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Cross-Linked Polyolefins: Opportunities for Fostering Circularity Throughout the Materials Lifecycle

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ABSTRACT: Cross-linked polyolefins (XLPOs) constitute a significant portion of the plastics commercial market, with a market size of a similar order of magnitude to those of polystyrene and polyethylene terephthalate. However, few aspects of XLPO materials circularity have been examined relative to thermoplastic polyolefins. The cross-linking of polyolefins imparts superior performance properties, such as impact strength, chemical and electrical resistance, and thermal stability vs thermoplastic analogues, but it also makes the reprocessing of XLPOs to valuable products more challenging, as XLPOs cannot be molten. Thus, most XLPOs are incinerated or landfilled at the end of the first lifecycle, even though XLPO products are commonly collected as a relatively clean waste stream—providing a unique opportunity for valorization. In this review, we discuss approaches to improve XLPO circularity throughout the entire materials lifecycle by examining biobased feedstocks as alternative olefinic monomer sources and by assessing both traditional mechanical and advanced XLPO recycling methods based on industrial feasibility and potential product value. We also consider how advancing materials longevity can reduce environmental impacts and lifecycle costs and how recyclable-by-design strategies can enable better end-of-life opportunities for future generations of XLPO materials. Throughout this review, we highlight XLPO circularity routes that have the potential to balance the performance, circularity, and scalability necessary to impart economic and environmental viability at an industrial scale.

KEYWORDS: circularity, sustainability, lifecycle management, cross-linked polyolefin, cross-linked polyethylene, recycling
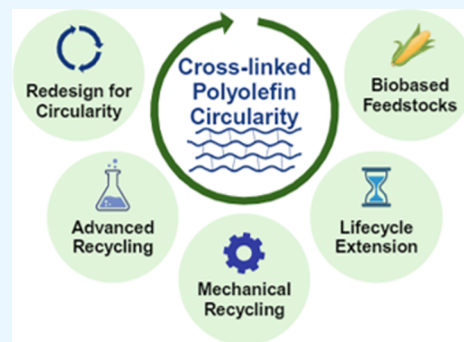
1. INTRODUCTION

Achieving polymer circularity is critical to address the adverse effects commonly associated with linear materials' lifecycles, such as greenhouse gas (GHG) emissions from the manufacturing and accumulation of plastics waste. Polyolefins (POs), encompassing polymers such as polyethylene (PE) and polypropylene (PP), constitute a substantial share of the global plastics market. Over 180 million metric tons of POs are produced from virgin feedstocks, and greater than 150 million metric tons of POs are discarded globally each year, which results in vast quantities of plastics waste.[1] PE alone, the highest volume PO, accounted for over 65% of major resin (*i.e.*, unprocessed plastic) manufactured globally in 2022, with a market of 124 million metric tons and >4% compound annual growth rate (CAGR) since 2018.[2] Cross-linked PE (XLPE or PEX) — the largest volume cross-linked PO (XLPO) — comprises ~5−10% of the total PE market with an expected 6−8% CAGR,[1] which makes XLPO one of the most abundant commercial polymers—with a market size of a similar order of magnitude to those of polystyrene and polyethylene terephthalate.[3]

XLPOs have superior performance properties relative to thermoplastic POs (*e.g.,* better impact strength, chemical and electrical resistance, thermal stability) that are critical to their use in applications such as pipelines, storage tanks, foams, and cable insulations.[4,5] For instance, XLPO is commonly leveraged in plumbing and radiant heating systems because it can maintain its structural integrity at higher temperatures than thermoplastic POs.[6] XLPO is also often employed in cables to insulate the metal conductor(s) (*e.g.,* copper) because of XLPO's electric, heat, and moisture resistance.[7] XLPOs can be derived from various types of POs, including PP, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) for distinct characteristics tailored to specific use cases.[4] For example, LDPE- or LLDPE-based XLPE is preferred in applications requiring flexibility, such as wire and cable insulation, whereas HDPE-based XLPE is favored in applications requiring substantial rigidity, such as pipes.[4] It is worth noting that
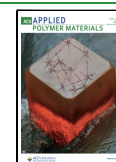
even though the majority of commercial XLPOs are XLPE, cross-linked PP, blends, and copolymers are likely to grow in interest as there can be performance and sustainability advantages to incorporating these other macromolecules (*e.g.,* PP has increased thermal, ultraviolet (UV), and chemical resistance and higher rigidity than PE).[8−11] XLPOs are usually highly cross-linked materials; for example, ASTM standards for XLPE tubing require a 65 to 89% degree of cross-linking.[12] To achieve such cross-linking in POs, there are three primary strategies—peroxide, radiation, and silane cross-linking (Figure 1). Peroxide and radiation (with electron beam radiation being
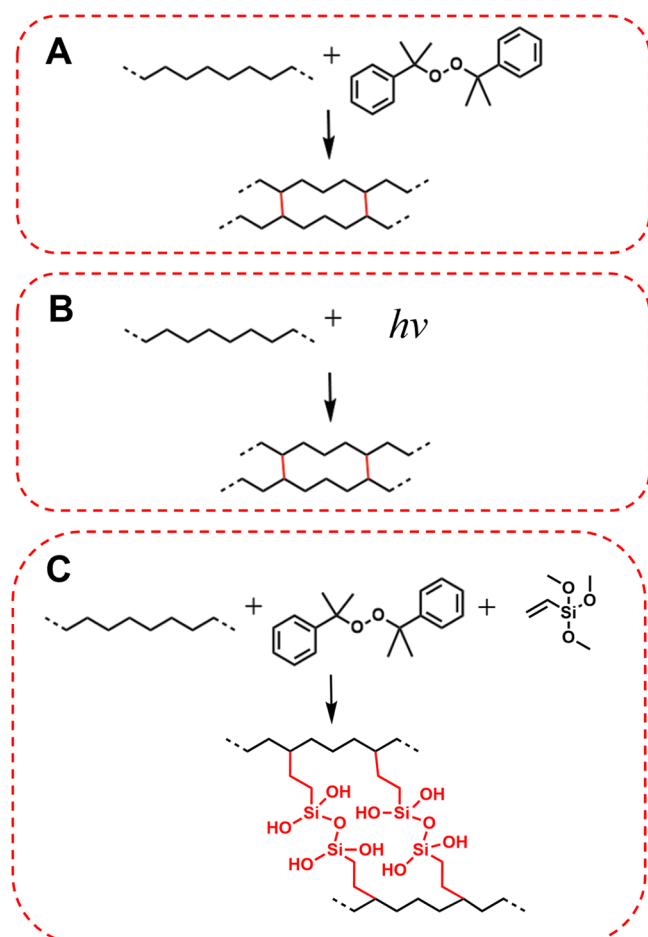

Figure 1. Overview of XLPE chemistry. A) Peroxide-cured XLPE, B) Radiation-cured XLPE, and C) Silane-cured XLPE (Si-XLPE). In radiation- and peroxide-cured XLPE, cross-links consist of C−C bonds, whereas in Si-XLPE, cross-links contain siloxane bonds.

the most prominent) methods generate free radicals that result in the formation of cross-links between PO chains.[13−15] Silane cross-linking (also known as moisture cross-linking) operates by the radical grafting of alkoxysilane cross-linkers to the PO backbone, followed by a condensation reaction to cross-link the polymer chains.[14,16] Peroxide cross-linking is versatile and suitable for various applications because it offers a broad processing window and fast cross-linking of different form factors,[4] but this option requires precise temperature control during extrusion and has significant equipment costs.[15,16] In contrast, radiation cross-linking provides consistent results, but the technique is expensive and more suitable for thin-walled

specialty cable applications due to the penetration limitations of radiation.[14,15] For PP cross-linking, with either peroxides or radiation, cross-linking coagents are employed to reduce chain scission.[9] Silane cross-linking is cost-effective, requires minimal additional equipment, and is popular in low voltage cables and pipes;[15,16] however, the approach relies on moisture diffusion, which leads to longer cure times (particularly in dry environments), sensitivity to moisture content during curing, and susceptibility to premature cross-linking.[14,16] On an industrial scale, XLPOs are generally extruded and/or injection molded then cured with specific processing conditions that depend on the application.[14] For a more in-depth discussion of XLPO cross-linking techniques and manufacturing, a review by Ahmad and Rodrigue provides further insights.[15]

The starting PO material, cross-linking method, cross-linking degree, and other factors affect the material properties of XLPO. For example, peroxide-cured LDPE with a gel content of 83% and molecular weight between cross-links of ~20 000 g/mol had a melting temperature (T_m) of 110 °C, tensile strength of 18.8 MPa, and elongation-at-break of 550%.[17] In another example, silane-cross-linked HDPE with 70% gel content had a T_m of 133 °C, tensile modulus of 1023 MPa, tensile strength of 21.4 MPa, elongation-at-break of 389%, and crystalline fraction of 60%.[18] Furthermore, application-specific standards dictate the minimum material requirements for XLPOs. For example, IEC 60502−1 is used for XLPE cable insulation and requires a minimum tensile strength of 12.5 MPa and elongation-at-break of 200% with a 25% maximum variation after heat aging.[19] The specific application also imposes the standards used to assess properties such as the degree of cross-linking. For example, the wire and cable industry relies on hot set testing to assess cross-linking, in which a maximum permissible hot set elongation is 175%, as is delineated in IEC 60811−507.[20] Alternatively, the pipes industry has specific cross-linking degree requirements that depend on the cross-linking mechanism (minimum gel content is 70% by peroxides, 65% by radiation, and 65% by silane cross-linking), as is delineated in ASTM F876−23 for pressure tubing.[12] Such regulatory standards ensure consistent performance of XLPOs across applications.

The high performance of XLPOs comes at the expense of circularity. XLPOs cannot be molten, and hence, most commercial XLPOs follow a linear lifecycle and are land-filled/incinerated after the first use. This end-of-life outcome is environmentally unsustainable, contributes to pollution and resource depletion, and poses economic concerns. Although efforts have been made to collect XLPO waste at the end of its lifecycle, challenges persist in handling and efficiently recycling XLPO, which emphasizes the urgent need for scalable XLPO circularity processes.[21] For instance, MTB Recycling (one of the largest cable recyclers in Europe) has an annual recycling capacity of 40,000 t of cables; however, the recovery and sale of copper and other metals is their major focus, and finding profitable solutions for the plastic cable components remains a challenge.[21] As XLPO products are already collected and separated, such scenarios provide a unique opportunity for valorization. Previous reviews have focused specifically on XLPE recycling but have not covered the broader sustainability of XLPOs throughout the entire materials lifecycle.[15,16,22] Broader PO circularity reviews tend to focus almost exclusively on thermoplastic POs with few including XLPO recycling.[23−25] Thus, there is an opportunity to holistically examine the
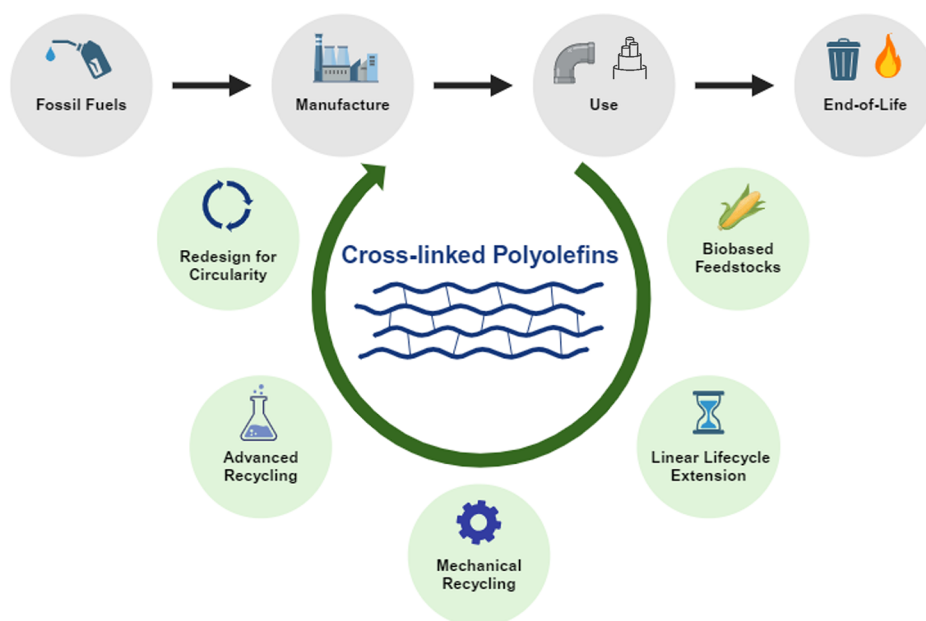
Figure 2. Overview of materials circularity strategies for XLPOs vs the current linear lifecycle. Created with BioRender.com.

circularity and sustainability challenges, innovations, and opportunities for XLPOs from feedstock to end-of-life.

This review discusses sustainable solutions to improve the circularity of XLPOs throughout the entire materials lifecycle with a focus on strategies that have the potential to be economically and environmentally viable at an industrial scale. An overview of the materials circularity approaches considered in this review is shown in Figure 2. Strategies explored include employing biobased feedstocks to generate olefinic monomers, and examples in which such feedstocks are already in use commercially are highlighted. Existing methods that extend the first XLPO lifecycle are emphasized to maximize the material's time in the "circularity loop" and reduce the amount of virgin feedstock consumed. Mechanical recycling processes and applications for ground XLPO as a filler/aggregate are discussed, and advanced recycling strategies that de-cross-link/deconstruct XLPOs are assessed on the basis of product value, scalability, and circularity. Additionally, XLPOs that are recyclable-by-design via dynamic covalent chemistries also are addressed, and key factors for evaluating these redesigned materials as alternatives to conventional XLPOs are proposed. The review concludes with considerations of future challenges and opportunities for sustainable XLPOs to balance high-performance demands with scalability and circularity.

2. BIOBASED OLEFINIC MONOMER FEEDSTOCKS

The majority of all commercial POs are synthesized from petroleum-derived monomeric feedstocks, which raises concerns about GHG emissions, limited availability of fossil fuels, and global resource stability.[1,26] Biomass feedstocks have emerged as a promising alternative to petroleum for polymer production,[26] with global biobased polymer manufacturing reaching 4.5 million tons in 2022 and a forecasted CAGR of 14% through 2027.[27] More specifically, the biobased PO market is predicted to grow by 20x over the next ten years.[28] Braskem's "I'm Green" PE is the largest-scale bio-PE on the market with 179 kton sold in 2022 and is the first certified bio-PE.[29] Other examples of commercial biobased POs include Dow's ENGAGE REN Polyolefin Elastomers[33] and Avient

Corporation's Maxxam BIO POs.[30,31] Braskem's plastics are synthesized from sugarcane ethanol;[29] Dow's polymers are derived from tall oil (a byproduct of wood pulping);[30] and Avient's materials incorporate renewable fillers from cellulose fiber and olive seed powder.[31] There are numerous pathways to produce biobased POs, each with advantages and limitations. For example, ethylene can be synthesized biologically through sugar fermentation to dehydrated ethanol or catalytically, as shown in Figure 3A and discussed in the recent review by Dutta.[32] Examples of pathways to produce bio-PP are shown in Figure 3B.[33] An important consideration to the overall sustainability of biobased POs is the source of the feedstock (i.e., whether it is a first-, second-, or third-generation feedstock). First-generation biomass sources are food crops, and thus, could potentially compete with food production and raise concerns about arable land usage.[34] Second- and third-generation biomass (comprised of cellulosic and waste residues/algae for second- and third-generation, respectively) encompass a range of nonedible biomass sources including agricultural/industrial residues, municipal solid waste, and algae.[34] Future research could investigate the synthesis of XLPOs from second- and third-generation biomass to potentially alleviate food system and environmental concerns, as discussed in a review on the manufacture of bio-PE from wood waste by Mendieta et al.[35] Yet, it is critical to note that just because a biomass feedstock is second/third generation does not necessarily make it more environmentally friendly. For instance, a lifecycle assessment (LCA) on the manufacture of lactic acid from edible corn vs corn stover found that the manufacturing of the corn stover lactic acid had ~47% increased monetized environmental costs than edible-corn lactic acid, mostly due to the additional pretreatment steps required for the corn stover-based feedstock.[36] Therefore, beyond the selection of a non-petroleum feedstock, it is also important to certify the sustainability/carbon neutrality and evaluate the economic/environmental viability of proposed biobased polyolefins. A number of sustainability certification systems exist and were reviewed by Ramirez-Contreras et al.[37] One example is the International Sustainability and Carbon
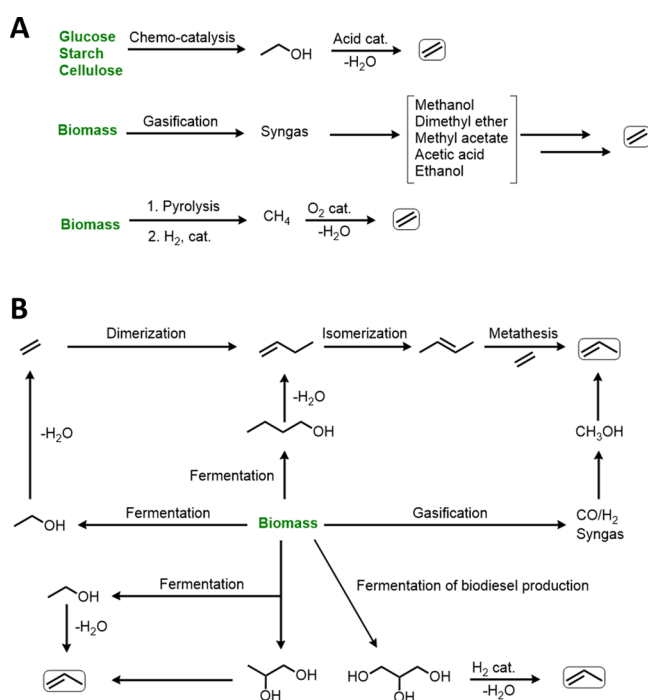
Figure 3. Examples of pathways to produce bio-olefins. A) Catalytic pathways to synthesize bio-PE and B) Fermentation and gasification pathways to synthesize bio-PP. Panel A adapted from ref 32. Copyright 2023 American Chemical Society. Panel B reproduced with permission from ref 33. Copyright 2015 De Gruyter.

Certification (ISCC) framework, which was developed to provide a globally applicable certification system for the sustainability of raw materials and products.[38] Other methods for the evaluation of proposed circularity solutions include technoeconomic analysis (TEA) and mass balance accounting (a metric for quantifying circularity) that can apply both to bio-XLPOs and the rest of the strategies described herein.[39−41]

Despite their potential for environmental impact reduction, bio-XLPOs have yet to be produced commercially. Bio-olefinic monomers can be leveraged to synthesize bio-XLPOs with identical chemical structures (as depicted in Figure 3), manufacturing, and properties vs their petroleum-derived analogues, in a similar manner to the commercially available thermoplastic bio-POs described above.[42] The biggest obstacle for drop-in biobased feedstocks is cost—for example, the price of bio-PE currently is ∼1.3−1.5x higher than the price of the petroleum-derived equivalent.[43] Yet, for scenarios in which either fossil fuel prices increase or governments enact carbon taxes or similar policies, drop-in alternatives could become more commercially viable.[44,45] Biobased XLPOs could improve the sustainability of the monomer feedstock by eliminating the need for virgin fossil fuels and adding temporary carbon sequestration during the biomass growth stage; however, the specific strategy to make bio-XLPO must be evaluated to ensure that the overall process, from feedstock to polymer, leads to a reduction in environmental impacts.[46] Furthermore, because the structure of the monomers and final product are identical to traditional XLPOs, the same end-of-life concerns with regards to sustainability exist for bio-XLPOs.[41] Thus, although bio-XLPOs can reduce environmental impacts during XLPO production, renewable feedstocks must be used in conjunction with the approaches presented in the following sections to improve overall XLPO circularity.

3. EXTENDING XLPO'S FIRST LIFECYCLE

The optimization of XLPO design for longevity decreases carbon emissions by lowering replacement frequency and reducing demand for raw materials and manufacturing. Additionally, the extension of XLPO's first lifespan mitigates materials disposal challenges, which delays entry into the recycling stream, and thus postpones the need for recycling infrastructure and potentially energy-intensive reprocessing. Sustainability is enhanced because a longer lifespan for XLPO contributes to more efficient management of resources throughout the material lifecycle. An LCA comparing the use portion (often associated with power loss) to the manufacture portion of XLPE cables revealed that manufacture amounts to >2x more global warming potential (GWP; expressed in kg of CO_2 equivalents) than use for both overhead and underground cables, (Figure 4) − emphasizing the environmental
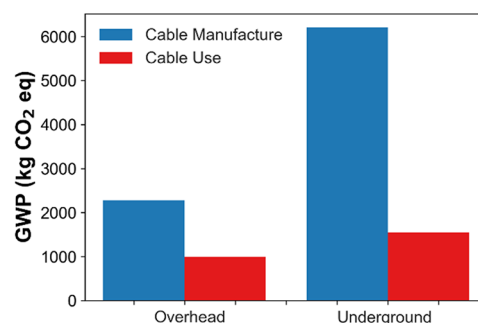

Figure 4. Comparison of GHGs emitted during manufacture and use for overhead and underground cables measured in GWP expressed in kg of CO_2 equivalents. Adapted from ref 47. Copyright 2010 American Chemical Society.

significance of materials longevity.[47] Another LCA suggested that 1 trillion kg of CO_2 equivalents are emitted as a result of additional power generation required to compensate for transmission and distribution infrastructure-related power losses (determined by the combination of power generation and uncertainty analysis across 142 countries).[48] Infrastructure technical losses that result from limits such as aging (i.e., less efficient) or failing cables require power plants to generate more than 1 kWh to deliver 1 kWh to a customer, and thus, extending XLPE cable's longevity can improve infrastructure efficiency, decrease the required excess power generation, and reduce GHG emissions.[48] In an additional example, XLPE pipes, when substituted for traditional copper pipes in residential water plumbing, reduced building costs by up to 63% and GHG emissions by 42%.[49] These GHG and cost savings are mostly due to higher copper installation costs and increased required maintenance, as copper is more prone to corrosion and leaking than XLPE.[49] Copper pipes generally have a longer lifecycle than XLPE pipes (50 vs 25 years for copper vs XLPE, respectively), but future research into XLPE formulations to increase longevity to be above that of copper could result in further cost and GHG savings.

The lifetime of cables has no single determining factor; XLPO insulation plays a considerable role in cable performance, but other variables such as incidents (e.g., weather events, mechanical damage from digging), voltage, ampacity, temperature, and the installation environment are also contributors. Thus, improving cable insulation is beneficial but not the only aspect to consider to enhance overall cable sustainability. One
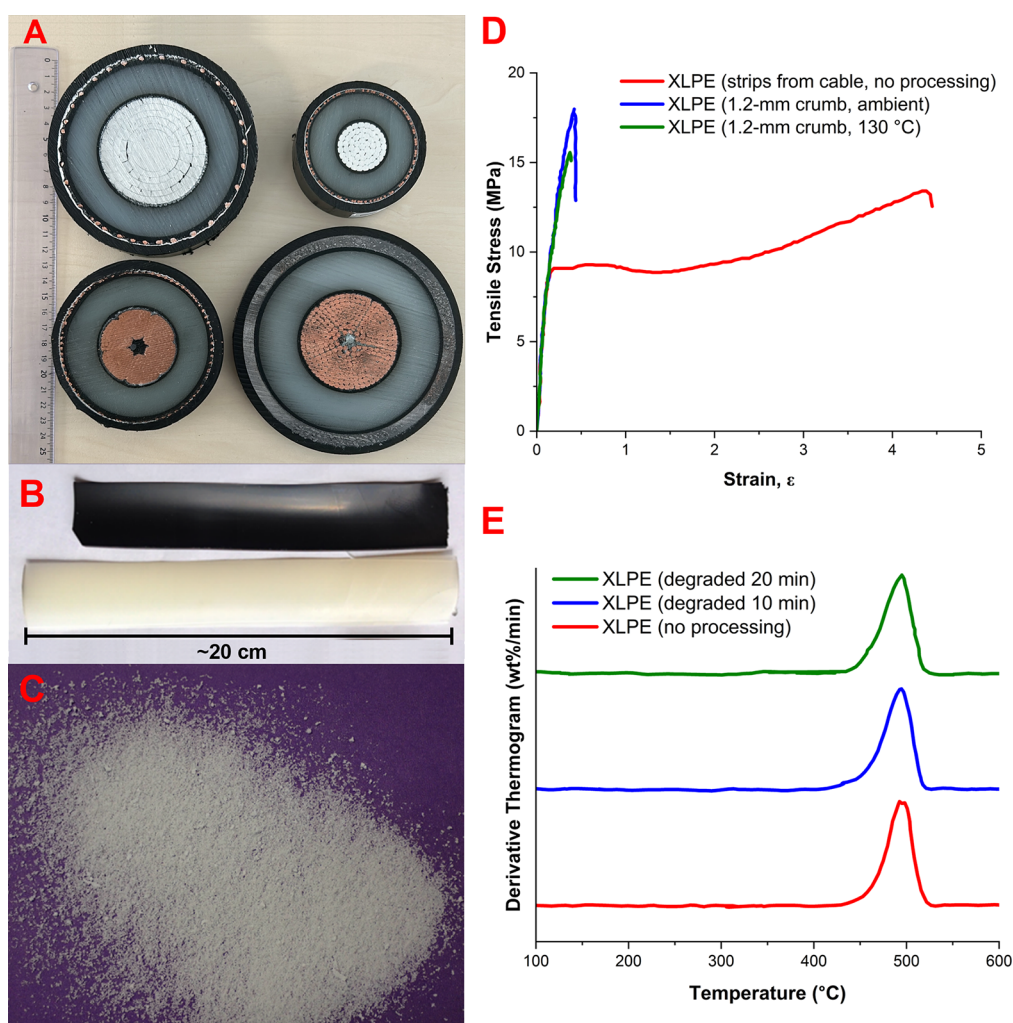
Figure 5. Photographs of a spent XLPE power cable at different stages of mechanical recycling and XLPO recyclate properties. A) Complete cross sections of XLPE power cables, B) cable sample with the outer black semiconductive shield (above) removed from the natural XLPE insulation layer (below), and C) ground XLPE obtained on a conventional Wiley cutting mill with a 3 mm sieve. Particle size distribution is as follows: 25% > 500 μm, 38% from 355−500 μm, 18% from 300−355 μm, and 19% from 75−300 μm. D) Tensile properties of injection-molded samples of ground XLPE recyclate vs unprocessed XLPE and E) thermal stabilities of XLPE after varying times of thermomechanical reprocessing. Panel D adapted with permission from ref 17. Copyright 2000 John Wiley and Sons. Panel E adapted with permission from ref 62. Copyright 2016 Elsevier. Panels D and E replotted using PlotDigitizer.[63]

important aspect of insulation performance is that cables may be exposed to electrical stress in a moist environment (*e.g.*, when directly buried in the ground) and are therefore subject to water-tree-growth deterioration.[50] Water treeing is a phenomenon in which branching degradation channels, which originate from water contact under electric fields, develop within the insulation of power cables and impair performance and longevity.[51] A medium voltage cable lifecycle cost study can provide insights into the advantages of prolonging the lifespan of XLPO materials in this regard. For this scenario, the anticipated 25-year lifespan of XLPE was compared to the anticipated 40-year lifespan of water tree-retardant XLPE (TR-XLPE).[52] TR-XLPE is a specific formulation of XLPE designed to resist water treeing through the incorporation of a low-level, nonmigratory additive package to enable longer service life.[51] The study revealed a substantial decrease in lifecycle costs for TR-XLPE, with ∼50% total cost savings over the materials lifecycle relative to traditional XLPE.[52] The analysis incorporated testing of field-aged cables and accelerated laboratory testing, including the examination

of cables buried for 17 years, and showcased the retention of dielectric strength that was augmented by data from accelerated wet-aging tests.[52] This significant economic improvement emphasizes the benefits linked to the deliberate selection of materials designed for enhanced longevity. There are also other methods to prepare XLPOs under assisted electric fields that can enhance electric breakdown strength, decrease conductivity, and potentially improve durability/longevity without additional additive incorporation.[53] Although negative environmental impacts are anticipated to decrease by prolonging XLPE cable longevity, future LCA is needed to confirm this conjecture; moreover, the effect of additive packages on recyclability needs further investigation.

4. TRADITIONAL MECHANICAL RECYCLING AND APPLICATIONS FOR GROUND XLPO

Mechanical recycling is the most widely adopted recycling technique and is presently considered the most economically feasible method at an industrial scale.[54] This approach involves reprocessing plastic waste into secondary raw materials and

products through physical means.[54] Mechanical recycling has been reviewed extensively for thermoplastic polymers such as POs and also has been applied to XLPO waste for reclamation and reuse.[24,55] Unlike many other polymers, sorting XLPO poses fewer challenges, benefiting from specific point sources as opposed to the complex mix found in larger post-consumer recycling plants. Yet, inherent limitations emerge, especially if the cross-linked structure undergoes significant alteration during manufacturing or use.[56] One of the major challenges with the mechanical recycling of XLPOs is that neither XLPO nor its resulting recyclate can be molten. Consequently, the recyclate is often incorporated in a blend or composite for processing and is effectively positioned as a filler.

Mechanical recycling typically includes collection, sorting, materials comminution (e.g., grinding to controlled particle sizes, typically 50−900 μm, depending on the specific mechanical recycling process),[17,56−58] cleaning, reprocessing at different weight ratios, and providing reinforcement for various polymer systems.[24,59−61] Based on the XLPO source, the recyclate often contains contaminants—for example, cable recyclate may include 1−2 wt % metal contamination.[17] Figure 5A-C illustrates examples of spent XLPE cable, representative cable stripped down to XLPE, and XLPE cable ground into smaller particles, respectively. Figure 5D-E compares the tensile properties and thermal stabilities of ground XLPE recyclate to unprocessed XLPE. Figure 5D shows the lower elongation-at-break and higher tensile stress for injection-molded, ground XLPE recyclate relative to injection-molded, unprocessed XLPE (blue vs red curves).[17] A higher temperature injection-molding process appeared to slightly decrease the ultimate tensile strength of the final product (green vs blue curves).[17] Figure 5E illustrates the similarity in thermal stability before and after two recycling times in a thermomechanical batch mixer.[62] These two examples are representative of the general trend for XLPOs in which mechanical recycling has a larger effect on tensile properties and a smaller effect on the thermal stabilities. Additionally, in-depth recyclate characterization should be incorporated in future mechanical recycling studies to understand how material degradation resulting from the grinding process impacts XLPO microstructure.

4A. Applications as a Filler. To overcome potential degradation in performance, recycled XLPO often is blended with virgin PO to achieve desired properties, and fundamental technical variables such as XLPO loading, particle size, and layer separation have been examined to optimize these formulations. Ground, recycled XLPOs generally are reintroduced into virgin thermoplastic materials at relatively low weight percentages (i.e., 1−25 wt %). The addition of XLPO often improves some properties and worsens others—for instance, higher loadings of XLPE in an XLPE/HDPE blend increased impact strength by ∼30% but decreased flexural strength and modulus by ∼10%.[57] As a balance must be struck between raising the XLPO loading and maintaining required performance properties, several studies have investigated the optimal XLPO-to-virgin-material ratio for specific processing applications. For example, Diaz et al. demonstrated that up to 35 wt % ground XLPE from cables could be used in a PE matrix for rotational molding applications without a significant reduction in tensile and flexural properties.[56] Lindqvist et al. incorporated 25−50 wt % loadings of XLPE from both cable manufacturing waste and end-of-life cables into blends with PP and found that higher XLPE loadings (50 vs 25 wt %)

increased strain-at-break and impact strength, but decreased elastic modulus and stress-at-break.[58] Furthermore, the blends containing XLPE from end-of-life cables experienced more severe degradation upon aging at 105 °C for six months, although the addition of an antioxidant/metal deactivator (Irganox MD 1024) was successful in retaining mechanical properties over an extended period (accelerated aging for 6000 h).[58] In comparison to XLPO loading, particle size appears to have a lesser impact on the overall performance of XLPO blends. For instance, Freitas et al. found that particle size significantly affected only the tensile strength out of five mechanical properties tested (impact strength, tensile strength, tensile strain-at-break, flexural strength, flexural modulus) in XLPE/HDPE blends,[57] and White et al. demonstrated that the particle size did not appreciably change the material properties for blends containing reprocessed XLPE when subjected to injection molding under high pressure.[17] Beyond investigating XLPO loading and particle size, Diaz et al., showed that multilayer molding improved external appearance and mechanical property retention relative to monolayer molding of an XLPO/PE blend and may enable higher loadings of XLPO going forward.[56] Possible next steps should focus on further optimization of these blends and characterization of XLPO blends' material performance (e.g., thermal stability, UV resistance) beyond the mechanical properties mentioned above.

XLPO blends have already found utility in, or been proposed for, a variety of applications as illustrated by the examples below. Ground XLPE from cable scrap has been compounded into virgin PE matrices that could be used for injection molding of cable guards and packaging articles, extrusion of internal cable jackets, and rotational molding of parts.[59] Finely ground XLPO foam has been introduced as a filler to HDPE (up to 30 wt %), which increased impact strength and tensile strength-at-break by over 400% and 40%, respectively, without significantly affecting other mechanical properties.[60] XLPE foam aggregates also have been incorporated in non-woven, geotextile composites for floating covers employed in odor/air emission control from manure storage structures.[61] These applications grant the recycled material an additional life, though work to determine how many times remolding may be possible is critical to assess the true "circularity" of such materials. Particular attention must be paid to the amount of contamination (particularly from metals in cables and additives in all XLPO formulations), as higher contamination levels can lead to greater degradation over material lifetimes.[58]

The behavior at the particle interface and the compatibility between XLPO and the matrix are important considerations for XLPO blends. As XLPO particles are cross-linked, the chemical/physical bonding at the interface with the continuous matrix is likely relatively weak (compared to the interface of a comparable blend without cross-linked particles), leading to poor interfacial adhesion. Lindqvist et al. investigated the compatibility of ground XLPE particles from cable manufacturing waste at 50 wt % loading in a PP matrix using scanning electron microscopy.[58] The XLPE particles appeared well dispersed with no visible voids at the interface between the particle and matrix; nonetheless, sharp edges around the particles suggested that the interaction between the two materials was indeed low.[58] Fortunately, analysis of blending recycled ground tire rubber into thermoplastic matrices may offer insight into various techniques to enhance XLPO/matrix compatibility.[64] These techniques include the use of

compatibilizers or coupling agents, nanofillers, and energy treatment, as well as processes like devulcanization and revulcanization to improve the interfacial adhesion and dispersion of the ground tire rubber.[64] Similarly, compatibilization approaches have been applied to mixed plastics waste recycling, in which material streams consist of multiple immiscible polymers.[65] For example, compatibilizers in the form of block copolymers, non-reactive polar polymers, and reactive functionalized polymers can improve adhesion in plastic/plastic blends.[65] Similar compatibilization strategies may be beneficial to the performance of ground XLPO blends.

4B. Applications as an Aggregate.

Aggregates for building materials are traditionally dominated by sand, gravel, or crushed rock, which can comprise a majority of the total mixture (e.g., ~80 vol % or 90 wt % for asphalt).[66] Traditional aggregates face concerns such as resource scarcity and adverse impacts on the environment in the mining region.[67] Mechanically recycled XLPO finds extensive use as an aggregate in construction materials to alleviate these environmental concerns and decrease the overall material weight because XLPO is significantly less dense than traditional aggregates.[68] For example, Vidales-Barriguete et al. incorporated XLPE cable waste directly (without any selection or pretreatment) into gypsum boards, such as drywall panels.[69] XLPE-containing boards exhibited increased elasticity and marginally improved thermal conductivity and surface comfort while remaining within the necessary compliance values for flexural strength.[69]

Concrete and cement applications also benefit from the incorporation of mechanically recycled XLPO as an aggregate.[70] For instance, Reiterman et al. partially replaced natural sand with crushed cable waste in cement, which slightly improved freeze–thaw resistance and reduced bulk density.[68] Although the compressive and flexural strengths of the hardened screed were reduced proportionally with the amount of cable waste, these properties remained within the specified technical requirements.[68] Notably, this example of cable waste used a mixture of XLPE, poly(vinyl chloride) (PVC), and PE, and it highlights the robustness of such applications to handle less pure XLPO product mixtures.[68] The elasticity of XLPO also led to improved cracking resistance properties to concrete and cement.[71] Another study assessed the viability of the incorporation of up to 15 vol % XLPE waste as a partial substitute for traditional stone aggregates in concrete.[72] Increased XLPE content improved workability and ductility, decreased unit weight and cracking, and maintained compliance with industry standards for compressive strength, as shown in Figure 6.[72] This enhanced ductility makes XLPE-containing concrete more suitable for applications that are particularly susceptible to cracking, such as irrigation canals.[72] One remaining concern is the risk of aggregate products entering the environment as leachates or microplastics, especially for use cases such as canals. Assessment of this risk is necessary for such applications before full-scale implementation.

A particularly promising avenue for the application of mechanically recycled XLPE is as an aggregate or binder replacement in asphalt, similar to recycled ground tire rubber. XLPE powder has been used as an asphalt modifier to improve thermal stability and significantly reduce melt viscosity, thereby improving asphalt processing.[73] The incorporation of waste XLPE also increases material resistance to rutting/fatigue and elasticity of bitumen.[74] Additionally, the inclusion of XLPE can

Figure 6. Photographs of representative failed concrete samples from a uniaxial compression test with XLPO content varied from 0 to 15 vol %. Concrete cylinders were prepared at a water-to-cement fraction by mass of 0.50, and compression tests were conducted according to ASTM C39. Higher XLPO contents led to more ductile and workable concrete that was less susceptible to cracking. Adapted with permission from ref 72. Copyright 2024 Elsevier.

decrease the density of asphalt to enable more lightweight structures, improve permanent deformation and temperature resistance, and retain similar water resistance to conventional asphalt.[75] Although applications as an aggregate or filler may not result in the higher-value products that can be achieved with advanced recycling techniques, there are a number of existing applications for mechanically recycled XLPO that are already industrially feasible and can be immediately implemented more broadly to improve the circularity of XLPO and the longevity of the systems into which repurposed XLPO is incorporated.

5. ADVANCED RECYCLING AND MATERIALS VALORIZATION

Advanced recycling involves the breakdown of XLPOs to create new products and can be classified as de-cross-linking, depolymerization, or deconstruction. De-cross-linking breaks only the cross-links while keeping the polymer backbone intact, depolymerization converts the polymer back to the original monomer, and deconstruction cleaves the polymer into smaller units (Figure 7). Each of these recycling
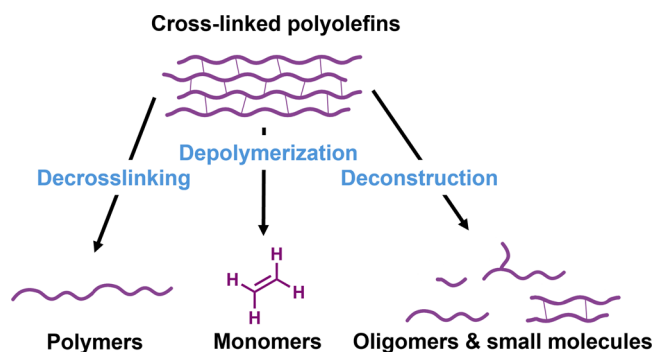

Figure 7. Overview of XLPO recycling strategies and classification of primary product(s). Specifically shown with ethylene as the monomer. Oligomers include linear, branched, and partially cross-linked PE.

methods leads to varying types of products with enormous ranges in material properties, and thus, each approach may be suitable for different applications.

Although a process-based differentiation can be made, herein, advanced recycling strategies were viewed from a product perspective (i.e., recycling thermosets into thermoplastics or recycling thermosets into lighter hydrocarbons, oils, and monomers). The primary reason for this approach is that POs are chain-growth polymers with C–C backbone bonds that require a large amount of energy to break, and PO degradation typically proceeds heterogeneously, which yields a

Table 1. XLPO Recycling Strategies with Associated Advantages and Limitations

Major Recycling Product	Strategy	Advantages	Limitations
Thermoplastics	Mechanochemical milling[77−80]	Reprocessable products, inexpensive	Thermal stability, batch process
	Ultrasonic extrusion[81]	Reprocessable products	Cost, backbone degradation
	Supercritical fluid de-cross-linking[65,82−86]	Reprocessable products	Higher temperatures and pressures, cost, scalability
Oligomers, small molecules, and monomers	Pyrolysis[87]	Higher conversion rates	Lower-value products, pollution concerns
	Catalytic deconstruction[88]	Higher-value products	Higher costs, requires further development
	Liquefaction[89]	Capable of handling waste mixtures	Higher costs, requires further development

mixture of products, including gases, oils, char, and wax, with wide molecular weight distributions that depend on the feedstock and process conditions.[76] Furthermore, due to the more homogeneous molecular structure of peroxide- and radiation-cured XLPOs, it is virtually impossible to break down the structure into small molecules without de-cross-linking. Conversely, it is difficult to selectively target only the cross-links without some cleavage of the main chain. An overview of the advantages and limitations of the advanced recycling methods discussed in this section is shown in Table 1.

A major consideration for recycling XLPO is the cross-linking chemistry employed, such as peroxide or silane-curing. For example, peroxide-cured XLPE is generally more homogeneously cross-linked than silane-cured XLPE (Si-XLPE); hence, Si-XLPE typically breaks down in a more localized (i.e., less uniform) manner than peroxide-cured XLPE.[90] Si-XLPE is more sensitive to property degradation, potentially because of its higher heterogeneity enabling XLPE degradation to occur in local centers with increased reactivity.[90] Furthermore, the type of bonds in the cross-link significantly impacts the approach and ease of cleavage. An unsubstituted C−C bond's dissociation energy is ∼72−87 kcal/mol, whereas a siloxane bond's dissociation energy is typically >120 kcal/mol, therefore ∼1.4−1.7x more energy is required to break a siloxane bond vs an unsubstituted C−C bond.[91] Additional considerations include the degree of cross-linking, additives, cost, and sustainability.

5A. Recycling Thermosets to Thermoplastics. Mechanochemistry, in the form of solid-state milling, is a de-cross-linking strategy that has gained recent prominence, with popular strategies including pan-milling and continuous twin-screw extrusion.[77,80] Pan-milling, also known as solid-state-shear milling, is a poplar mechanochemistry strategy that grinds material between two rotating planes equipped with teeth designed to induce a combined compression and circumferential shearing impact.[78] Pan-milling aims to selectively de-cross-link XLPO, without significant cleavage of the polymer backbone, by preferential breakage at the cross-links as the highest stresses and moments are likely to accumulate at these sites during milling.[79] Pan-milling has been used to recycle waste XLPE cables into phosphogypsum-containing composites for applications such as waterproofing.[92] In addition to XLPO-related uses, solid-state shear milling has broader applicability in recycling rubber tire waste and has been used to prepare thermoplastic vulcanizates from 50/50 XLPE/tire rubber blends.[93]

Cross-linking in both Si-XLPE and peroxide-cured XLPE has been effectively reduced via pan-milling in several studies, with gel fractions (measured by Soxhlet extraction) decreasing from 77 to 14 wt % and 70 to 15 wt % after 20 cycles for Si- and peroxide-cured XLPE, respectively.[77,79] After milling Si-XLPE, Fourier-transform infrared (FTIR) spectroscopy analysis showed a large reduction in the peak at 1030 cm^{-1} (corresponding to the siloxane bond −Si−O−Si−) in the milled vs unmilled Si-XLPE.[77] Taken together, the gel content reduction and FTIR spectra demonstrate the deconstruction of the cross-links. The molecular weight of the soluble fraction of the XPLE was measured via gel permeation chromatography (GPC) − i.e., GPC was performed on the 30 wt % that is not cross-linked in 70 wt % cross-linked XLPE.[77,79] Despite the authors' claims that an increase in the molecular weight of the soluble fraction for the milled vs unmilled Si-XLPE meant that the de-cross-linking occurred without breakage of the main chain, one could also conclude that the GPC traces indicate

that chain scission has occurred because the molecular weight of the soluble fraction after milling is ∼3x lower than the PE molecular weight before cross-linking.[77] Reconciliation of the molecular weight data is an essential component in future efforts to determine the extent of backbone degradation during milling. Rheology measurements (e.g., zero-shear viscosity) are one approach that has been implemented to indirectly measure the molecular weight of the de-cross-linked material.[80] This method reflects contributions for both the cross-linked and un-cross-linked portions of the polymer through the use of the empirical relationship between the melt viscosity and molecular weight, although differentiating between contributions from chain lengths, branches, cross-links, and fillers remains a challenge.[80] Mechanochemistry is considered a cost-effective and environmentally friendly method in comparison to other advanced recycling strategies to reprocess thermosets with the potential to retain better mechanical properties vs traditional mechanical recycling; however, studies are still necessary to address the energy intensity associated with numerous milling cycles, apply mechanochemistry strategies to radiation-cross-linked XLPE, and investigate whether milling results in small molecules that can leach out from the product in a future lifecycle.

Ultrasonically aided extrusion also has been investigated as a physical recycling approach, inspired by similar strategies that devulcanize cross-linked rubbers.[15,81] In this method, ultrasonic generators are used in conjunction with extruders to reduce melt viscosity, thereby improving processability.[94] Huang et al. investigated the de-cross-linking of peroxide-cross-linked HDPE and LDPE with twin-screw, ultrasonically aided extruders and found a reduction in gel content from 93 to 27 wt % and 93 to 61 wt % for cross-linked HPDE and LDPE, respectively.[81] Factors that impact the de-cross-linking include the screw design, extruder type, ultrasonic amplitude, and XLPE branching.[15,81] Long-chain branching in cross-linked LDPE enhances breakage of the main chain because long chains reduce the material's ability to change configuration when subjected to strong biaxial deformation, which possibly causes increased stretching in the XLPE and backbone degradation.[81] Ultrasonic extrusion has the potential for increased throughput; however, the abovementioned polymer backbone degradation and high costs may be problematic.[15]

Another advanced recycling strategy investigated for XLPO de-cross-linking leverages supercritical fluids, which are excellent plastics decomposition media.[65] Peroxide-, radiation-, and siloxane-cross-linked XLPEs have been de-cross-linked with supercritical alcohols, including methanol, ethanol, and propanol. Methanol is the most common reaction medium because of its relatively mild critical conditions [critical temperature (T_c) = 240 °C, critical pressure (P_c) = 8.1 MPa] and high efficacy.[95] For example, Cho et al. completely de-cross-linked XLPE in supercritical methanol, with the gel content decreasing from 88 to 0 wt %.[83] Other studies have proposed swapping supercritical alcohol for supercritical water to alleviate the toxicity concerns associated with methanol; however, supercritical water has a higher T_c and P_c, (T_c = 374 °C, P_c = 22.1 MPa), which makes potential recycling systems more expensive than those using supercritical alcohols.[82,84,96] Furthermore, de-cross-linking with supercritical water has only been demonstrated successfully on Si-XLPE, but the process has not been extended to peroxide- or radiation-cured XLPE.[82,84] A major concern associated with supercritical fluid de-cross-linking is that most proposed strategies were run
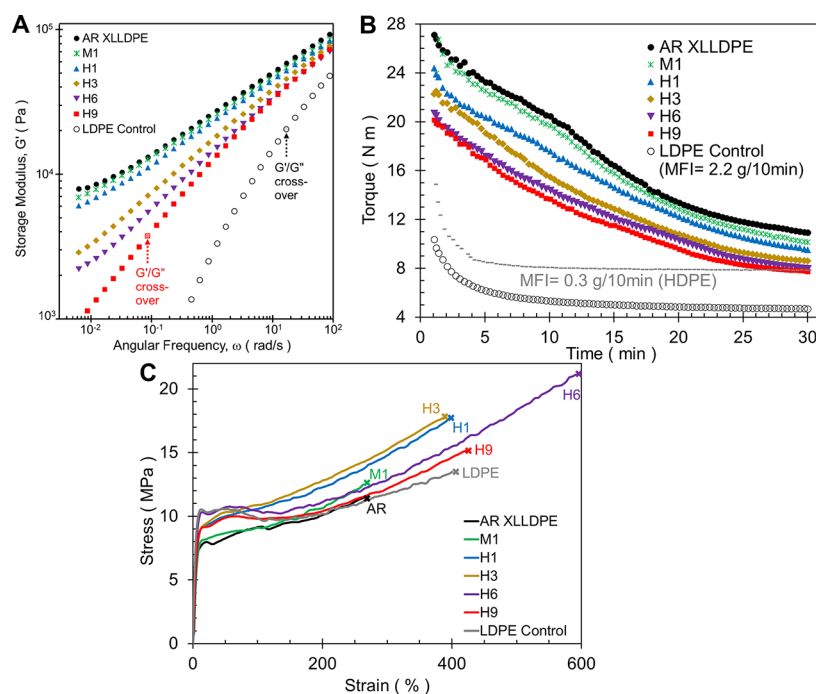
Figure 8. Tensile and rheological properties of de-cross-linked XLPE recyclates with XPLE and LDPE as controls. A) Storage modulus curves from parallel plate oscillatory frequency sweeps, B) torque rheometer outputs with an additional benchmark of commercial, extrusion-grade HDPE (dotted line), and C) representative stress—strain curves. G' is shear storage modulus, G'' is shear loss modulus, and MFI is melt flow index, a common industrial proxy for material processing. AR is as-received post-industrial XLLDPE, M or H refers to mild vs harsh screw configuration, and the subsequent number is the number of passes through the pulverization setup. Adapted from ref 80. Available under a CC-BY license. Copyright 2022 Zack et al.

in batch reactors, and thus need to be adapted to continuous setups to improve scaleup feasibility and costs.[85] Baek et al. de-cross-linked peroxide-cured XLPE in a continuous, multiscale single-screw extrusion process at a feeding rate of 7 mL/min with the XLPE in contact with the supercritical fluid for <2 min,[85] but this feeding rate is still relatively slow; hence more work is required to scale these systems and address concerns about industrial suitability stemming from higher costs.

The ultimate recyclate properties are important considerations for all the above de-cross-linking techniques. The work by Zack et al., which employed a solid-state shear pulverization de-cross-linking strategy on peroxide-cross-linked XLPE and achieved a minimum gel content of 2%, is presented as a case study of de-cross-linked XLPO recyclate performance.[80] Test results of the recyclate compared to un-cross-linked LDPE and unprocessed XLPE [referred to as cross-linked linear low-density polyethylene (XLLDPE)] as controls are shown in Figure 8A-C. Because the recyclate has a degree of cross-linking between those of the LDPE and XLLDPE, one may expect the recyclate to exhibit behavior between those of the LDPE and XLLDPE; this expected behavior is demonstrated in the parallel plate and torque rheology experiments. Conversely, the stress—strain curves show recyclate properties that are outside the ranges of either control, which suggests that the de-cross-linked recyclate is more branched, and with a deteriorated backbone, than the starting thermoplastic. Thermal properties of the recyclate [specifically, T_m, thermal decomposition temperature (T_d), and crystallization temperature] were impacted significantly less than tensile properties, similar to the mechanical recyclate discussed in the previous section. Together, these results provide a detailed picture of the impacts of the de-cross-linking process on the chain architecture and macromolecular structure and are generally representative of other recycling studies, such as those that employ ultrasonic and critical fluid de-cross-linking techniques.[81,85] Even in a de-cross-linking study that showed reduced gel content to 0%, the tensile and rheological properties of the de-cross-linked XLPO did not match those of thermoplastic PO, further emphasizing the impact of de-cross-linking strategies on molecular

architecture and therefore also crystallinity.[83] Future studies should investigate how these changes impact the ability of the de-cross-linked XLPOs to be successfully re-cross-linked in a closed-loop recycling approach, and if possible, how the properties of the recycled XLPOs compare to those of virgin materials.

5B. Recycling Thermosets into Oligomers and Small Molecules.
Pyrolysis is a compelling route to handle mixed plastics or difficult-to-recycle materials at relatively high temperatures.[65] Plastics waste pyrolysis primarily yields liquid and gaseous hydrocarbons, char, and wax, and the distribution of products depends on operating conditions such as temperature, pressure, catalyst choice, type of feedstock, and reactor design.[97] The generation of syngas (a mixture of H_2 and CO) from pyrolysis is also a focus of current research because syngas is a valuable intermediate in the synthesis of numerous industrial chemicals, ranging from liquid fuels and lubricants to alcohols, aldehydes, olefins, and ammonia.[98] Yet thus far, there has been little research on syngas production from XLPO pyrolysis. In one study, Singh et al. used pyrolysis and CO_2-assisted gasification (performed at 900 °C, with syngas yields of 80 and 250 wt % for pyrolysis and gasification, respectively, wherein the gasification yield is >100% because the yield is calculated on an XLPO-basis, but the CO_2 also reacts to produce syngas) of XLPE to generate syngas with a similar energy heating value to natural gas.[87] More work is needed to understand the kinetics and transport phenomena associated with these processes in large-scale reactors.[87]

Catalytic approaches, such as catalytic pyrolysis, also have been considered for the recycling of XLPOs, as the leveraging of catalysts typically enables lower operating temperatures and results in liquid products.[88] For example, Straka et al. investigated the catalytic pyrolysis of XLPE from cable and pipe manufacturing scraps with Ru-based catalysts at 450−470 °C.[88] The process achieved an 87−91 wt % yield of hydrocarbon oil, a possible intermediate to synthesize value-added products such as solvents, industrial oils, lubricants, and fuels.[88] Thermogravimetric analysis and differential scanning calorimetry techniques have been used to illuminate the consequences of cross-linking degree on the pyrolytic decomposition behavior of

peroxide-cross-linked XLPE, both in the presence and absence of a typical fluid cracking zeolite catalyst.[89] The inclusion of a catalyst enabled a ~60 °C decrease in pyrolysis temperature, but the catalyzed process was more sensitive to the degree of cross-linking, with higher operating temperatures required for increased degrees of cross-linking—as the cross-linked matrix was suggested to hinder the mobility of PE chains and hence the interaction with the catalyst's active sites.[89] Future efforts are appropriate to determine the catalyst's effect on deconstruction yields and product distributions, and there is a significant opportunity to leverage other catalytic deconstruction approaches (*e.g.*, hydrocracking, hydrogenolysis) to recycle XLPO.

Other advanced recycling technologies, such as hydrothermal and solvothermal liquefaction that run at high temperatures and pressures in the presence of water and organic solvents, respectively, can depolymerize XLPOs and yield monomers, platform chemicals, or fuel oil.[99] Liu et al. investigated the depolymerization of LLDPE and XLPE from cable waste in water, acetone, and methanol under liquefaction conditions with the resulting product streams containing gas, oil, and solid fractions.[99] Acetone liquefaction at 350 °C for 90 min (optimal performance conditions) achieved a conversion of 75%, oil yield of 39%, energy recovery of 40%, and higher heating values of 44 MJ/kg for the oil samples, along with a lower-boiling-range molecular distribution.[99] The oil fraction contained alkanes and alkenes within carbon ranges of C_{14} to C_{31} and C_{16} to C_{21}, respectively.[99] Although the study did not include a detailed compositional analysis of the gas phase, it is expected that this product stream mostly would include short alkanes and alkenes because of the lack of selectivity of random chain scission. Liquefaction is a promising strategy to transform spent XLPOs into valuable chemicals/fuels at the end of its first materials lifecycle; however, future work is necessary to optimize the process to reduce reaction temperatures/times and selectively tune mixtures for specific applications.

Most of the above approaches are still in their experimental stage and have been validated only at laboratory scale. The petrochemical industry is investigating the pyrolysis of XLPO into fuel as the most feasible, large-scale, XLPO advanced recycling technique, and preliminary results suggest that the product of pyrolysis-treated XLPE is a suitable cracker feedstock to make new PE.[100] To realize this technology at scale, it is important to streamline the fragmented XLPO waste collection process and supply chain. Furthermore, detailed TEA/LCA of the advanced recycling methods would be beneficial to identify the most promising approaches, highlight the remaining challenges, and evaluate industrial scalability.

6. REDESIGNING XLPOS WITH DYNAMIC COVALENT CHEMISTRIES

It remains critical to develop sustainable end-of-life solutions for the XLPOs already produced, but inherent difficulties in reprocessing will continue to be a challenge for XLPOs. Thus, there is an opportunity to redesign the next generation of XLPOs with end-of-life options in mind (*i.e.*, "recyclable-by-design"). Recyclable-by-design polymers can be achieved through the incorporation of dynamic covalent chemistries in which traditional covalent cross-links are replaced with reprocessable bonds (*i.e.*, those that can exchange or disassociate under certain stimuli, such as heat, light, pH, or solvent). These dynamic covalent chemistries include covalent adaptive networks (CANs), dissociative reactive networks, and vitrimers (*i.e.*, a specific set of CANs in which bonds exchange under a heat stimulus without an intermediate state of disconnection).[101,102] There are many proposed dynamic covalent chemistries with great potential for reprocessability that have been the subject of several recent reviews,[101,103,104] including one specifically focused on PO vitrimers by Ahmadi et al.[105] In this section, the most common dynamic chemistries that have been applied to POs (shown in Figure 9) and key
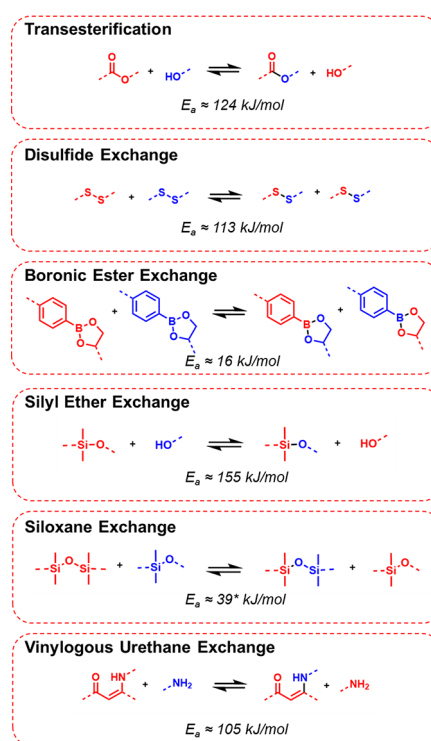

Figure 9. Highlighted dynamic covalent chemistries and activation energies (E_as) required for the exchange reaction.[102,106−110] Examples of the reprocessing conditions for each dynamic covalent chemistry are as follows: transesterification—compression molded at 210 °C,[106] disulfide exchange—compression molded at 160 °C,[107] boronic ester exchange—compression molded at 150 °C,[111] silyl ether exchange—melt processed at 150 °C,[109] siloxane exchange—reprocessed in dibenzo-18-crown-6 ether with a KF catalyst at 160 °C,[108] and vinylogous urethane exchange—extruded at 160 °C.[110] *Siloxane exchange is the only exchange reaction whose E_a was calculated in the presence of a catalyst.

considerations for success on an industrial scale are highlighted. Dynamic covalent chemistry-based POs are promising alternatives to XLPOs, yet dynamic covalent chemistry is a relatively new arena for this application. Thus, it is important to note that more study is required, particularly concerning material longevity, before dynamic covalent chemistries can be implemented in XLPO-related spaces, as discussed below.

In addition to the dynamic covalent chemistries shown in Figure 9, another option to redesign XLPOs for circularity is to substitute thermoplastic POs for XLPOs when possible. For example, Green et al. completed several studies on the substitution of a blend of slow-crystallized thermoplastic PEs for XLPEs in cable insulations.[112] These blends have acceptable electrical properties (*e.g.*, low dielectric loss), decent thermal properties (*e.g.*, T_m ~ 130 °C), and sufficient reprocessability, as the blends are not cross-linked.[112] Others have investigated XLPO alternatives such as thermoplastic PE−PP copolymer blends that form physical cross-links[113] and thermoplastic PP, which was covered in a review by Li et al.[114] Additional testing is required to understand whether these thermoplastic alternatives can meet all the technical specifications (*e.g.*, mechanical properties, chemical resistance, durability) required of XLPOs for many applications. Other dynamic covalent chemistries not shown in Figure 9 that have been applied to POs are Diels−Alder and imine chemistries.[115,116] Both chemistries have been more commonly

Table 2. Comparison of Critical Thermal and Mechanical Properties of XLPE vs Dynamically Cross-linked PE

Dynamic Chemistry	Type of PE	T_m (°C)	Tensile Strength (MPa)	Elongation-at-Break (%)
Transesterification[106,121,124]	HDPE/LDPE	128−133/105	17−21/16−20	620−710/400
Disulfide Exchange[107,123]	HDPE/LDPE	130/106	Not reported	Not reported
Boronic Ester Exchange[102,111,125]	HDPE	124−128	15−27	436−675
Silyl Ether Exchange[109,126]	PE-HEMA[a]	72	3	250
Siloxane Exchange[108]	HDPE	127	19−20	380−400
Vinylogous Urethane Exchange[110]	LDPE	97−110	16−17	85−105
Commercial XLPE[122]	LDPE	90−105[b]	16−22	350−550

[a]Hydroxyl functionalized PE, specifically ethylene-hydroxyethyl methacrylate copolymer. [b]Normal operating temperature range for cables.

applied to polyolefin-based rubbers. For example, Diels−Alder reactions have been employed after grafting maleic anhydride on the backbones of ethylene/propylene and ethylene/vinyl acetate rubbers.[117] Dynamic imine bonds also have been used in ethylene/propylene rubber by first introducing aldehyde pendent groups to the chains and then adding an amine cross-linking agent.[118] These chemistries exhibit excellent reprocessability, but further characterization is needed to determine important performance metrics, such as T_m and tensile properties.[115,116]

A comparison of several important thermal and mechanical properties of PE vitrimers and commercial XLPE is shown in Table 2. In addition to the HDPE and LDPE vitrimers and properties included in this table, several studies also have applied dynamic chemistries to other POs, such as PP and LLDPE.[11,119] The T_ms of the dynamically cross-linked PEs are closely related to whether they have an HPDE or LDPE backbone, as the T_ms of LDPE and HDPE are 95−105 and 120−140 °C, respectively.[120] PP has a T_m near 165 °C, and thus, PP vitrimers generally have higher T_ms than PE vitrimers.[120] For instance, Kar et al. synthesized transesterification-based vitrimers from HDPE and PP with T_ms of 133 and 166 °C, respectively.[121] Therefore, PP-based vitrimers may be a better fit than PE vitrimers for higher-temperature applications. In terms of mechanical properties, the tensile strength and elongation-at-break for many of the dynamically cross-linked chemistries are within the range of commercial XLPE. A notable exception to the mechanical property trends is silyl ether exchange-based vitrimer, in which lower tensile strengths and elongations-at-breaks are exhibited relative to the other vitrimers in Table 2. There is an opportunity to increase these metrics by adding bulkier substituents onto the silyl ether group.[109] Vinylogous urethane exchange chemistries also possess lower elongations-at-break, but future work to produce HDPE vinylogous urethane exchange-based vitrimers would be expected to increase those values. It is also worth noting that XLPOs do not have a T_m, like vitrimers can, and a normal operating temperature range is provided instead. In cables, the standard operating temperature rating for XLPE is 90−105 °C, the emergency overload temperature is 130−140 °C (i.e., an elevated temperature outside of normal operation that a cable can withstand for a limited time period), and the short circuit rating (i.e., the highest temperature that a cable can withstand for ~0.5 s) is 250 °C.[122] Thus, vitrimers that would be molten by 130 °C, let alone 250 °C, would not be an acceptable substitute for cable applications with current formulations, and some amount of chemical cross-linking and/or high degrees of entanglement may be required to achieve the thermal properties necessary for cable insulation.[113,123]

The critical properties that recyclable-by-design POs must meet to be commercially viable as XLPO substitutes ultimately depend on the application. These use case-specific performance properties include thermal stability, electrical and chemical resistance, weatherability, and durability. Silyl ether/siloxane exchange chemistry has been reported as the most thermally stable dynamic cross-linker ($T_{d,5}$ = 427 °C), and thus, is of particular interest for cable applications.[108,109] It is also worth noting that siloxane chemistry is the most chemically similar to Si-XLPE. Therefore, siloxane chemistry may have the potential to perform the closest to Si-XLPE, which makes siloxane vitrimers promising for traditional Si-XLPE applications, such as low-voltage cables and pipes. Additionally, impact strength, stress-crack resistance, and electrical and chemical resistance are key XLPO metrics that have not been broadly characterized for dynamically cross-linked POs germane to cables. An example of the type of electrical testing required for cables is the conduction of breakdown voltage tests on thin films or mini cables to assess dielectric strength, as was done by Green et al.[112] Breakdown testing in this study demonstrated that their recyclable-by-design formulations outperformed XLPE and LDPE controls.[112] Moreover, many applications for XLPOs are exposed to a variety of elements (e.g., UV radiation, water, wind) and are expected to last decades. Industrial characterization commonly determines the durability and weatherability of XLPO formulations with accelerated aging tests, and these tests are necessary to further the translation of dynamic covalent chemistry research efforts.[127]

The scalability of initial processing approaches and retention of thermomechanical properties after multiple reprocessing cycles are important factors in determining the industrial feasibility of recyclable-by-design chemistries. Traditional XLPOs generally are compounded via extrusion, and therefore, many of the previously mentioned studies implemented reactive extrusion synthesis strategies that are expected to be economically scalable and feasible by leveraging existing industrial extrusion systems.[102,106,108,110,111,121,125,126] Rheological investigations or the common industrial metric, MFI, can provide further insight into the processability of dynamically cross-linked PO formulations. Additionally, curing methods/times and any other processing steps required must be taken into consideration when evaluating the scalability of these chemistries. To demonstrate reprocessability, the dynamic cross-linked POs must retain mechanical properties over at least three reprocessing cycles. For instance, Tellers et al. synthesized LDPE vinylogous urethane-based vitrimers that exhibited >80% retention of tensile strength after four cycles of reprocessing.[110] It is also of critical importance to consider the potential trade-offs between fast reprocessing and performance properties, as materials with faster stress relaxation times may

display larger creep.[103] Dynamic covalent chemistries with lower activation energies (E_as) will be easier to reprocess but less creep resistant, which can worsen lifetime material performance.[103] To improve creep resistance, one strategy is to increase E_a; however, if the vitrimer's E_a is too high, a catalyst may be necessary or the reprocessing conditions may become too costly.[103] Of the chemistries described in this section, boronic ester exchange has the lowest E_a of ~16 kJ/mol, whereas the rest of the chemistries (other than silyl ether exchange, which was not reported) have E_as > 100 kJ/mol.[102,107,108,110,121,126] Other than raising the E_a, the introduction of a level of permanent cross-linking in addition to dynamic cross-linking is highly effective at reducing creep and retaining reprocessability.[103,128] For example, with the incorporation of 40 mol % permanent cross-links into a disulfide-based vitrimer, creep resistance was reduced by ≥65%, and reprocessability was maintained.[128] Creep is also highly temperature dependent, as demonstrated by disulfide-based CANs synthesized by Bin Rusayyis et al.[123] The CANs exhibited excellent creep resistance at 70 °C (0.75% creep strain after ~14 h subjected to continuous 3.0 kPa stress) but significantly lower creep resistance at 90 °C (~7.1% creep strain under the same 3.0 kPa stress).[123] Overcoming creep resistance continues to be a challenge for the commercial implementation of dynamic covalent chemistries, and thus, future research is needed to identify those chemistries best suited to balance performance and (re)processability for XLPO applications.

Along with balancing (re)processing and creep resistance, there are other remaining concerns before these chemistries can be translated to commercial scales. Silyl ethers and boronic esters are susceptible to irreversible hydrolysis when exposed to heat and water.[107,108] Boronic ester, disulfide, and dynamic vinylogous urethane bonds are susceptible to oxidation, and thus premature exchange, which limits robustness.[103,104] Transesterification and silyl ether/siloxane exchange chemistries can have high costs, along with potential leaching and corrosion concerns associated with catalysts.[103,104] To better understand and overcome these remaining challenges, further characterization, in particular for longevity and application-specific properties, is required. As previously mentioned, introducing some amount of permanent cross-links and/or physical cross-links into dynamically cross-linking applications may be necessary to balance performance properties and recyclability.[113,123] Furthermore, most of the research to date has focused on the introduction of dynamic cross-links to upcycle plastics waste and has compared the properties to thermoplastic POs but not XLPOs. One exception is the study by Fenimore et al. on disulfide exchange-based POs directly compared PO vitrimer properties to those of analogous XLPOs.[107] It was found that the LDPE vitrimers had similar levels of cross-linking to traditional LDPE-based XLPE and that the vitrimers could be formulated to have similar thermomechanical properties to virgin XLPE (specifically for elastic storage modulus (E') rubbery plateaus of 0.52 vs 0.55 MPa for vitrimers and XLPE, respectively).[107] Although challenges remain, this study is an example of the type of direct comparison to traditional XLPOs useful in further studies to assess the promise of dynamic cross-linked materials. Finally, LCA also is needed to determine whether these chemistries lead to a reduction in environmental impacts relative to traditional XLPOs.

7. OUTLOOK: REMAINING CHALLENGES AND DIRECTIONS FOR FUTURE RESEARCH

There are many promising research directions for translating the work done on thermoplastic POs to XLPOs. In particular, a number of catalytic and pyrolysis strategies have been successfully applied to thermoplastic POs, as described in recent reviews.[129,130] For instance, several catalysts have been identified to cleave the C−C bonds in POs to yield liquid and gaseous hydrocarbons.[131−134] Hancock et al. used Ru nanoparticles on a carbon catalyst to convert PE into liquid alkanes under relatively mild reaction conditions (200−250 °C, 20−50 bar H_2).[134] Wang et al. converted LDPE to diesel, wax, and lubricants over a Ru supported on tungstated zirconia catalyst (250 °C, 50 bar H_2 for 2h).[132] In another example, Liu et al. leveraged the synergistic effects between POs and biomass in a co-pyrolysis process to enhance the desired product yield (e.g., syngas).[135] Biological deconstruction is also a promising advanced plastics recycling option that is energy-efficient and highly selective.[130] For instance, Sowmya et al. isolated the fungus *Penicillium simplicissimum* from a local dumpsite to biodegrade PE, and nuclear magnetic resonance spectroscopy confirmed the formation of aromatic and alkene protons, groups absent from the starting PE.[136] Although biological deconstruction has not been studied on XLPOs to the best of the authors' knowledge, there is an opportunity to examine whether any of the previously identified thermoplastic PO degradation enzymes and microorganisms also can act on XLPO substrates.[136,137]

Opportunities also exist for the translation of other areas of materials research to XLPOs, such as functionalization, devulcanization, and compatibilization. Learnings can be applied from other cross-linked systems, in particular vulcanized rubbers, to XLPOs and vice versa. A number of devulcanization methods have been probed, especially in the context of waste tire rubber, which could provide insight into XLPO de-cross-linking.[138] Compatibilization has been investigated to improve the adhesion of rubber wastes in blends to improve the overall performance properties of the recycled material, an approach that could be applied to the XLPO blends discussed in Section 4.[139] Moreover, PO functionalization research can be applied to XLPOs. Maleic anhydride grafting is the most common strategy to functionalize C−H groups, but there has been a growing interest to activate C−H bonds through other means, resulting in the selective conversion of C−H bonds to bonds such as C−C, C−N, C−B, and C−S, as reviewed by Williamson et al.[140] POs also have been functionalized by the introduction of in-chain double bonds via dehydrogenation or by oxidation.[141] These valorization approaches open the door for other chemistries to be harnessed to broaden the scope for recyclable-by-design XLPOs or to functionalize ground XLPOs for higher-value applications. In short, a considerable number of opportunities exist by applying adjacent areas of materials research to XLPOs.

Manufacturing steps, such as cross-linking and curing can consume considerable energy, release undesired byproducts from the decomposition of organic peroxides, and contribute significantly to the overall environmental impact of an XLPO product.[142] For example, manufacturing emits >2x more GHG emissions vs use for cables, as discussed in Section 3.[47] In recognition of this point, there has been recent work to reduce curing times/temperatures and choose synthesis procedures

that avoid the generation of toxic byproducts.[142] There are additional opportunities to increase circularity in the production of XLPOs with regards to material inputs, such as upcycling thermoplastic PO waste to XLPO (*i.e.*, substituting recycled POs as a material input for virgin PE) or incorporating biobased cross-linkers. For instance, Fenimore et al. employed post-consumer recycled (PCR) LDPE and HDPE to synthesize PE vitrimers,[107] and Dey et al. used biobased cross-linkers to synthesize PCR−PP vitrimers with 90% retention of mechanical properties after five reprocessing cycles.[143] Biobased peroxides also have been developed for the formulation of industrial hardeners, although they have not yet been applied to XLPO systems.[144] The effects of the PCR purity and biobased cross-linkers on the long-term properties of XLPOs require additional evaluation, and future research should investigate if other steps within XLPO manufacturing (*e.g.*, transportation, formulation design, compounding, product distribution) can be streamlined to further alleviate environmental impacts.

A remaining challenge for XLPO circularity is the impact of additives on the strategies discussed throughout this review. Common additives used in XLPOs include stabilizers such as antioxidants, color concentrates, flame retardants, and carbon black (for conductivity or UV-weathering resistance).[145−147] Additive packages vary from product to product, which adds another layer of uncertainty to XLPO circularity solutions, and the specific additives present have been shown to have significant consequences for thermoplastic PO recycling, especially for catalytic approaches. For instance, phenolic antioxidants reduced catalyst activity by 50% in the deconstruction of HDPE employing a $Pt/WO_3/ZrO_2$ catalyst system.[148] Another example that highlights the impact of additives on the ultimate recyclate value is the difference in the price of natural vs colored mechanically recycled HDPE ($0.75 vs $0.23/lb for natural and colored HDPE, respectively in the United States in 2021).[149] As additives are critical for the processing and performance of commercial XLPOs, it is vital to investigate the impact of additives on proposed recycling processes and develop solutions in the case that they interfere. Such remedies could include preprocessing steps to strip additives out of XLPOs, screening process conditions for robustness, or developing additive formulations more tolerant to the chosen circularity method.

Balancing performance, cost, scalability, and circularity poses a major challenge in achieving complete circularity for XLPOs. Many XLPO applications necessitate high-purity materials to achieve extended lifecycles, which will have a large effect on the choice of circularity strategy. For instance, using upcycled POs in XLPO formulations could improve circularity and reduce costs but likely would demand stringent purity standards, or robust formulations and applications capable of handling any impurities to achieve the required performance. Furthermore, sustainable solutions will need to be either cost-competitive or subsidized with current methods to break into the market. Inevitably, there will be no one-size-fits-all remedy to improving the circularity of XLPO. Nonetheless, by employing a combination of circularity strategies discussed in this review and those yet to be uncovered, a significant opportunity exists to markedly improve the lifecycle circularity of both current and future XLPOs.

8. CONCLUSIONS

The circularity of XLPOs has been relatively overlooked by the sustainable materials research community, yet numerous approaches present opportunities to enhance the circularity of this substantial and growing plastics waste stream. This review has highlighted solutions spanning the materials lifecycle, such as using biobased feedstocks, extending materials longevity, enabling circularity through mechanical and advanced recycling methods, and redesigning chemistries for circularity in next-generation XLPOs. Recent advances in plastics design, especially those targeting thermoplastic POs, offer promising future research directions for increased XLPO sustainability, but challenges remain to balance performance, cost, scalability, and circularity. Overall, there are several opportunities to transition from the current linear lifecycle of XLPOs to a more circular lifecycle and from the laboratory to industrial application.

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■ ABBREVIATIONS

CAGR	compound annual growth rate
CAN	covalent adaptable network

E_a	activation energy
E′	elastic storage modulus
FTIR	Fourier-transform infrared
GHG	greenhouse gas
GPC	gel permeation chromatography
GWP	global warming potential
G′	shear storage modulus
G″	shear loss modulus
HDPE	high-density polyethylene
ISCC	International Sustainability and Carbon Certification
LCA	lifecycle assessment
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MFI	melt flow index
P_c	critical pressure
PCR	post-consumer recycled
PE	polyethylene
PEX	cross-linked polyethylene
PO	polyolefin
PP	polypropylene
PVC	poly(vinyl chloride)
Si-XLPE	silane-cross-linked polyethylene
T_c	critical temperature
$T_{d,x}$	thermal decomposition temperature or temperature at which x% mass loss occurs
TEA	technoeconomic analysis
T_g	glass transition temperature
T_m	melting temperature
TR-XLPE	water tree-retardant cross-linked polyethylene
UV	ultraviolet
XLLDPE	cross-linked linear low-density polyethylene
XLPE	cross-linked polyethylene
XLPO	cross-linked polyolefin

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