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]

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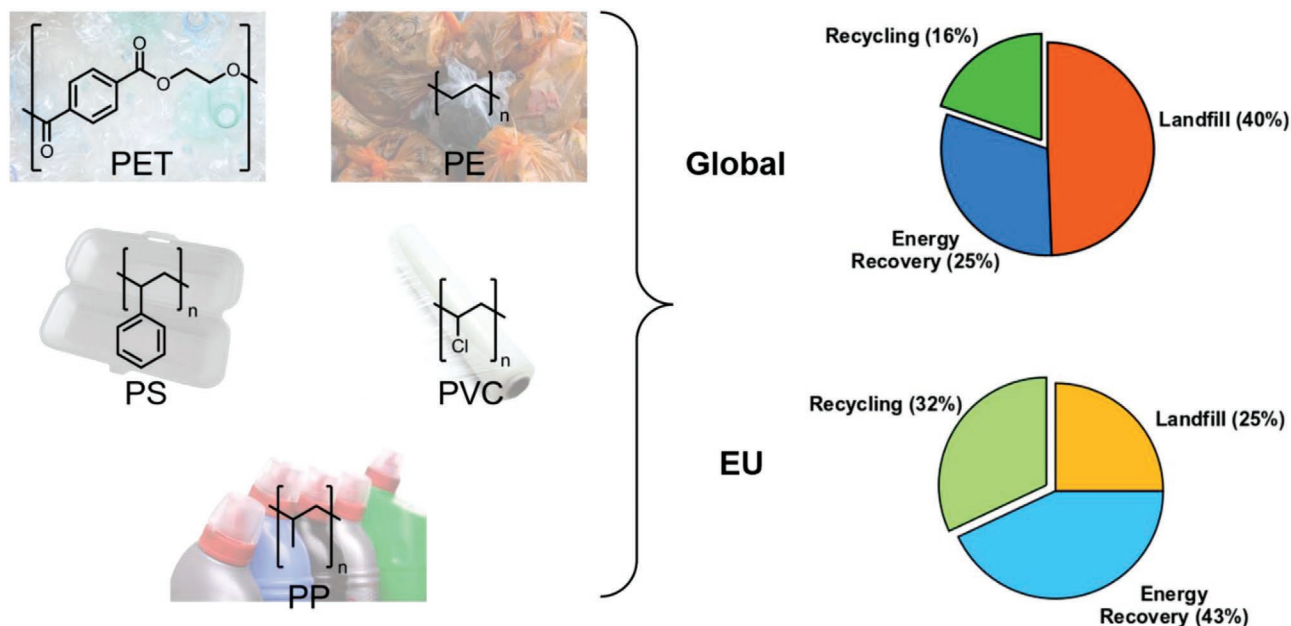**Rapid Communications**
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Figure 1. The main packaging polymers: poly(ethylene terephthalate) (PET), polystyrene (PS), polyethylene (PE), polypropylene (PP), and poly(vinyl chloride) (PVC) and current global and EU plastic waste management rates.[1,2]

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]

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 preconsumer 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 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

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 rudimentary 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
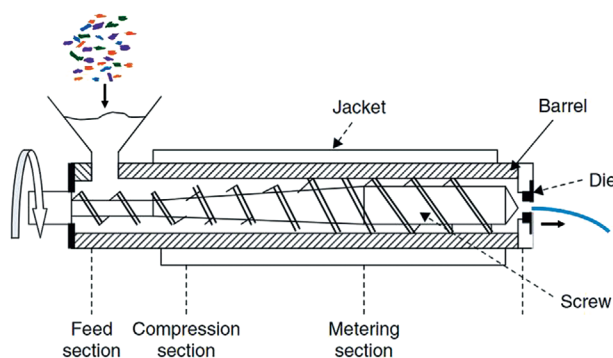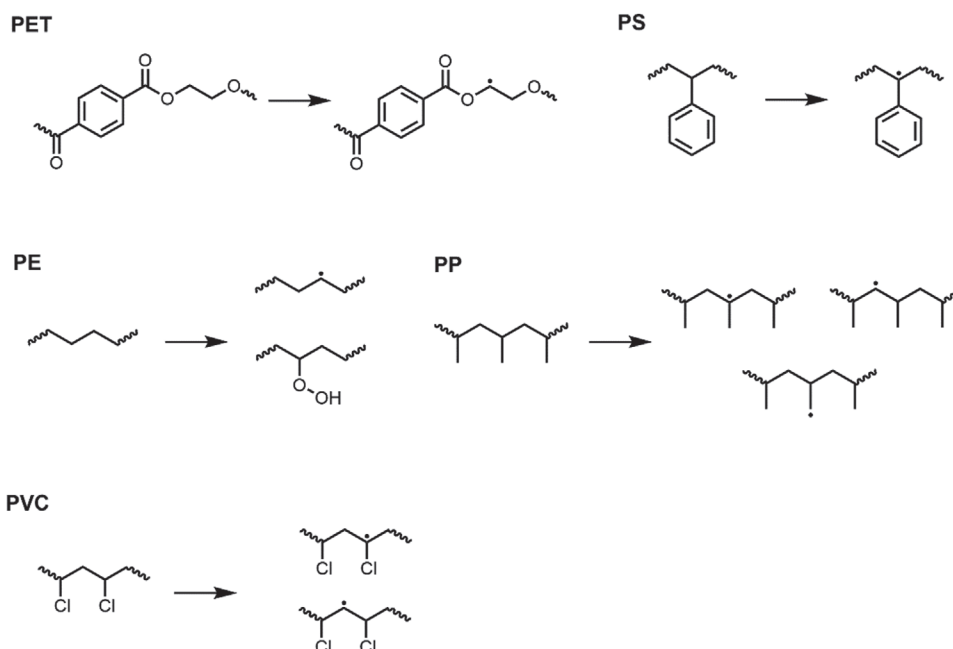

Figure 2. Schematic representation of a single screw extruder. Reproduced with permission.[43] Copyright 2009, Elsevier.

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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]
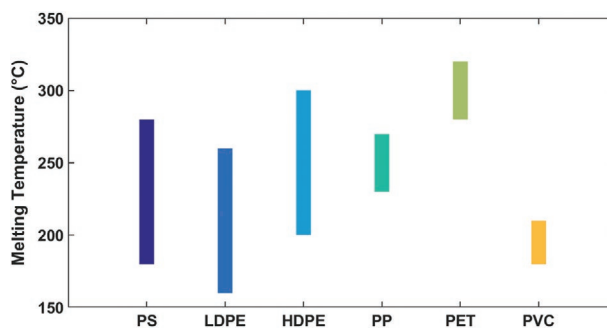

Figure 3. Processing ranges for the six most common packaging polymers.[60]

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
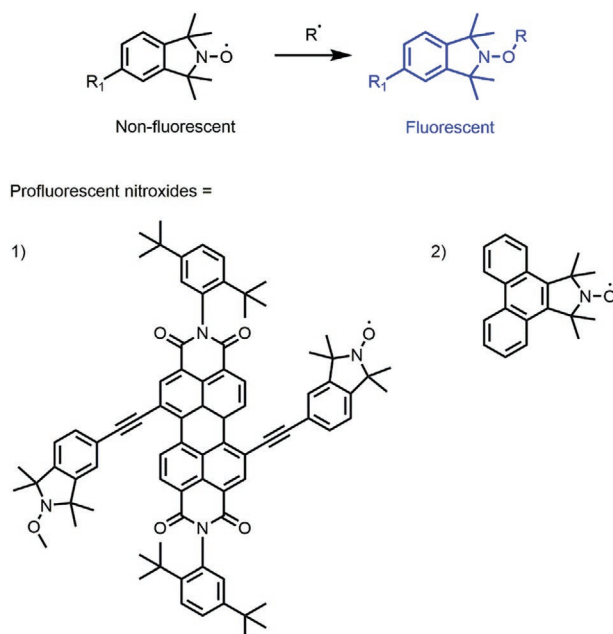

Figure 4. Profluorescent nitroxide compounds used by 1) Lussini et al. and 2) Micallef et al. to monitor radical based aging in polymeric materials.[70,71]

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.

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

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