVC and PVA can undergo during extrusion which can induce acidolysis or hydrolysis of PET.



Scheme 3. Reaction pathways PET undergoes during mechanical recycling.

smaller average sizes formed with increased recycling,[99] causing increased embrittlement and Young's modulus.[42]

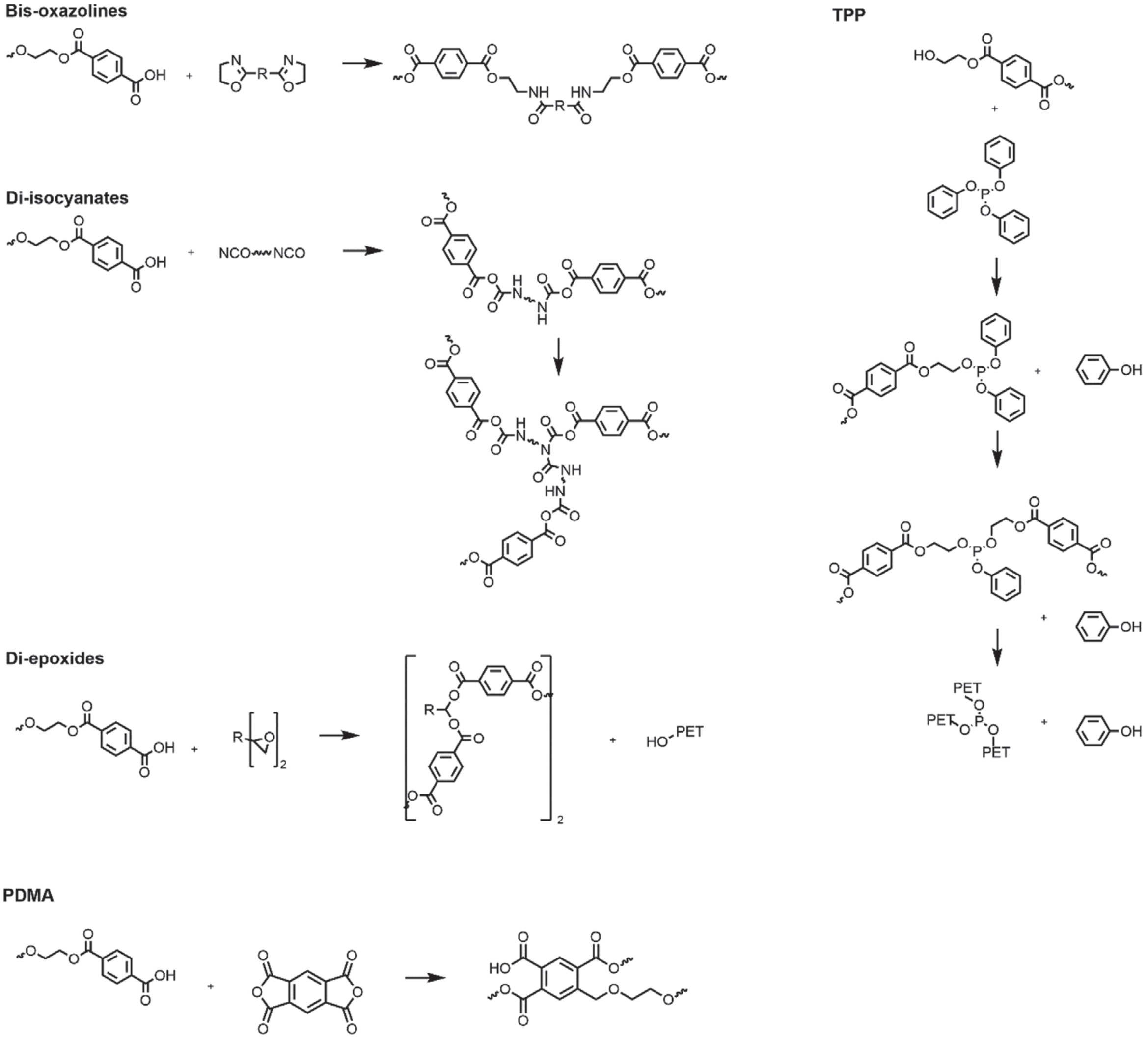
3.2. Improvements to Poly(ethylene terephthalate) Recycling

Improvements to PET mechanical recycling are well researched.[50,53,99–102] Much of the modern research builds from initial efforts by La Mantia and Vinci[47] Their article investigates the maximum number of extrusions PET can undergo before it is unsuitable for (re)manufacturing. Beyond three recycling cycles changes in the material properties are less pronounced (Figure 6), as degradation reactions are slow due to polymer size.[47] This result confirms the molecular weight dependence on degradation kinetics where the larger the polymer chain, the faster the degradation kinetics.[47,48] To promote chain extension, protect chains, improve mechanical properties and add value to the recyclate, additives are often incorporated during PET recycling.[43,99] To circumvent the effects of the thermal oxidation, metal-based stabilizers such as tin mercaptide or lead phthalate have been reported, as has extrusion in inert atmospheres.[50,53] Solid state polymerization (SSP) can also be used to react hydroxyl and carboxyl end groups of existing and broken chains to reverse scission. To prevent the radical attack on chains, radical scavengers such as organic phosphates are used. Gooneie et al. reported the efficacy of ((1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octan-4-yl)methoxy)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DP), an additive that additionally imparts flame retardant properties. The decomposition products of DP act as radical quenchers and delay the on-set of PET crosslinking;[50] the authors do not discuss the potential impact on β-scission due to radical attack. Of these methods, reactive chain extension shows the largest promise in improving PET recyclate quality.

3.3. Chain Extender Use in Poly(ethylene terephthalate)

The uses of chain extenders that reverse some of the damage caused by PET chain degradation are inexpensive and convenient, promoting reactions inside processing equipment. These oligomers target reactive chain ends to fuse chains back together and increase molecular weight. The extenders can have two or more reactive groups to maximize the number of reactions between chains, leading to both branched and linear topologies.[99,101–103] Chain extenders can also help to compatibilize two different grades (i.e., PETs with significantly different structures or molecular weight) by reacting the chains together and reverse the chain scission induced by thermo-oxidative processes.[84] Common chain extenders include oxazolines, isocyanates, epoxides, lactams, hydroxyls, carboxylic acids, and organic phosphites and phosphates.[99,101–103] Examples of commonly used multifunctional extenders are shown in **Scheme 4** and their functionalities are present in commercial extenders such as Joncryl derivatives.

Increases in chain length can be dynamically measured in-situ by monitoring increases in torque values as chains extend. Cavalcanti et al. report using triphenyl phosphite (TPP) to successfully extend the chains through their carboxyl and hydroxyl terminal groups.[99] Incarnato et al. describe using pyromellitic dianhydride (PMDA) as a chain extender in reactive extrusion in an attempt to induce long chain branching of PET (**Figure 7**). The presence of entangled networks from PMDA branching promotes increased intrinsic viscosity (η*), decrease in melting temperature and increase in cold crystallization temperature.[100] The use of PDMA increases the torque of virgin PET quicker than TPP, by similar factors (≈2–3) and at lower weight percentages (Figure 7). This difference is somewhat surprising as multifunctional extenders usually outperform bifunctional


Bis-oxazolines
Di-isocyanates
Di-epoxides
PDMA
TPP

Scheme 4. Common reactions between chain extenders: bis-oxazolines, di-isocyanates, di-epoxides, pyromellitic dianhydride (PMDA), triphenyl phosphite (TPP) and PET.

extenders, suggesting that both the extrusion conditions and extender reactivity play significant roles. PMDA has also been used to chain extend PET, polyurethanes, PLA, and other specialty polymers.[104–108]

Chain extenders are now commonplace in industrial settings.[101,109–111] Tavares et al. report that incorporation of Joncryl PR 002, a multifunctional epoxide oligomer, is more effective in recycled PET than in virgin streams.[109] They report that less than 1% of the Joncryl additive is required to reverse the decrease in molecular weight due to extrusion induced chain scission.[95] In contrast, Duarte et al. report that a blend of Joncryl 4368 and 4370 increases the molecular weight of vPET more effectively than post-consumer recycled PET, although they agree that 1% of the additive is required to reverse the effects of process induced degradation.[109,112] The increased effectiveness of the multifunctional chain extenders such as PDMA, TPP, and Joncryl additives is owed to increased reaction site numbers between end groups.[96] The type of reactive site also affects chain extension: di-isocyanates are more reactive than di-epoxides with PET terminal groups for chain extension.[101] Benvenuta Tapia et al. report the use of reversible addition-fragmentation chain-transfer (RAFT) polymerization to produce poly(styrene-*co*-glycidyl methacrylate-*b*-styrene-*co*-acrylonitrile triblock copolymers, where the epoxide based chain extender increases the molecular weight and viscosity of rPET in reactive extrusion and matching similar thermal properties to vPET, with a direct correlation between the concentration of glycidyl methacrylate (GMA) and mechanical properties (**Figure 8**).[102]

While promising, it is important to note that these chain extenders may not be suitable for food-grade PET production

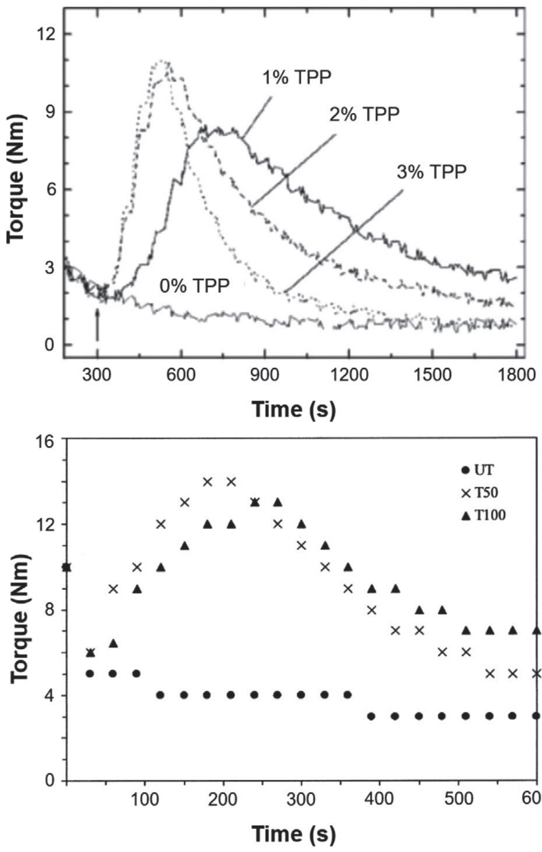


Figure 7. Top: The effect of TPP on the torque of PET processed at 260 °C and 60 rpm. Bottom: The effect of PDMA at 0.5% and 1% on torque for PET processed at 280 °C at 100 rpm. Reproduced with permission.[99] Copyright 2007, John Wiley and Sons. Reproduced with permission.[100] Copyright 2000, Elsevier.

due to potential migration and regulatory issues. Unreacted small oligomers, phosphites, or other molecules may leach through materials into packaged products and induce cytotoxicity. They may also disrupt crystallinity or crystallization rates.[102] Many chain extenders have poor thermal stability, creating more risk from multiple extrusions.[101] In some cases chain extension can produce excess acid groups during the extension process, which then increases degradation rates, as most acutely observed in TPP-extended PET.[99,102]

The dominance of PET in packaging research efforts focus on improving the mechanical recycling process.[53,102] While inclusion of additives can improve the properties of the recycled PET, their exact effects, especially at end-of-life, are not well understood and thus can further complicate recycling. Despite these risks, commercial use of chain extenders is growing and indeed upgrading deteriorated recyclate.[109,112] Future research should focus on the applicability and mechanism of action of extenders over larger numbers of extrusion cycles to understand the impact on a circular plastics economy. Continual reprocessing of chain-extended PET is under-investigated and may impact degradation mechanisms or recyclate variability.

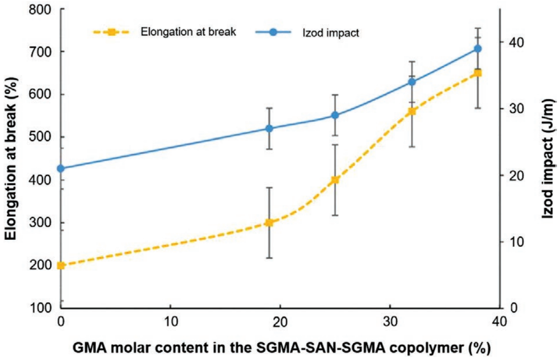
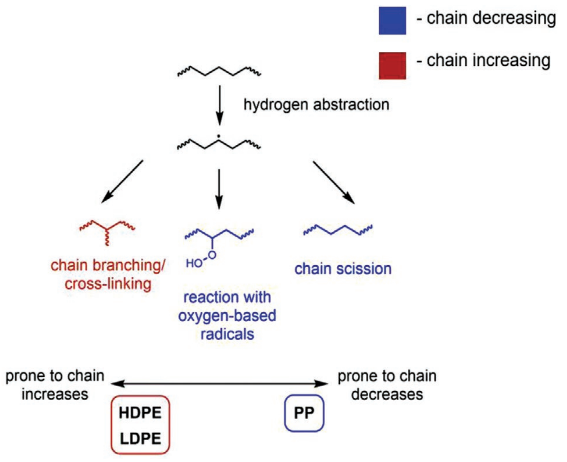


Figure 8. Elongation at break and Izod impact versus GMA content during chain extension of rPET. Reproduced by permission.[101] Copyright 2018, Springer Nature.

4. Mechanical Recycling of Polyolefins

Degradation during the mechanical processing of polyolefins can form a variety of carbon based molecules such as alcohols, aldehydes, ketones, acids and cyclic ethers and esters and short-chain hydrocarbons.[113] Constructed solely with carbon and hydrogen bonds, each of the three main polyolefins used in packaging (HDPE, LDPE, and PP) have different degradation mechanisms to each other, and are significantly different than other packaging polymers (**Scheme 5**). Radical attack does generate macroradicals along the polymer backbone, but following initial attack β-scission of the polymer chain forms other macroradicals. Intramolecular radical transfer can occur to form a variety of other radical species, with recombination or dissociation of these radicals forming shorter, branched, or crosslinked polymer chains. Reaction of polymer macroradicals with any oxygen-based radicals will introduce carboxylic acid, carbonyl and hydroxyl end groups which may in turn promote further degradation.[114–121] HDPE and LDPE show higher crosslinking



Scheme 5. General reaction scheme of polyolefins undergoing extrusion.

rates whereas PP is more prone to chain scission (Section 4.1.1, 4.1.2, and 4.2).[122] Attack of polyolefin chains occurs primarily in the amorphous phase of the polymer as oxygen struggles to diffuse through highly crystalline domains.[51]

4.1. Polyethylenes

PEs are structurally simple polymers with remarkably high strengths that have promoted widespread use in packaging. HDPE (0.952 g cm^{-3}) has a high degree of crystallinity and is stronger yet less elastic than the more loosely packed LDPE (0.924 g cm^{-3}). The less crystalline LDPE is more transparent and elastic than HDPE and so is widely used for film production. The difference between the two polymers' densities can alter their degradation mechanisms during extrusion, as described below.[123]

4.1.1. High-Density Polyethylene

HDPE shows competing mechanisms of chain scission and chain branching during extrusion, depending on extrusion conditions. Pinheiro et al. report that in oxygen rich environments, the carbonyl concentration in HDPE increases due to thermo-oxidative chain scission of the polymer backbones via the creation of stable carbonyl end groups.[117] In low oxygen environments, the shear-induced degradation instead causes chain scission and double bond production to dominate over chain branching.[114,117] During continuous extrusion the polymer chains progressively decrease in length, shortening the chains and making them less susceptible to shear forces.[48,117] However, the short chains are still susceptible to attack from the longer chain macroradicals at double bonds. The reaction between shorter polymer chains containing double bonds and longer macroradicals produces long chain branching.[117] Researchers have also confirmed simultaneous chain scission and branching using less direct experimental methods.[44,117,118] Oblak et al. performed 100 consecutive extrusions on HDPE (**Figure 9**). They note that there are significant structural changes in the material during the first 30 cycles but an oscillatory plateau in properties is then observed. They speculate that chain branching is the dominant chain chemistry occurring during the first 30 cycles, chain scission between 30 and 60 extrusion cycles whereas above 60 extrusion cycles chain crosslinking predominates, resulting in up to a five-fold increase in viscosity.[44] This crosslinking is overcome by reducing screw speeds whereas chain scission reactions can be enhanced by changes in screw speed, meaning that the challenges of continued recycling of HDPE are easier to mitigate than for PET.

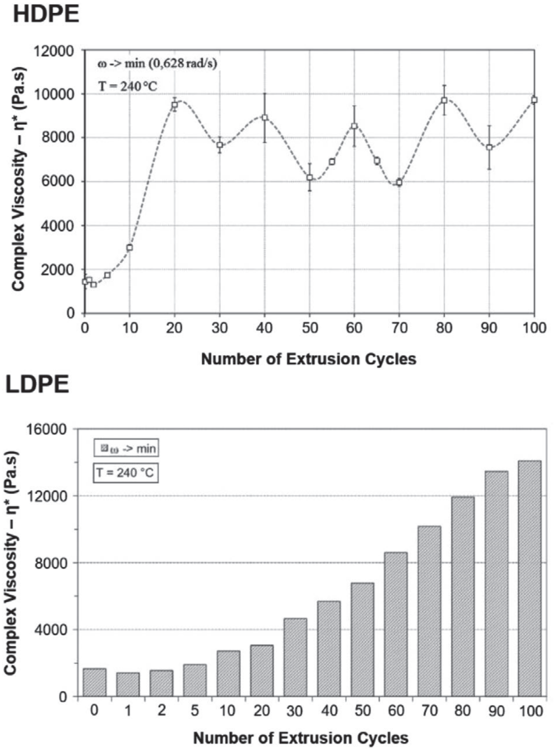
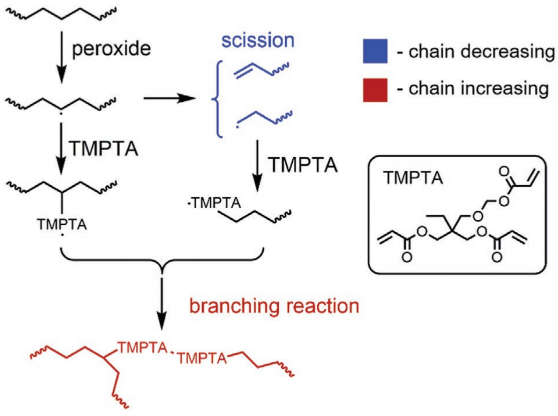


Figure 9. Complex viscosity versus number of extrusion cycles for top: HDPE and bottom: LDPE. Reproduced with permission.[44] Copyright 2015, Elsevier. Reproduced with permission.[131] Copyright 2012, Elsevier. Trend lines are reproduced from original sources.

While degradation of HDPE extrudate can be minimized through extruder control, the inclusion of stabilizing additives is also commonplace (Section 4.1.3). Reactive extrusion of HDPE includes direct post-polymerization functionalization, grafting or crosslinking.[116] Control over crosslinking is realized using radiation, moisture and thermo-chemical methods.[116,124,125] Peroxides have been used to induce crosslinking between chains to minimize chain scission and maintain mechanical properties.[124–126] Kim and Kim employed trimethylol propane triacrylate (TMPTA) to minimize the chain scission and disproportionation side reactions induced by peroxides (**Scheme 6**),[124,127] although the melt flow index (MFI) reduced by more than a factor of 10 on inclusion of TMPTA,



Scheme 6. Reaction scheme for controlled degradation of PE using peroxides and trimethylol propane triacrylate (TMPTA).[127]

suggesting decreased crosslinking yet Su and Huang report increased branching with TMPTA use in PP.[124,127] Chain linking to other polyolefins in blended systems, and using epoxides, diamines, acrylates, phosphates and silanes is also reported.[128,129] Other efforts to improve HDPE include grafting with initiators or polymerizable monomers such as parabenzoquinone, vinyl silanes, maleic anhydrides, styrenics, oxazolines, and acrylics, although the target in these instances is often specialist PEs rather than packaging polymers.[116,124]

4.1.2. Low-Density Polyethylene

LDPE has a highly branched structure, inhibiting packing and reducing density. Branched structures are more susceptible to crosslinking or chain branching reactions during extrusion, with more end groups and lower thermal stability. Increases in LDPE molecular weights during recycling is observed using rheology, thermo-rheology, GPC and FT-IR studies (Figure 9).[120,130,131] While degradation mechanisms that increase molecular weight predominate during LDPE reprocessing, an underlying competition between chain scission and chain branching remains. As LDPE is extruded, it shows initial chain cleavage followed by recombination and chain branching. In the presence of oxygen, radical chain reactions will enhance scission rates. In inert atmospheres and low oxygen conditions macroradicals will cross-react to induce higher rates of chain branching. The affinity of LDPE for chain scission decreases as it branches due to a decrease in the radius of gyration.[120] This accounts for differences observed by Dostá et al. for LDPE and Oblak et al. (Figure 9) for HDPE.[120,131] As it is predominantly found in packaging with short circulation times, LDPE is not usually stabilized against reprocessing degradation posing problems for circular recovery and recycling systems.[51]

4.1.3. Stabilizer Use in Polyethylenes

PEs often require stabilizers to limit thermo-oxidative degradation during melt reprocessing and maintain recyclate quality. These additives also improve UV radiation stability.[74] Combinations of UV inhibitors, thermal stabilizers and anti-oxidants are vital as the ketones and peracids that can form as degradation products form at different rates under UV and thermo-oxidative stresses.[72] Additives are chosen for their solubility, dispersion and stabilization in the host matrix, and to minimize their evaporation and volatization during processing. Phenols such as Irganox 1010 (Figure 5) are common antioxidants, functioning as both hydrogen bonding stabilizers and alkyl peroxy radical traps.[74] The combination of phenolic and phosphate-based antioxidants is often more effective than a phenolic compound alone.[77] Antagonistic effects can also occur between stabilizing systems. In systems stabilized with hindered amine light stabilizers (HALS) and hindered phenols, nitroxyl radicals produced from photooxidation react with the phenolic groups, disrupting the redox system responsible for stabilization. Peña et al. report that a three-additive system overcomes the majority of antagonistic effects and suggest carbon black as a third additive due to its adsorption-desorption properties.[80] Again, decisions that mitigate an immediate problem propagate during subsequent use; the aforementioned use of carbon black prevents sorting and darkens recyclate, decreasing both quality and price during subsequent processing cycles.

Due to the migration of antioxidants and potential carcinogenicity, research efforts have focused on the development of safer, sustainable or natural antioxidant alternatives or the inhibition of migration through covalent bonding to the polymer chain.[73] Many of these risks are unknown, with limited cytotoxicity data known for antioxidants or metal-based catalysts often used in their synthesis. Natural antioxidants include bio-derived phenols such as caffeic acid, ascorbic acid, α-tocopherol (vitamin E), curcumin, quercetin, and β-carotenes.[74,132] Inclusion of 0.2 wt% vitamin E provides a higher level of protection than the same weight percentage loading of synthetic counterparts Irganox 1010 and 1076.[74,132] Similarly, studies by Tatraaljai et al. and Zia et al. on the inclusion of curcumin during PE processing showed improved chain protection compared to Irganox with improved water barrier properties.[74,133,134] In an attempt to promote the use of bio-derived antioxidants, Iyer et al. discuss the inclusion of very low cost antioxidants stemming from natural agro-wastes (**Figure 10**). The agro-waste stabilisers are not as effective as the commercial alternative Irganox 1010 but still protect against embrittlement of LDPE (Figure 10).[74] The use of stabilizers can increase the lifetime of plastic products and can provide protection against thermo-oxidation during mechanical recycling. As is now a common feature in this review, there is little understanding of the impact of these stabilizers over multiple processing cycles.[79]

4.2. Polypropylene

PP has a high volume to weight ratio, a challenge for landfills[135,136] even as it has glossy appearance, good optical properties, and high tensile strength make it an essential packaging polymer.[125] The presence of tertiary carbons along the PP backbone[122,137] are more prone to shear degradation, introduces a more reactive methine functional group and increases flammability.[91,122,138] Repeated recycling of PP reduces molecular weights owing to thermo-mechanical and thermo-oxidative chain scission, increasing the degree of crystallinity to afford higher elastic moduli and reduced elongation at break.[139,140]

PP radical degradation is very similar to that of PE with hydroperoxides abstracting hydrogen atoms from the polymer chains.[122,137] The spherulitic structure focuses degradation at these spherulite boundaries, segregating catalyst residue and additives in the amorphous phase (**Figure 11**).[137,141] Macroradicals produced combine or undergo β-scission.[91,119,122] As the methine proton is more reactive, the formation of peroxyradicals is enhanced but the resultant radical is stabilized versus PE.[138,142] At lower temperatures, PP is stable to processing for up to five extrusion cycles. Beyond five cycles and/or at higher temperatures, significant chain scission limits performance, contrasting with the chain branching and crosslinking observed in PEs.[140]

To counter the radical attack on the polymer chains during extrusion, PP also requires stabilization. Both phenolic and hindered amine systems are common.[143] PPs spherulitic structure

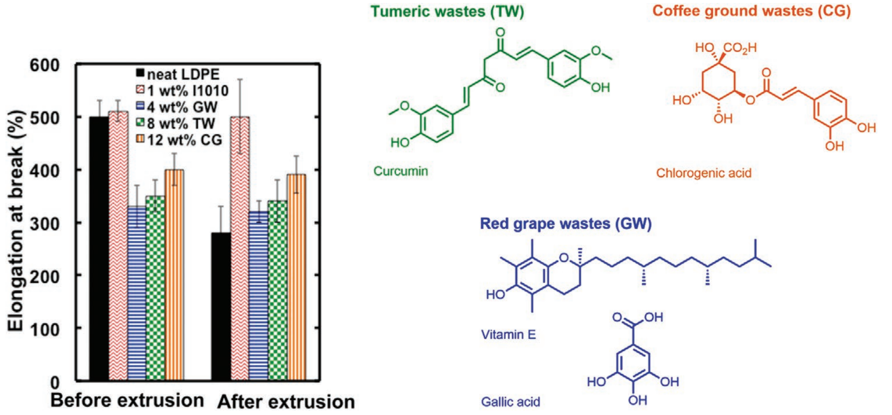


Figure 10. Elongation at break values for LDPE extruded with antioxidant agro-wastes. Reproduced with permission.[75] Copyright 2015, American Chemical Society.

impacts the distribution of stabilizers and antioxidants (Figure 11).[141,143] Smaller spherulites allow a uniform distribution of stabilizers throughout the polymer matrix, improving radical capture reactions and thus efficacy.[141,143] Taniike et al. reported that the distribution of the stabilizer within the PP polymer matrix is independent of the type of antioxidant or stabilizer.[141] Bio-derived agro-wastes include tannin wine seed extracts, seed polyphenol extracts and virgin wine wastes can stabilize the product and delay the onset of MFI oxidation degradation for up to 100 h.[144] Lignin, a natural phenolic polymer, can also successfully stabilize PP and recycled PP (rPP) at concentrations between to 2–5 wt%. The lignin acts as both an anti-oxidant and as a filler to increase the rigidity of the polymer matrix. Synergistic effects are reported when lignin is combined with Irganox 1010 due to increased diffusion of the commercial antioxidant throughout the polymer matrix.[145] These stabilisation methods have not been tested under extrusion conditions, so their applicability to protect over several reycling life-cycles is unkown.

The migration of stabilisers in PP is also under-investigated, raising potential human and environmental health concerns, compounded by the localisation of these chemicals in more mobile amorphous regions. To prevent antioxidant loss through volatization and migration, Gao et al. describe the grafting of antioxidants onto nanosilica particles.[142] Reduced loss of antioxidant increased the stabilisation effects after accelerated thermal aging (**Figure 12**).[142] The migration of antioxidants from the polymeric material can also be purposefully exploited. Controlled release of antioxidants from PP matrices can provide both antioxidant protection of the polymer matrix and to contained food products. Thymol and carvacrol were incorporated at 8 wt% in PP, with both active antioxidants released into food-like simulants and remained in the polymer over 15 days.[146]

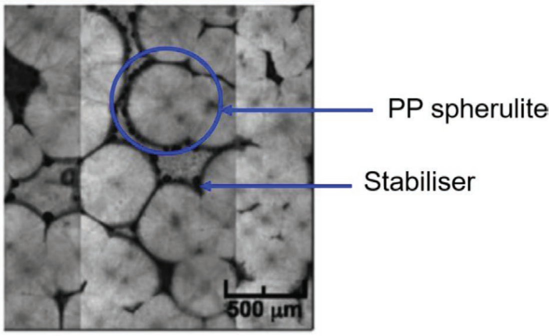


Figure 11. Optical image showing the spherulitic structure of PP. Reproduced with permission.[142] Copyright 2012, John Wiley and Sons.

4.3. Polyolefin Blends

Polyolefin blending has been an active area of research for several years due to the mixed polyolefin (MPO) waste fraction separated using flotation sorting of plastic wastes.[77,131]

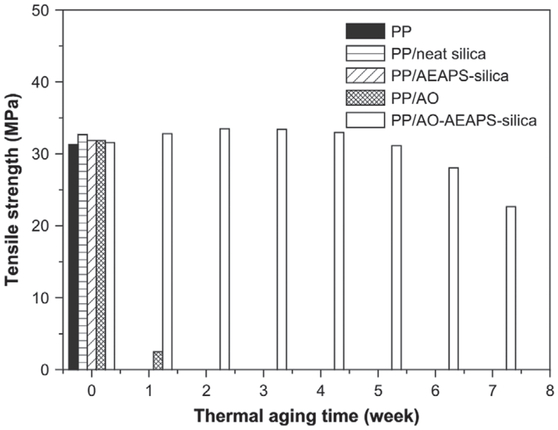


Figure 12. Effect of thermal aging on tensile strength of PP samples stabilized with AO and coupled to silica using AEAPS. Reproduced with permission.[142] Copyright 2008, Elsevier.

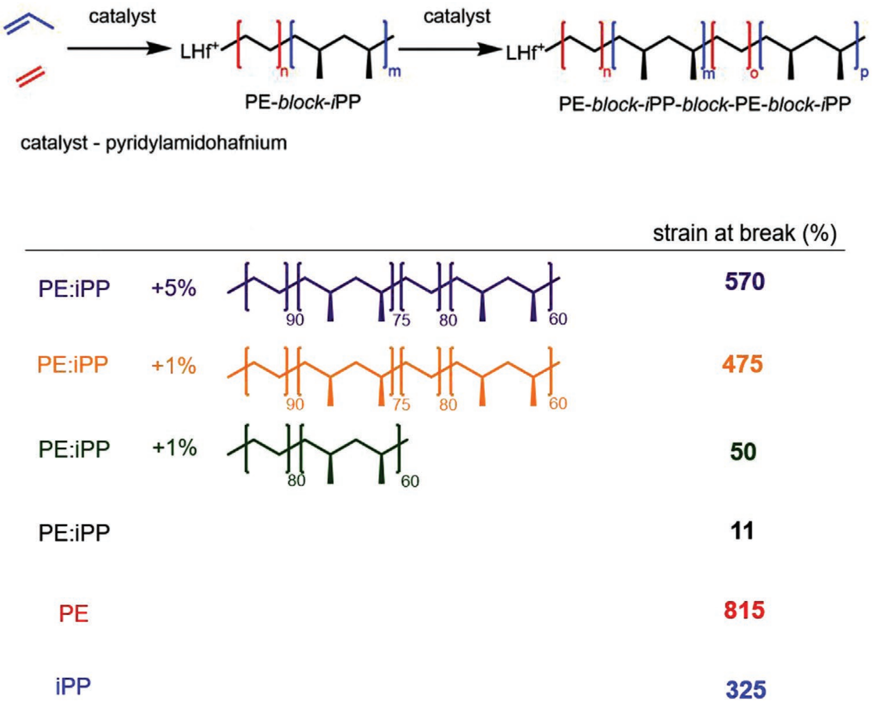


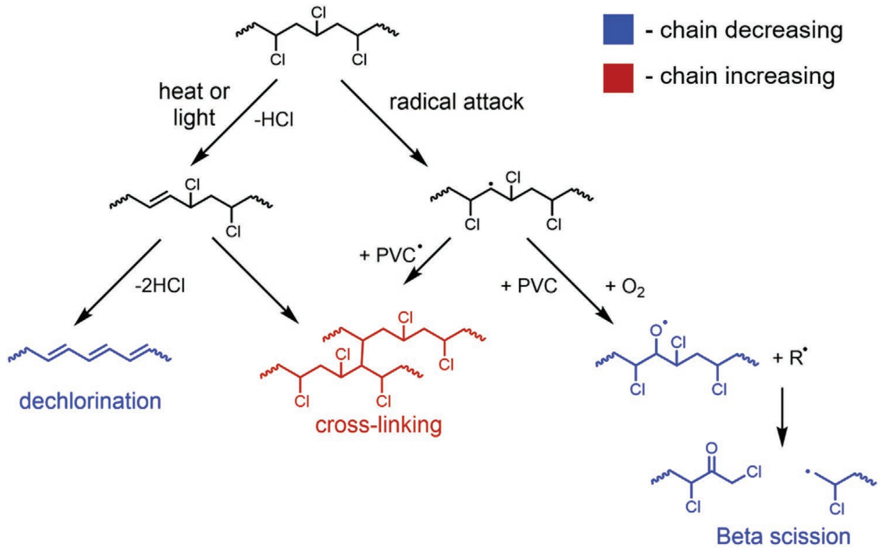
Figure 13. Synthesis of PE/iPP copolymers using an isoselective pyridylamidohafnium catalyst. Tensile testing of PE/PP blends stabilized with different wt% of PE:iPP copolymer.[151]

Recycled MPOs require minimal sorting, are easily produced and much cheaper than pure PP and PE recyclates. Yet the produced recyclates have significantly diminished mechanical properties due to poor adhesion between polymer phases.[131,147,148] These adhesion issues prevent the use of these blends for manufacturing purposes due to lower Young's moduli and reduced elasticity (iPP:PE blends shown in **Figure 13**).[89,149–151] Poor adhesion can be explained by presence of noncrystallizable oligomers at the interphases generated during synthesis.[148] Appropriate choice of catalyst during polyolefin synthesis can minimize the presence of these oligomers and promote adhesion across MPO interphases.[148] The mechanical behavior of polyolefin blends can be altered by modifying the majority phase as shown by research conducted by Van Belle et al. [150] Blends of LDPE/HDPE, LDPE/PP and LLDPE/HDPE have transitional tensile behavior in which tensile behavior will transfer to the majority phase. Blends of PP/HDPE cause brittle behavior, unlike the shear yielding seen for the mono-polymers.[150]

Recently, Eagan et al. report synthesizing a novel polyethylene-block-isotactic polypropylene (PE-*b*-iPP) copolymer to successfully "stitch" two polyolefin polymer phases together (Figure 13). The resulting copolymer stabilized blend showed large tensile property improvements when compared to conventional unstabilized PE-iPP blends due to aforementioned interlocking entanglements between the two phases.[92,151,152] More recently, this research group has presented polyethylene grafted with isotactic polypropylene copolymers (PE-*g*-iPP) as blending agents for PP and PE with similar compatibilising effects as multi-block copolymers.[153] The grafted compatibilisers are formed by copolymerising macromonomers in the presence of a hafnium pyridylamido catalyst rather than by living polymerisation. These new copolymer compatibilisers Thus, providing an economically favourable method to compatibilised MPO wastes.[153] Successful compatibilization of polyolefins is of great interest to the recycling industry. The qualities of one polyolefin can be used to enhance that of another. HDPE, though of lower cost and of higher mechanical properties than LDPE, produces poor quality films with increased haziness and lower toughness. Wu and Wang report that blends of PP/LLDPE/HDPE (10:30:60) show improved toughness and decreased haze compared to pure HDPE films due to partial compatibility and crosslinking between the three polymers.[154] A polyolefin-wide blending technology that is independent of composition remains a challenge, with research requiring testing of many different blend compositions to find optimum ratios, highlighting the need for systematic solutions for improved polymer waste stream sorting processes.

5. Mechanical Recycling of Poly(vinyl chloride)

PVC is ubiquitous in food and construction industries as it is robust, light, flexible and has excellent oxygen and water barrier properties.[155–157] However, at end-of-life PVC degradation



Scheme 7. Common degradation mechanisms PVC undergoes during extrusion.

causes release of chlorinated products into the surrounding environment.[143] Mechanisms of degradation during recycling include thermo-oxidation, crosslinking, functionalization of chains and hydrodechlorination (**Scheme 7**).[53,158,159] Pyrolytic treatment of PVC is generally not advised due to the possible release of highly toxic and corrosive HCl gas, with impact on both the environment (i.e., acid rain) and plant (i.e., reactor corrosion).[158,159] PVC is unstable to both thermal and photo-induced stress. PVC waste streams must be pure and highly stabilized against unwanted degradation to enable useful mechanical recycling.

5.1. Degradation Mechanisms of Poly(vinyl chloride)

Thermal and optical degradation promotes hydrodechlorination to form internal double bonds (Scheme 7), significantly decreasing mechanical strength. The initial double bond formation promotes subsequent reactions, leading to polyene sequences along the chain. These polyene sections absorb light, discoloring the polymer.[158–162] High degradation levels and a lack of oxygen both induce reactions whereby double bonds facilitate PVC chain crosslinking.[53] Secondary reactions, especially in the presence of oxygen, can introduce many other chain structures and functionalities.[158,160] Radicals are generated by the cleavage of the C-Cl bond or from the abstraction of hydrogens, with environmental oxygen reacting to produce oxygenated species that eventually form carboxylic acid end-groups. Oxygen can also react with the polyene sections of the chain.[160] However, PVC polyene formation occurs under both N_2 and O_2, so control of degradation is challenging and elimination of all substantive degradation is unfeasible.[161] As with other packaging polymers, contaminants can catalyze the hydrodechlorination and mechanical performance losses.[158]

5.2. Stabilization of Poly(vinyl chloride)

PVC is generally extruded with stabilizers that neutralize HCl released and thus prevent attack on polymer chains. Some stabilizers have the added ability to replace chlorine atoms lost from the polymer backbone.[159] Stabilizers are consumed during processing of the polymer during its first life, necessitating further stabilization when recycled. Stabilizers can be metal based such as lead, calcium-zinc, sulfur organotins, and metal soaps.[159,163] Although no longer in used (as of 2015), the presence of both lead-based and sulfur-based stabilizing systems react to form lead-sulfide which appears as dark sports in the material and have potential human and environmental toxicity concerns, especially as much of this legacy material remains in use.[159,163,164] Inclusion of inexpensive bases such as $CaCO_3$ can also prevent the release of HCl during processing. As it also acts as a filler, inclusion of $CaCO_3$ improves the mechanical properties of the material (i.e., elastic modulus, elongation at break, and impact strength by up to 20%), and indeed is retained over multiple life cycles.[159,164] However, high amounts of these fillers leads to embrittlement, necessitating increase addition of plasticizers that further complicate the chemical composition of PVC and necessitating filler inclusion at low loadings.

5.3. Plasticizer Use in Poly(vinyl chloride)

This PVC embrittlement occurs even in the absence of fillers and stabilizers, necessitating plasticizers in nearly all applications.[165] Plasticizers weaken intermolecular interactions within materials by increasing free volume (**Figure 14**), thus lowering the glass transition temperature (T_g), decreasing stress at break and increasing elongation at break.[166,167] Nearly nine times more plasticizer than stabilizer was used in PVC in 2006

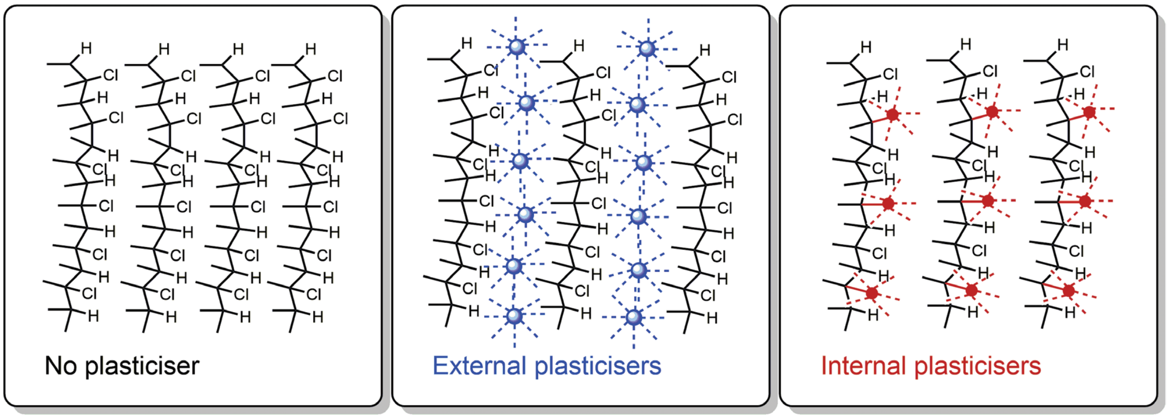


Figure 14. Schematic representation of internal and external plasticizers in PVC.[167]

(5.8 million vs 0.67 million tons). As plasticizers are rarely used in PET and HDPE, PVC accounts for 80–90% of plasticizer use up to 2005.[165] As the most common phthalate plasticizers are a threat to human health, this has increased calls for the exclusion of PVC from packaging polymers and many other applications.[165,168–170] Phthalate plasticizer concentration increases with each recycling cycle, exacerbating these issues,[170] especially as phthalates migrate to external surfaces during thermal aging, reducing its efficiency and increasing environmental exposure over time.[171]

These concerns have understandably led to tough restrictions on phthalate use, creating real challenges for PVC mechanical recycling, including through the European PVC recycling scheme VinylPlus.[172] New, non-toxic, plasticizers include citrates, carboxylates, phosphates, sebacates, and epoxidized oils.[167,173] One of the most commonly used and commercially available alternatives to phthalates for use in food-related packaging is Hexamoll DINCH, a 1,2-cyclohexane dicarboxylic acid diisononyl ester, which complies with global regulations in medical device, toy and food contact industries.[174,175] Investigation into other phthalate-free plasticizers is ongoing. US patent US2017/0096543 A1 describes the invention of an ester-based plasticizer, through the reaction of pentaerythritol and a monocarboxylic acid, that can achieve similar effects at lower concentrations, but to our knowledge these results have not been peer reviewed.[174] The use of epoxidized oils as a replacement to phthalates is another promising development, although issues with flammability and migration have limited commercial development to date.[167] Many alternative plasticizers are under-explored, with toxicity and migration issues key unknowns that need resolution prior to incorporation into plastics in circulation.

Internal plasticity, through substitution of the PVC chlorine atoms, can be used in place of external plasticity (Figure 14). Lu et al. report the chemical modification of PVC by reacting the common plasticizer diisononyl phthalate with the polymer chain to produce a self-plasticizing polymer with decreased phthalate migration. Nucleophilic substitution of the chlorine atoms with thiophenol groups with K_2CO_3 or *N*,*N*-diisopropylethylamine also plasticizes the system, with lower T_g values observed.[166] Self-plasticizing PVC was also explored by Jia et al.[167,176–180] The use of phosphorous containing castor oil derivatives (EAMR-DOPO),[167] dehydroabietic acid derivatives,[178] cardanol based groups,[177,179] mannich bases of waste cooking oil,[178] and aminated tung oil methyl esters[180] have all been used in self-plasticization of PVC. Self-plasticized plastics can reduce both plasticizer migration and toxicity, although this second has not been conclusively evidenced in real-world systems.[176] Further research must be conducted into the robustness of self-plasticized materials, as substituted PVCs are expected to be less stable during mechanical recycling.[178] Nevertheless, self-plasticizing PVC is a promising route to upgrade recyclate and minimize unintended consequences.

It bears mention that the recycling process is not the only contributor to negative environmental impact for PVC; originally, PVC synthesis was energetically expensive and required exceeding toxic chemicals like Hg(l) and Cl_2(g).[165] Greener methods to produce vinyl chloride monomers are emerging.[181] However, the real solution may be in alternatives to PVC, although the financial challenges of infrastructure investment, legacy polymers in long-term use, and the lack of understanding of the ecotoxicology and recyclability of alternatives means that the recycling of PVC remains an essential area of research.

6. Mechanical Recycling of Polystyrene

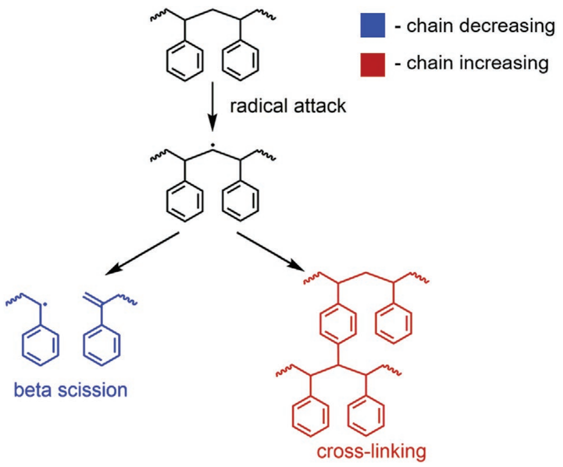
PS exists in three forms: solid, expanded foam and a polybutadiene reinforced form (HIPS), all of which are used in packaging. Polystyrenes are challenging to collect and recycled due to their low densities.[182] Solid PS can be mechanically recycled into other useful products whereas expanded polystyrene (EPS) usually requires a solvent-based or mechanically based method to de-foam and reduce its volume before reprocessing.[183,184] Solvents used to de-foam EPS do not cause degradation of the chains but care must be taken to minimize the environmental and carbon impact of the solvent of choice.[184] Noguchi et al. report the use of the bio-derived solvent, *d*-limonene a natural vegetable oil from citrus fruits, to de-foam and shrink EPS.[185]

This technique reduces the volume of the EPS foam by twenty times and is promising for recycling because the residual oil acts as an antioxidant that protects chains from radical induced scission. While an expensive process, *d*-limonene is food-derived and potentially more environmentally friendly than other solvents such as toluene (although the carbon footprint may be significant higher), but most significantly it selectively dissolves EPS while leaving expanded polyolefins and labels intact.[182,185] As an alternative to *d*-limonene, other natural oils such as star anise oil, eucalyptus oil, thyme oil and chamomile oil can be used to successfully reduce EPS foam volume without lowering molecular weights.[182] To eliminate solvent cost and impact, Trezek et al. describe the use of an apparatus to mechanically reduce the size of the foamed polystyrene.[186,187] Recycled EPS (rEPS) can be re-gassed to enhance its foamed characteristics, although the added cost compared to virgin polymer continues to depress recycling rates.[183,188]

6.1. Degradation Mechanisms of Polystyrene

PS is susceptible to radical attack; thermal scission causes the formation of a macroradical species (**Scheme 8**). The radical reaction continues by intramolecular radical transfers before β-scission of the chain through an unbuttoning reaction forming small dimers and trimers.[126,174,175] As with other polymers, PS chains can crosslink under certain, usually low oxygen, reaction conditions.[176] The degradation of HIPS differs due to the presence of the polybutadiene chains, with degradation starting in the unsaturated double bond of the polybutadiene and then propagating through the PS chains.[51,189,190] Although not directly used to produce electric components, PS is used in electrical and electronic equipment packaging. As the waste associated with electronics is rising, efficient recycling of polymers for electronics and their packaging is imperative.[183,190]

A decrease in molecular weight, viscosity, and elongation at break is observed as PS is mechanically recycled. Recycled polystyrene is primarily downcycled into disposable cutlery and products.[191] Remili et al. report that by the tenth reprocessing cycle the molecular weight of PS decreased by nearly 50%.[192] Chain scission dominates during reprocessing, as confirmed both by molecular weight and rheological measurements. Both chain scission and crosslinking compete in HIPS reprocessing.[189,190] At higher temperatures or cycles, chain scission begins to dominate over crosslinking and the elongation at break of HIPS decreases.[189] Vilaplana et al. report that after nine reprocessing cycles the elongation at break of HIPS decreases by 38%, a smaller decrease than seen in PET but still significant for product manufacture.[190]



Scheme 8. General reaction scheme for mechanical recycling of PS.

Mechanical recycling is not the primary method used to recycle EPS as foam density differences and additives impact the process and prevent true circularity. Dissolution/precipitation techniques are widely applied to PS due to their ability to reduce EPS volume and provide a high quality rPS comparable to the virgin material.[193]

6.2. Filler Use in Polystyrene

While understudied compared to other packaging polymers, fillers can reinforce the PS polymer matrix. Nagalakshmaiah et al. recently report the production of a cellulose nanocrystal (CNC)-PS composite material using twin screw extrusion and avoiding the time and resource intensive solvent casting methods.[194] Mini-emulsion polymerization was used to modify the CNC and minimize thermal and dispersion instabilities. The compatibilizing copolymer poly(styrene-*co*-2-ethylhexyl acrylate) was used to plasticize the polymer, lowering the T_g and mechanical performance.[194] Incorporation of montmorillonite clay increases the viscosity of HIPS and counteracts chain scission reactions during degradation.[189] However, inclusion of clay again decreases the mechanical properties due to poor dispersion of the clay. However, extrusion shears clay agglomerates, which reduce in size, disperse better in the polymer matrix, and recover the mechanical properties.[189,195] Similarly, Remili et al. report that the inclusion of Cloisite 15A clay in PS (5 wt%) protects the chains from degradation and maintain polymer mechanical properties after recycling (**Figure 15**).[192] The observed increase in PS molecular weight is attributed to crosslinking from radical recombination reactions; the clay prevents chain mobility and thus limits the movement of radical fragments produced by chain scission.[192,196] Unlike the nanoclay used in HIPS, the Cloisite 15A clay in PS leads to improved properties such as the Young's modulus and hardness of the recycled composites.[192] This may be due to the difference in the clay structures present in the polymer matrix, as montmorillonite clay forms random agglomerates while the layered Cloisite 15A can better trap radical fragments. Gutiérrez and Alvarez investigate the reactive extrusion of PS and native/oxidized corn starch using zinc octanoate to catalyze the crosslinking reaction. Composite films showed higher elasticity due to their compact structure, although this has not been explored in mechanical recycling.[197]

As with PVC, PS recycling is less prevalent than other polymers – both due to inherent challenges in its operation and the

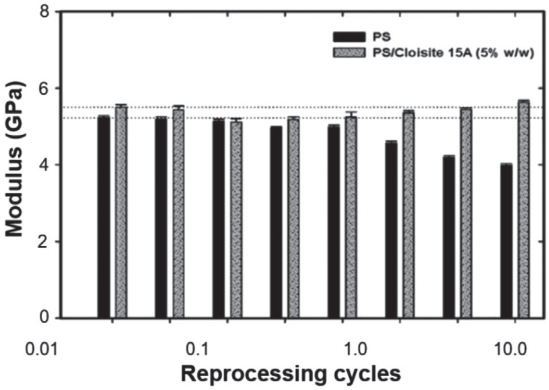


Figure 15. Young's modulus versus number of reprocessing cycles for PS compounded with and without 5%w/w Cloisite 15A. Reproduced with permission.[192] Copyright 2011, Elsevier.

potential that regulations may minimize the material in circulation in the future.

7. Applications of Complex Polymer Blends in Mechanical Recycling

As discussed, blending technologies may recover value in systems where polymer waste sorting is not feasible and can minimize problems of contamination in polymer waste streams. Blending of polymers with dissimilar chemical polarities is challenging and especially difficult when systems are contaminated with multiple polymers. A high number of entanglements and increased polymer block size positively affects the mechanical properties of the material.[141,152]

Co-monomers such as those described by Eagan et al. can be used to compatibilize other blends.[151] For example, poly(ethylene-*co*-vinyl acetate) and poly(styrene-*b*-ethylene/butadiene-*b*-styrene) are used to compatibilize blends of HDPE, PVC and PS, with gamma radiation then used to induce crosslinking reactions.[198] Though the radiation improved the uniformity of blends, the elasticity and tensile strength of the blends suffers,[198] making it difficult to justify the use of energetically costly radiation as a recycling solution, although important research in this field is continuing.

PET-polyolefin blends are often compatibilized by grafting polyolefins with functional groups that can interact with PET end groups such as maleic anhydride, acrylic acid, ethylene-vinyl acetate copolymers, maleimides, or glycidyl methacrylate.[199] Mi et al. report blending PP and PET using in situ microfibrillation and multi-flow vibrate injection molding paired with polyolefin grafted maleic anhydride (POE-*g*-MA) to control the blend morphology of PP and PET.[91] Two different morphologies of each polymer were used; PP spherulites and orientated structures denoted as "shish-kebabs" and PET spherules and fibers (**Figure 16**). Blending the PP spherulites with the orientated microfibrillar PET led to improved mechanical properties whereas blending the orientated PP with the PET spherules gives improved impact strength. Both the PET fibers and PP "shish-kebabs" cannot coexist as the PET fibers disrupt the flow of PP.[91] Bottle grade PET can be improved through incorporation of GMA grafted onto PP with styrene as a co-monomer, increasing the materials impact strength due to enhanced interactions between chains.[199,200] PET present

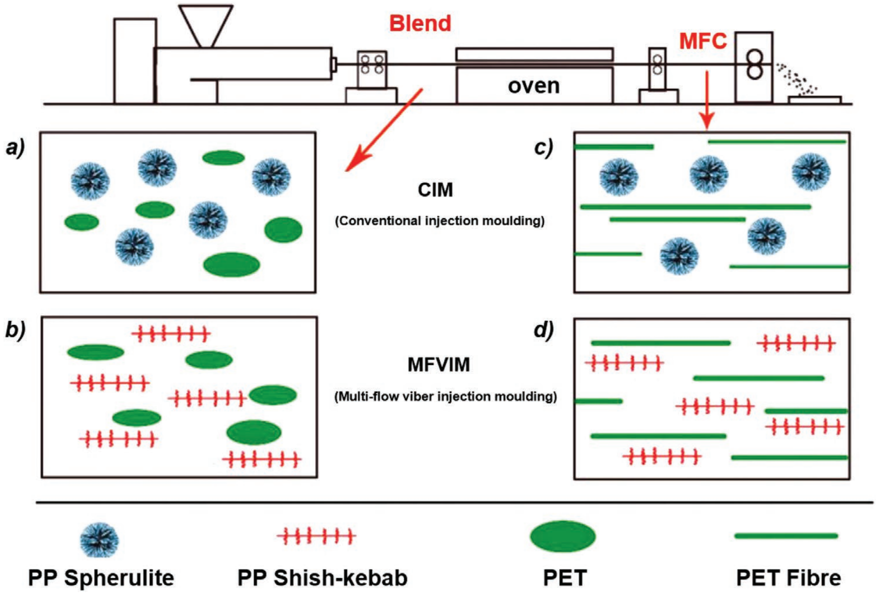


Figure 16. Experimental set-up used to produce a) blends b) microfibrillar composites c) blends, and d) microfibrillar composites via a,c) CIM and b,d) MFVIM. (a–d) Reproduced with permission.[91] Copyright 2019, MDPI.

as the minor phase in PP, compatibilized by poly(styrene-*co*-(ethylene-butylene)-styrene) grafted with maleic anhydride (SEBS-*g*-MA), is encapsulated by the hydrophobic PP protecting the PET chains from degradation. The PP-PET blend is said to be stable up for three extrusion cycles which is similar to reports of mechanical recycling of pure PET streams,[47,140] although this has not yet been explored for real-world systems and the lack of food-grade PP is an additional challenge for retaining material value.

Compatibilized blends cannot always be used to produce high quality products. Ragaert et al. report a secondary use for the product of the sink fraction of waste sorting destined for incineration which also uses SEBS-*g*-MA as a compatibilizer. They sort this discarded fraction using IR to remove the majority of PVC, resulting in a broadly PET (73%) and PP (17.6%) based mix. The authors report the properties of the blended material with and without SEBS-*g*-MA compatibilizer while also developing a new roofing tile with the moniker "greentile,"[90] recovering value of a waste fraction destined for incineration or landfill.

PLA and PET are problematic packaging partners, as they are difficult to separate due to their similar density ($\approx$1.25 g cm^{-3} PLA and $\approx$1.35 g cm^{-3} PET), physical appearance and IR signature from similar polyester backbones. Thus contamination of PLA in PET waste streams is common due to imperfect waste sorting. PLA degrades into the parent lactic acid at PET processing temperatures, with the acids catalyzing the degradation and esterification of PET. As PLA is also one of the most popular "biodegradable" plastics, it is rarely collected for mechanical recycling.[95] Gere and Czigany report using an ethylene-butyl acrylate-glycidyl methacrylate (E-BA-GMA) terpolymer to produce a compatibilized blend of PET-PLA.[201] The blends show increased toughness but a decrease in their elastic moduli. The authors also incorporated the chain extender Joncryl ADR 4368 which may be a true source of mechanical improvements observed. The compatibilized blends have higher thermal stability compared to their non compatibilized counterparts, although reprocessing was not explored.

Blending technologies can also exploit the degradation mechanisms of different polymers. Li et al. report compatibilizing PP and PS by inhibiting degradation reactions within the extruder, using tetraethyl thiuram disulphide (TETD) to form dithiocarbamate radicals to react with the macroradicals formed by polymer degradation.[202] The authors combine the TETD with di-*tert*-butyl peroxide (DTBP), which abstracts hydrogen atoms from the PP backbone and accelerates β-scission of the polymer, to effectively control the degree of degradation of the polymer. The reaction produces a PP-*g*-PS copolymer in situ which then acts as a compatibilizer between the PS and PP fractions.[202] Another additive, dicumyl peroxide, in combination with a low molecular weight unnamed polyester (molecular weight of 3000 with 30 mol% double bonds), was used to improve the stiffness of co-mingled plastic waste (65% PE, 11% PS, 10% PP, 7% PET, 9% other plastics) by inducing crosslinking of the polymer chains. Schadler et al. suggest that inclusion of the unsaturated polyester acts as a higher modulus filler to improve the flexural modulus of PE and the co-mingled plastics. When the crosslinking agent is added, gel formation results and the modulus of both PE and co-mingled plastic increases.[83]

While polymer blends can offer enhanced mechanical properties and retain value in poorly sorted polymer waste, reprocessing is rarely considered. The behavior and degradation mechanisms of the blended materials is an essential area for further study, both in how the polymer blend behaves with multiple degradation temperatures and mechanisms and the influence on broader waste management systems in propagating this contamination.

7.1. Complex Polymer/Filler Blends

As discussed for specific polymers above, fillers can be used to reduce the effects of damage caused by chain degradation during mechanical recycling. Incorporation of fillers can improve the Young's modulus, elongation at break and impact strength of recyclates but reduce polymer processability.[83,137,203] Fillers in polymer blends migrate to the interfaces between the fractions, dictated by both filler structure and thermodynamics. This decreases the interfacial tension between the two polymers by minimizing the energetic difference between particles in the bulk and at the interface.[21,93] Fillers must be chosen with the chemical polarity of the polymer matrix in mind. Incorrect matching of filler to polymer leads to poor adhesion and poor transfer of stress and strain across the polymer, thus decreasing the mechanical properties of the resulting material. Coupling agents, such as silanes or titanates, can be added to improve adhesion between the filler and the polymer.[83,134,204]

The use of fillers within recycling must be carefully planned with processing in mind. Changes to processing properties, such as viscosity, can damage processing equipment due to excessive torques or require recalibration of large industrial processes. Incorporation of fillers in recyclates changes the rheological behavior of the final extrudate.[127,203,205] Low viscosity values are obtained at low shear rates due to brittle regions with high filler concentration.[203] Processing of viscous polymers, such as those with high filler content, requires increased energy which in turn drives up processing costs.[203] The balance between improved recyclate properties, filler quantity and financial costs remains challenging.

Naturally derived fiber fillers are growing in popularity due to their renewable nature and potentially lower environmental impact.[206,207] Fiber fillers, such as starch, cellulose, chitin, chitosan, soya, wheat gluten, gelatine, and lignin, reinforce polymers by acting as physical compatibilizers in blends.[208] Augier et al. and Petchwattana et al. both report on successful inclusion of wood fibers to improve recyclate quality over multiple processing cycles. Petchwattana et al. note that wood fiber filler combined with recycled PVC (rPVC) is stable for up to 5–7 cycles while Augier et al. note improvement in the strength of the material above 10–20 extrusion cycles without compromising other mechanical properties (**Figure 17**).[209,210] Naturally derived fiber fillers also work on PP and HDPE.[206,207,208] Unfortunately, these naturally derived fiber fillers are prone to degradation, can disrupt the polymer matrix and suffer from adhesion issues which then require yet another additive in coupling agents.[138,208,212] Detailed accounts of natural fiber

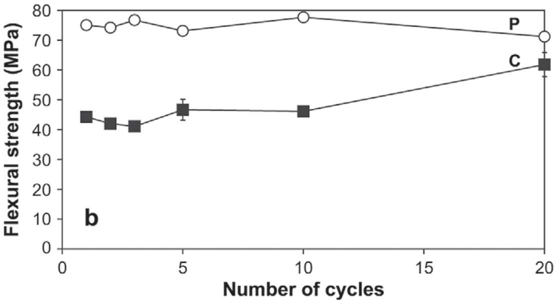


Figure 17. Flexural strength versus number of reprocessing cycles for PVC reinforced with wood fibers (C) and without fibers (P). Reproduced with permission.[209] Copyright 2007, Elsevier.

composites and treatments to improve them can be found in previous published reviews.[213,214]

Particle fillers such as glass fiber, talc, $CaCO_3$, and wollastonite produce cheap composites with enhanced stiffness, creep-resistance and heat-deflection.[215] Stiff composites can be used in specific applications such as heavy-loaded bridges, replacement of automotive parts and fire-retardant materials.[215] Glass fibers can even interact synergistically with a second filler to enhance mechanical properties further and produce high strength materials. Although theoretically advantageous, glass-fiber enforced polymers are very challenging to process.[215] Glass-fiber stiffened polymers suffer from rapid degradation within polymer processing equipment due to their higher viscosities.[204,215]

Fillers can often be tailored to fit specific product requirements. Fire retardants, while not essential in most packaging applications, are highly relevant to protecting electronic equipment. Inorganic fillers such as metal hydroxides, carbonates or phosphates can be used as flame retardants, although high percentages cause adhesion problems within the polymer.[216] Use of ammonium polyphosphate as a fire-retardant filler in flammable PP reduces the flammability of the polymer but the filler migrates out of the polymer matrix with time and degrades within the extruder.[196] Other fire-retardant additives include aluminum trihydrate, zinc borate, melamine, graphite, titanium dioxide, flax and magnesium hydroxide.[217,218]

In more recent developments, nanoparticle fillers have been incorporated to improve the stability of polymer blends. Unlike polymeric compatibilizers, nanoparticle fillers are unspecific. Taguet et al. propose that the effectiveness of a nanoparticle for stabilization is optimized when the particle radius is significantly larger than the radius of gyration of the polymers to be blended. Minimizing interparticle interactions and having equal adsorption-affinities for both polymers increases nanofiller efficacy.[93] A variety of different organically coated nanofillers have been used to stabilize blends of recycled and virgin polymers. The most advanced of these is organic modified montmorillonite clay, which has been used to improve blends of rPET/HDPE, rPET/PP/HDPE, and rPET/rPP.[219–221] Montmorillonite clay has also been reported to improve the properties of PP and PS (Sections 4.2 and 6.2). Studies also suggest that it may enhance other degradation reactions through side reactions caused by surfactants, contaminants, metals presence in the clay, or collapse and re-aggregation of the clay into agglomerates.[189,192]

The environmental impact of the additional use of compatibilizers and fillers in conjunction with other additives must also be considered (**Figure 18**). The recyclability of the fillers themselves may differ from the host polymer matrix and may require costly separation before recycling of the polymer. The extensive filler research has facilitated quick and low-cost upgrades to mechanically recycled polymers (r-polymer), allowing polymers that may have been destined for landfill to be repurposed into secondary uses where impact strength is prioritized over flexibility.

8. Secondary Uses for Recyclate

If circular systems are not possible, where mechanical recycling can return waste plastic back into the original product, minimizing the fraction sent to landfill remains essential. A common strategy is downcycling of plastic waste into secondary products, reusing the resource in other products such as building materials, lubricating greases, textiles or other packaging (**Figure 19**).[90,183,222–227]

Recycled LDPE, HDPE, and PP in blended or pure form has been used in lithium semi-solid colloidal dispersions as a thickening agent in a liquid lubricant.[222–224] Recycled polyolefins have been used in multi-layer food packaging (including with alternative materials such as paper), however these r-polymer are more prone to small molecule diffusion suggesting a regulatory challenge for use in food packaging.[228,229] To combat this, recycled polymers have been used as central layers between virgin polymers in multilayer films. Multi-layer polymer film production is challenging and requires careful viscosity matching in order to produce defined layers.[230] Radusin et al. report using rPE between layers of virgin PE in food packaging with minor aesthetic issues such as a loss of transparency and a mild color change.[229] Previously, researchers also incorporated rLDPE between layers of virgin polymer and used gamma radiation to induce crosslinking between the layers. They found no negative effect on the permeability of the packaging however, the food-safe 5–10 kGy (according to the Codex Alimentarius Commission) dose used to irradiate the packaging was found to produce harmful radiolysis products within the packaging layers.[228,231] Recycled PET has also been incorporated in multilayer packaging between layers of virgin food-grade polymer.[19] However, multi-layer packaging is challenging to recycle; the recycling process is not always economically or environmentally favorable due to sorting and separation challenges.[232,233]

Solid plastic wastes, such as PE, MPOs, PS, and HIPS have also been used as replacements for wood or other building materials to produce outdoor furnishings.[90,183,225] PS can be reprocessed into TV backsets or as bitumen replacement in asphalt mixtures to alleviate the increase of electronic equipment waste.[211,212] Composites or reinforced recyclate can be used in part to aid in construction of load-bearing structures such as bridges.

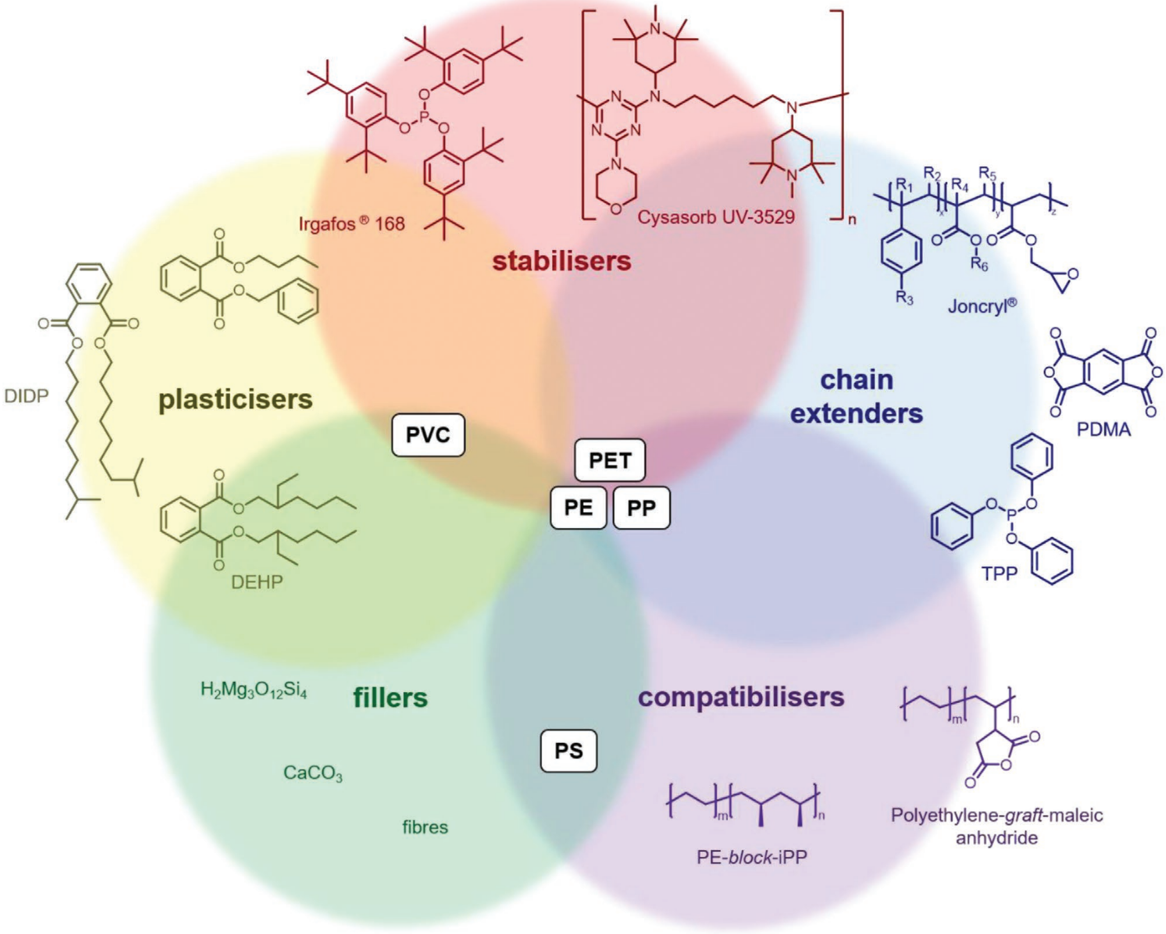


Figure 18. Common polymer additives used to improve polymer recyclates.

Figure 19. Schematic representation of downcycling routes for recyclate.

Due to growing concern regarding “fast fashion” (clothing designed to be worn a low number of times before disposal),[234] clothing brands have developed methods to use recycled polymers as a route to reducing environmental impact,[234–238] although it is clear that social practice also needs to change. Large multinationals such as Nike, Adidas, The North Face, Timberland, Speedo, Patagonia and Levi Strauss & Co., have devised and/or sponsored development of new fabrics with recycled content, principally PET bottles and black plastic trays.[234,239] New fabrics are produced by a mechanical process involving grinding and melting of polymer waste to draw fibers that can be woven.[235–237,239] Emerging companies such as TALA, Rothy’s and Looptworks use only recycled material to produce both their clothes and packaging.[240–242] Efforts to ensure these new processes are robust, including proper life-cycle assessment and tracking of potential formation of micro and nanoplastics is essential to assess the potential impact of this new market for mechanical recycling.

9. Conclusions and Outlook

The current linear plastic economy is not sustainable. Increasing environmental pollution entering our oceans and land, coupled with micro and nanoplastic pollution in our natural systems highlights the importance of reusing and recycling these essential materials. In many applications alternatives are either unavailable, exceedingly expensive or have higher carbon footprints, confirming that mechanical recycling must remain a major part of our waste management strategy. Mechanical recycling of plastic packaging is well researched, with significant progress have been made in the last 50 years. While this review captures the key developments in the published literature, there are undoubtedly innovations locked away as trade secrets by plastic reprocessors.

Although degradation mechanisms differ across polymers, changes in chain length and mechanical properties are a consistent challenge. Material property deterioration, costs and sorting issues are the primary hurdles faced for efficient mechanical recycling. Minimizing degradation by the inclusion of antioxidants, chain extenders, blending technologies, fillers, plasticizers is complicated by the lack of standards over grades of polymer, and the role these additives play in creating further variation in recyclate quality. The discrepancies in recyclate composition lead to lower economic value and higher risk in incorporating high levels of recycled content by industry.

Waste management systems should be actively considered when designing polymers, blends and mechanical recycling processes. If we are to justify the continued use of plastics –which we should – we must have better control over their material life cycle and pursue solutions that can maintain their value over repeated uses and reprocessing. Creating this consistency will lead to improved recycling rates, increased recycled content in products, and minimize the plastic we export, landfill, incinerate, and litter. We note the likely limitations of mechanical recycling systems, and while outside the scope of this review recognize the important transition between waste management systems that exploit both mechanical and chemical recycling methodologies. Together they are essential tools to a truly circular plastics economy.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

circular economy, extrusion, mechanical recycling, packaging, plastics, polymers

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