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Critical Review of Molecular and Physical Property Changes of Recycled Polymers

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Abstract

With the constant and ever-increasing utilization of polymers in industries such as food packaging, automotive, and textiles, understanding their impact on the environment has become vital. Common polymers such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and nylon have become the foundation of conventional materials, but not without directly impacting the environment through its production, usage, and disposal. Primarily, the environment suffers from petrochemical polymers' non-biodegradable nature. Through polymer recycling, many of these petrochemical polymers can be reintegrated into the production cycle, and research on the topic is plentiful with new and upcoming methods to optimize the process and minimize their global impact. Comparing different recycling methods for common polymers and understanding their effects when combined with virgin polymer resins provides insight into the most effective method of recycling polymers. The focus is on quantifying the efficacy of mechanical and chemical recycling methods as well as the effect of fillers and additives in recycled polymers. Through a multitude of characterization techniques such as mechanical testing, Fourier-transform infrared spectroscopy (FT-IR), and differential scanning calorimetry (DSC), the physical and molecular changes recycled polymers undergo can be quantitatively determined. By comparing property changes of common polymers, the impact and efficacy of recycling methods can be explored. Further understanding of deviations in properties when comparing industrial and lab-scale recycling methods provide knowledge on their overall impact on the environment. As such, achieving properties comparable to virgin polymers with the aid of recycled polymers is the aim for creating a better, more sustainable environment.

Introduction

Plastics have become an ever-present feature in this world. Their prevalence in almost every facet of the average person's life has not only simplified day-to-day tasks, but also expanded to include products from a variety of industries. From packaging materials used for food to the materials that protect people in vehicles to the clothing worn by the average person, the versatility of polymers is unmatched. The availability and widespread use of polymers since the 1950s as such has led to modern innovations but at the cost of a reliance on fossil fuels for their production. Single-use plastics for food packaging being one of the largest use-cases has led to an environment wherein cheap, simple-to-use products are constantly produced with little regard to their after-effects [1]. Plastic production has been incessant as over 8.3 billion metric tons of virgin polymers have been produced at an alarming rate of 330-380 million metric tons per year as of 2016 [2, 3]. Typically non-biodegradable, petrochemical polymers post-consumption accumulate in the form of landfills and only a mere 7-9% are recycled [4].

The environmental burden placed due to the production of petrochemical polymers combines two major facets: the production process involving non-renewable resources and the non-biodegradable nature post-consumption [5]. In recent times, the environmental impact of these plastics extends as far as the marine environment with the lack of degradation of polymers drastically affecting the ocean as a whole [6, 7]. To minimize the environmental impact, polymer recycling and re-integration with virgin polymers has been touted as the first step. But due to the complexity of plastics produced in the form multilayer and blended mixtures of materials, the mechanical separation process is both difficult and, in some cases,

cost ineffective. Re-extrusion of recycled polymers to yield similar properties as the virgin feedstocks is one of many ways of recycling, but the delicate balance of retaining mechanical and thermal properties while integrating the maximum amount of recycled polymers further complicates the overall efficiency of the process. In addition, incineration as a form of energy production provides an alternative method for hard-to-separate polymeric blends but at the cost of greenhouse gas emissions and further damaging effects to the environment [8]. Recycling as such is still the primary method of reducing the environmental consequences of petrochemical polymers.

In order to more efficiently recycle the polymers produced, understanding both the degradation of virgin polymers and characterization of re-integrated recycled polymers are vital. Quantification of the physical, chemical and molecular property changes through a variety of characterization methods allow for greater improvements in the recycling process [9]. As virgin polymers are rarely used alone, the impact of fillers and additives within the recycling process is vital information for understanding the overall process [10]. Therefore, conventional petrochemical polymers such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and nylon as well as polymer composites including fillers are the focus herein.

Overview of Polymers and Polymer Recycling

The petrochemical polymer industry has vastly expanded since its first use, as has the prevalence of polymers in daily usage. Their impressive mechanical and thermal properties, high availability/abundance, and cost-effectiveness in production, have yielded a reliance on an unsustainable quantity of polymer production. Not all petrochemical polymers contribute equally, but the most common, conventional polymers in the scope of this paper are defined as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and nylon. PE, most renowned for its usage as low-cost, flexible film packaging when produced as low-density polyethylene (LDPE), is regarded as the most well-known and widely produced polymer. Due to variations in density and branching as high (HDPE), low (LDPE), and linear-low density (LLDPE) polyethylene, their applications vary accordingly and the variations affect mechanical properties such as flexibility and rigidity. LDPE is used primarily for flexible film packaging, HDPE for stiffer molded plastics, and LLDPE for flexible sheets and films with increased tensile strength. PP, the second most widely produced polymer, is used in flexible barrier films and rigid molded plastics due to its impressive flexural strength [11, 12]. By contrast, PS has versatile applications with expanded PS used for foam and thermal insulation, and high impact PS for rigid packaging applications. PET, with its barrier properties, high temperature and moisture resistance, and notable mechanical strength, has made it the polymer of choice for plastic bottles. Nylon, known for its usage in packaging, automotive, and primarily textile industries, provides increased strength and elasticity with specialized applications dependent on the tensile strength [13].

As the list of applications for these polymers increases, so too does the production, use, and disposal. Despite the thermoplastic nature of conventional polymers, landfilling and general disposal methods generate large quantities of non-degradable plastic waste [4]. From an economic perspective, polymer recycling provides an avenue for the conversion from a linear to a circular economy. The current single-use and disposal methodology that some plastics are designed with in a linear economy directly impacts resource depletion. With the intent of providing a use-case for end-of-life polymers, a circular economy relies on the restorative effect that reuse of polymers can provide [14]. The concept of a circular economy aims to repurpose most, if not all, materials produced so that waste generation is minimized.

Though performance of recycled materials can differ comparative to their virgin polymer counterparts, it is not economically feasible to continually produce new, virgin polymers. As such, polymer recycling can help alleviate the stress placed on resource depletion. Organizations such as How2Recycle provide simplified knowledge to further educate the general populace on the methods and impacts of recycling. As such, the impact of polymer recycling can be improved through both education and integration into a circular economy.

The environmental impact of petrochemical polymers is far-reaching, affecting marine life, global warming, and adding to the ongoing landfilling problem. In terms of marine life, PET bottles contribute to changes in marine life with its degradation potential causing adverse effects due to chemical contamination, pollution, and in some cases, physical harm to marine life [15]. Through the use of FT-IR, the degradation potential of PET within the marine environment can be quantified as they can persist in the marine environment for many decades [7]. Despite the deterioration of functional groups within PET in water, it takes decades for noticeable degradation to occur, adding to the accumulation of plastics in the ocean. Similarly, foamed polystyrene used in a variety of applications adds to the impact on the marine environment with the additives within the polymer adding an extra layer of complexity as they can leach out and adversely affect marine life. Despite the degradation potential of polystyrene, biodegradation occurs much slower, yielding slow breakdown into its constituents [6, 15]. With carbon emissions and global warming an ever-present issue, the effect can be quantified through life-cycle impact assessment of these polymers. Polymers such as PET and PS degrade at a slow rate in landfills and generate greenhouse gases such as carbon dioxide and methane during degradation [16]. Currently, the primary method of disposal of plastics is through landfilling which directly impacts the environment in many ways [4]. Landfilling not only consumes the available land but can also contaminate the land and generate greenhouse gases. Despite the importance of recycling polymers, the effect of polymers currently in landfills can be minimized to an extent by way of biodegradable additives [17]. In essence, the sustainability of polymers produced directly impacts the environment, and methods such as recycling provide an avenue to mitigate their impact on the environment.

Polymer Recycling Methods

As the usage of common polymers increases, so does the necessity for efficient and innovative recycling methods. The most well-known approaches to recycling can be divided into four categories based on the method applied: mechanical, chemical, radiation, and bacterial. Mechanical recycling involves collection of plastic waste material and recycling through mechanical techniques such as separating, chopping, grinding, crushing, and melting. The process involves physical separation of plastics through both size and density followed by removal of metallic contaminants to yield a mixture of processable plastic waste [18]. Further sorting of plastic waste is conducted in conjunction with Fourier Transform near infrared spectroscopy (FT-NIR) for polymer determination and manual sorting to ensure accurate separation. Characterization through FT-NIR allows for automated recognition of a variety of plastics such as polystyrene and polypropylene as waste materials travel along a conveyor belt [19]. The process involves real-time data collection of infrared spectra, processing, and identification of polymers in a mixture allowing for accurate separation following detection. Once sorted, the plastic waste is washed using steam, but other methods such as caustic washing can be used, dependent on their affinity to the plastic waste, to remove any organic contaminants [20]. The plastic waste is ground into flakes or crushed and

remelted for future use. This entire process is both arduous and time-consuming primarily due to separation of multi-component polymer mixtures found in everyday plastics.

By contrast, chemical recycling provides an alternative method to mechanical recycling wherein the polymer is reduced to monomeric components for re-use and repolymerization. The most widespread chemical recycling methods are through pyrolysis, depolymerization and targeted solvent-based recovery of polymers. Pyrolysis allows direct usage of plastic waste to produce energy and mitigates the need for separation of polymeric mixtures. By heating polymers in the absence of oxygen, the decomposition hydrocarbon products can be used as energy. PE and PS have previously been pyrolyzed using a Gray-King apparatus with thermogravimetric analysis (TGA) used as the method of evaluation [21]. By determining the appropriate temperature at which weight loss occurs in samples, the heating rate and production of stable radicals are quantified, yielding an effective method of producing energy and monomeric products through pyrolysis. Similarly, experiments in catalytic pyrolysis of HDPE, LDPE, and PP provide a simplified route of recovering monomers. The use of Ziegler-Natta catalysts, specifically in the pyrolysis process, improves naphtha-based gas yield and monomer recovery and suggests the potential for an integrated plastic waste recycling method [22]. The environmental concern with pyrolysis for energy production is that carbon dioxide emissions comparative to mechanical recycling are similar due to the energy requirements for operating each recycling process.

Similarly, depolymerization is the conversion of polymeric materials into their constituent monomers, typically, through the use of heat. The process applies to thermoplastic polymers and occurs when polymers are no longer thermodynamically stable due to thermal degradation. For example, the depolymerization of HDPE can yield plastic crude oil and its respective distillates through the use of magnesium carbonate as a catalyst. Through the depolymerization process, both motor gasoline and diesel can be produced allowing for a repurposing of, in this specific instance, HDPE storage boxes [23]. In the case of PET soft-drink bottles, depolymerization using metal acetate catalysts generates PET monomer and dimer for reuse. Despite the remnants of pigments from PET bottles, recycling through depolymerization produces monomers with properties unaffected by the pigments [24, 25]. Similarly, polystyrene depolymerization to yield styrene monomer provides an avenue for recycling up to 85% of the initial PS fed. Through the use of light and heavy cycle oils, varying high temperature and residence time, and concentration of polymer in solution, high yield of styrene monomer can be produced [26, 27]. Similar to depolymerization of common petrochemical polymers, nylon 6 can be partially depolymerized and then converted to its monomeric form through ring-closing reactions [28, 29]. The monomer produced through catalytic depolymerization and chemical conversion allows for end-of-life nylon 6 products to be recycled efficiently, reducing the impact of petrochemical polymers.

Solvent-based recovery occurs by repeated washes at specified temperatures and ratios to selectively dissolve polymers in mixtures. For example, solvent-based recovery of PP through the use of tetrachloroethylene produces powdered PP with minimal degradation due to solvent recovery [30]. Degradation of the recycled PP primarily occurs when reprocessing through extrusion or other methods, so minimal loss of mechanical properties occurs by way of solvent-based recovery. Similarly, PS recovered using ethyl acetate as solvent has minimal degradation through solvent evaporation, but extrusion and other reprocessing methods yields loss of mechanical and thermal properties with some increase in volatile compound content [31]. Simple solvent-based recovery, as such, provides a method of recycling polymers but reprocessing alters the overall mechanical and thermal properties when compared to virgin polymers. Solvent targeted recovery and precipitation (STRAP) is a newer, innovative process that isolates

polymer constituents within multilayer films and selectively dissolves them. The STRAP process has been applied to multilayer films to extract PE, ethylene vinyl alcohol (EVOH), and PET with almost 100% efficiency in separating the constituent polymers out [32]. The process involves selecting the appropriate solvent for each constituent polymer and selectively dissolving, separating the liquid containing said polymer, and precipitating with an anti-solvent. Switchable hydrophilicity solvent (SHS) extraction, similarly, allows for polymer film recovery by way of dissolution and ultrasonication. More specifically, varying the ratio of solid to liquid, time, and temperature of the multilayer film in the N,N-Dimethylcyclohexylamine solution allows for maximal extraction of the polymer film layers for reuse [33]. This process can be used for separating the different layers within multilayer packaging with minimal degradation or loss during the recovery process. The overall SHS extraction procedure can potentially be scaled up to plant level to reduce multilayer packaging waste and, in turn, reduce carbon dioxide emissions.

A more unique application of solvent-based recovery involves the use of electrospinning which extracts fibrous threads from solvent-dissolved polymer by applying a voltage source. In the case of expanded polystyrene (EPS), by dissolving EPS in a suitable solvent, transportation costs are minimized and the pelletizing step prior to recycling is eliminated [34]. Electrospinning the dissolved EPS fibers provides an alternative to conventional solvent extraction and produces a unique form of recovered polymer. With both solvent-based and depolymerization recycling methods, potential safety hazards exist as the volatile organic compound (VOC) level post-recycling must be monitored to minimize the toxicity of the recycled polymer.

Both radiation and bacterial recycling are newer, niche methods with further research required on their comparable efficiency to conventional mechanical and chemical recycling methods. Radiation-based recycling involves the usage of gamma and electron beam radiation to yield chain-scission within the polymer, like depolymerization. Gamma radiation has been applied to LDPE samples yielding degraded mechanical properties but with an increased threshold for crosslinking. For PP recycling, gamma radiation aids in the chemical recycling process by partially degrading PP and lowering the temperature threshold for pyrolysis [35]. The allure of radiation recycling is as a potential precursor to typical chemical recycling methods as it lowers the required energy threshold for chain-scission to occur. Bacterial recycling is an analogue to depolymerization and relies on degradation of polymeric chains through specialized bacteria into monomers, carbon dioxide, and/or water. As a general example, the degradation of PE in the marine environment can occur as microorganisms build up on the polymer surface. As the microorganisms attack the polymer, the surface becomes weaker and readily dissolves [36]. With PET, a type of bacteria known as *Ideonella sakaiensis* 201-F6 has been used to break down the polymer [37]. The bacterium produces two enzymes that hydrolyze PET and yield its constituent monomers. Though the research in polymer degrading bacteria is somewhat novel and ongoing, it provides an alternative to more common mechanical and chemical recycling methods.

Characterization and Degradation Mechanisms of Recycled Polymers

The plethora of wide-ranging polymers used have a shelf-life and at some point, will undergo degradation. Degradation is a complex mechanism, dependent on the polymer's primary backbone chain. A useful approach to understanding and characterizing how degradation occurs and the effects of degradation on polymers and polymer blends is to segregate polymers into two categories: polymers with a carbon-carbon (C-C) primary backbone and polymers with a carbon-noncarbon (C-X) primary backbone (where X

represents oxygen, nitrogen, etc., except carbon) [15]. Examples of C-C polymers include polyethylene, polypropylene, and polystyrene while C-X polymers include polyethylene terephthalate and nylon.

Degradation is generally described as a deficiency in polymer properties or a breakdown in the overall polymer structure leading to said deficiency [38]. Polymer degradation occurs by way of three main modes: photodegradation, thermal degradation, and ageing [39]. The first, photodegradation, occurs when polymers are exposed to light, more specifically ultraviolet (UV) light, and the photons are absorbed. The absorption process induces changes in the physical and chemical structures leading to chain-scission or cross-linking of polymer chains. The presence of oxygen within the system during photodegradation, known as photooxidative degradation, further accelerates the chain-scission that occurs [38]. In most polymers, like polystyrene, the effects of photodegradation are visually noticeable through discoloration or yellowing of the exterior surface. This discoloration occurs due to UV exposure wherein radicals form and oxidize chains within the polymer through cleavage of chains. The resultant carbonyl compounds are the source of the discoloration or yellowing [38].

The second, thermal degradation, occurs when the polymer is heated and starts to undergo chemical changes that affect the overall chemical composition. More specifically, changes in the functional end-groups as well as the formation of peroxide and carbonyl groups affect the chemical composition post-thermal degradation [40]. The elevation of temperature yields a variety of mechanical property changes like decreased strength, toughness, ductility, and chemical changes such as chain-scission or depolymerization [41]. The third, ageing, is a slower, more subtle, process that occurs as polymer chains relax from their initial conformation over time [38]. This structural relaxation is most often described in the form of physical property changes like loss of tensile strength and toughness, but also affects the gas permeability and overall structure of the polymer [42]. The effects of these degradation mechanisms are better quantified through a myriad of characterization techniques ranging from optical microscopy and Fourier-Transform Infrared Spectroscopy (FT-IR) to differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and mechanical testing as shown in *Figure 1*.

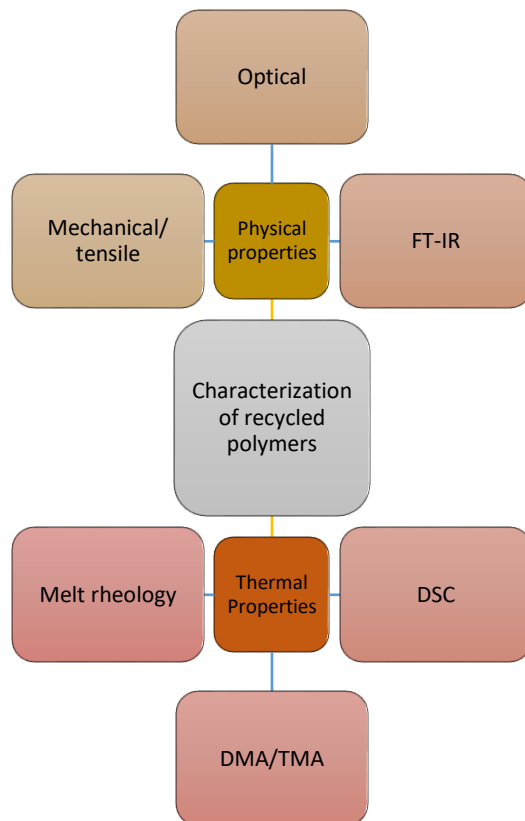


Figure 1. Methods used in the characterization of recycled polymers separated based on mechanical versus thermal properties affected.

From a chemical perspective, the mechanism of degradation is a result of the molecular changes that occur in the functional groups within the polymer, particularly in photooxidative degradation. The mechanism of action includes two major processes: chain-scission and crosslinking. Chain-scission is the cleavage of bonds within polymers to yield a reduction in molecular weight. Crosslinking is the formation of bonds by linking two or more polymer chains together [38]. Both processes alter the chemical structure of the overall polymer. Initiation occurs through the production of radicals where photons or heat yield hydroperoxide radicals [43]. Decomposition of the hydroperoxide radicals into alkyloxy and hydroxyl radicals allow for hydrogen abstraction to occur within the polymer chains. The resultant reactions can be categorized into Norrish I or Norrish II reactions where the Norrish I reaction generates further radicals and the Norrish II reaction cleaves bonds through chain-scission [38]. As this degradation process continues, the formation of carbonyl and vinyl groups on the polymer chain is indicative of chemical changes that occur. In fact, carbonyl content, through the carbonyl index, can be used as a direct reflection of the degradation that occurs within a polymer [44].

Characterization of C-C Polymers

The category of carbon-carbon primary backbone polymers includes PE, PS, and PP. The mechanical and thermal properties of each of these recycled polymers are characterized using a variety of methods. The primary use of recycled polymers is in addition to virgin polymers or as part of other polymeric blends.

Polyethylene

The first focus is on PE and its respective variants: HDPE, LDPE, LLDPE. Recycled HDPE in conjunction with LDPE were blended with the intention to produce traffic signs. The study involved comparing the mechanical and thermal properties of rHDPE and rHDPE with 25% LDPE blended from PCR waste materials. Mechanically, the tensile and flexion tests showed a decrease in yield strength, ultimate strength, elastic modulus, and bending modulus with the addition of LDPE. By contrast, thermal testing through DSC showed a slight decrease in the main fusion temperature [45]. The characterization showed that addition of LDPE to rHDPE potentially involves a compatibilization issue along with decreased mechanical properties. The mechanical properties of rHDPE/LDPE/LLDPE blends were further studied by Kukaleva, Simon et al. wherein the integration of LDPE and LLDPE were primarily characterized. Mechanically, the integration of LDPE improved both the toughness and stiffness of the overall blend when compared to rHDPE. The addition of LLDPE yielded worse tensile strength, impact strength, and Young's modulus primarily due to incompatibilities with rHDPE and immiscibility in general [46]. The difference in molecular weight between LDPE and LLDPE was considered a major factor in the miscibility with rHDPE, yielding worse mechanical properties in the rHDPE/LLDPE blends. The mechanical properties of recycled polyethylene blends typically yielded similar, albeit lower, results to rHDPE with improved flexibility due to the integration of LDPE. The impact of ternary blends of recycled PE variants was studied by Maleki, Farzin et al. to further clarify the impact of recycling and blending of PE. With regards to thermal properties, DSC was used to determine the effect on melting temperature and crystallization. The blends showed a decrease in crystallinity and slight decrease in overall melting temperature, but the overall thermal properties varied little when compared to the recycled constituents. Mechanically, the distinctions were more apparent as yield strength and toughness decreased while elongation at break increased [47]. The variation in mechanical properties when compared to non-recycled constituents can be attributed to the crosslinking and miscibility of chains within blends. Furthermore, thermal transitions in PCR polyethylene films were quantified by Curtzwiler, Williams et al. through the use of DSC. The presence of a shoulder peak near -108 °C correlates to the amount of PCR material present in the sample allowing an indirect method of degradation quantification in mixed waste blends [43]. As such, recycled PE blends typically yield lower mechanical properties while maintaining thermal characteristics.

Polystyrene

The second focus is on polystyrene and characterization of its thermal, mechanical, and optical properties. The addition of recycled PS to virgin PS in blends was characterized by Momany, Herzog et al. showing the effect of the addition of recycled materials. Thermally, DSC was used to determine the glass transition temperature and there was very little difference between the recycled and virgin PS. Mechanically, the effects of adding recycled PS became more apparent. Tensile strength remained comparable between recycled and virgin PS, but the decreased Young's modulus of recycled PS can be attributed to thermal degradation during the recycling process. The recycling process allows PS to undergo partial heat treatment wherein chain-scission can occur, negatively impacting the mechanical properties of the recycled material. Furthermore, the toughness of recycled PS was greater than virgin PS potentially due to the recycling process altering the molecular weight [48]. As the recycling process occurs, entanglement of chains and a decrease in molecular weight due to degradation directly impact the crystallinity of the polymer. Increased crystallinity as a result of this process allows for greater intermolecular bonding and increased toughness. As such, the mechanical and thermal properties of recycled polystyrene blends are comparable to virgin polystyrene dependent on the application. On the other hand, the optical properties of recycled PS are somewhat detrimental as considerable yellowing occurs from the ageing and processing

that can occur during recycling [49]. As processing methods such as extrusion involve heat, thermal degradation of chains can occur causing yellowing. In some cases, the discoloration associated with recycled PS can potentially be mitigated with blends of virgin PS.

Polypropylene

The third focus in carbon-carbon primary backbone polymers is polypropylene. With respect to its mechanical properties, recycled PP shows increased deterioration and loss of tensile strength and Young's modulus values but when blended with virgin PP, the effects can be partially mitigated [50]. Furthermore, in composites containing recycled PP, the rheological, mechanical and thermal effects are clearer. The decreased elongation at break and lowered impact energy at low temperatures are mechanical and rheological effects that occur due to the effects of recycling on PP. Furthermore, when integrated with virgin PP, the tensile modulus increases up to 14% as the recycled polymer is loaded until the effect plateaus [51]. The addition of recycled PP to virgin PP can contribute to interactions that allow the bonds within the blends to become stronger. Fracture resistance decreases with recycled PP loading as plastic degradation can occur throughout the recycling processing stages, thus weakening the interactions of the virgin and recycled polymer. Thermally, the use of melt flow index aids in quantifying the degradation and chain-scission that occurs in recycled PP [52]. With the use of DSC, thermal property changes within the melting and crystallization peaks can be identified. Increasing melting temperatures, specifically of the PP peak from -124 to -127 °C shows potential change in the aggregates formed and crystallinity of the blends when compared to virgin PP [51]. The optical properties of recycled PP are more related to the recycling process and as such vary. The opacity of films formed from recycled PP typically increases with harsher recycling procedures and is related to the crystallinity of the films [53]. This is due to the light scattering that occurs in the crystalline regions of the polymer. As the light shines through the amorphous and crystalline regions, obstructions within the crystalline region cause light scattering yielding more opaque optical properties. Overall, the optical properties of recycled polypropylene suffer but can be mitigated dependent on the recycling method chosen.

Characterization of C-X Polymers

Polyethylene Terephthalate

PET is one of the primary examples of carbon-noncarbon backbone polymers and plays a major part in the recycling industry. Recycled PET contains a variety of mechanical, thermal, and optical property differences that directly affects its usage in blends. Mechanically, toughness, elongation at break, and tensile strength decreases post-recycling with stress cracking a possible side-effect. Both yield stress and strain increased with rPET addition until a plateau point of approximately 80% rPET is reached showing the potentially diminishing returns on further rPET integration. The Young's modulus tends to increase until 40% rPET is added, but then sharply decreases which can be due to an increase in crystallinity with rPET integration [54]. The addition of other polymers such as polycarbonates can help mitigate the effect of loss of mechanical properties [55-57]. In terms of the thermal property changes, DSC and TGA show the primary differences when compared against virgin PET. DSC reveals that the addition of rPET decreases the overall crystallinity of the blends and decreases the crystallization and overall melting temperature. TGA shows that thermal stability slightly decreases as more rPET is added to blends, potentially due to the degradation that occurs in the recycling process [58]. Furthermore, the crystallization temperature is linearly proportional to the decrease in rPET concentration, meaning it can potentially be used as an indicator for the amount of recycled polymer within a sample[54]. FT-IR and

optical microscopy was used to determine changes in optical properties in recycled PET. FT-IR shows slight changes in the fingerprint region ($700\text{-}750\text{ cm}^{-1}$) that correlate with the crystallinity of the blend as is most likely due to the changes that occur in the recycling process. The optical properties, especially transparency, are affected linearly by the addition of rPET [55, 57]. Overall, rPET can provide minimal disruption to the thermal, mechanical, and optical properties in blends.

Nylon

Another common example of carbon-noncarbon primary backbone polymers is nylon. The mechanical properties of recycled nylon vary based on the degradation during recycling as nylon is affected primarily by reprocessing. Reprocessing allows for thermal and oxidative degradation to occur which in turn impacts the mechanical properties [59]. In addition, lower molecular weight as well as a broader molecular weight distribution caused by chain-scission alters the mechanical properties of nylon. Decreased tensile strength as well as elongation at break are common losses due to recycling [60, 61]. The absorption of water becomes a major issue that affects both mechanical and thermal properties. Water trapped within nylon can affect the mechanical properties during processing, so it becomes vital to dry and ensure little moisture is absorbed prior to recycling or reprocessing. DSC can be used to determine any changes in the melting temperature, but very minimal changes occur to the melting temperature [62]. Water presence acts as a plasticizer and increases the stiffness of the recycled nylon. In terms of optical properties, yellowing occurs as nylon reacts with the presence of water making recycled nylon difficult to use as a product on its own. Some of the mechanical and optical property differences can be mitigated by processing with virgin nylon, but the compatibility and processing methods directly affect how effective it will be.

Recycled Polymer Blends

In some cases, blends containing recycled PE and PP to improve flexibility have been studied. Thermal properties of recycled PE/PP blends were analyzed by melting and crystallization temperatures in DSC wherein the melting temperature of the blend remains similar to that of HDPE. Furthermore, the effect of recycling on the crystallization of blends showed increased crystallinity with recycled materials [12]. Through the use of melt flow rate measurements, the degradation of recycled polymers used in the blend is more clearly quantified. The higher melt flow index values show increased shear degradation attributed to the changes in PE during the recycling process. Mechanically, the elongation of blended samples improved, but at the cost of lower tensile strength and Young's modulus values. The blending of recycled PE/PP, as such, provides increased flexibility at the cost of mechanical strength. Furthermore, the mechanical properties of recycled PE and PS blends have been explored by Li, Silverstein et al., specifically on the flexural and compressive properties. The addition of PS to recycled HDPE reduced the flexural properties while maintaining the compressive properties when compared to virgin HDPE [63]. Primarily, the addition of PS showed immiscibility in specific cases and compressive properties comparable to virgin HDPE can be achieved dependent on the PS loading.

Effect of Fillers on Physical and Thermal Properties in Recycled Materials

Polymer composites have been in use for many decades with glass fiber reinforced polymers being the most common method of application [64]. The usage of fillers in polymer composites vary based on its primary application, but typically fillers allow for structural reinforcement, improved mechanical properties, or simply reduce the overall cost of production.

Growing concerns in the usage of glass fibers within polymer composites has led to the rise of natural fillers as an alternative. Natural fillers are a biodegradable, low-cost, non-toxic alternative that can improve mechanical properties of polymer composites due to their inherent material properties such as lower density when compared to typical fillers [65]. For example, wood fibers and flour are the most abundantly used natural filler mainly due to their low cost. Wood flour has been compounded as a low-cost filler in recycled polyethylene yielding similar mechanical properties, such as elastic modulus and tensile strength, and slightly worse ductility when compared against LDPE [66]. Rice husks are a natural byproduct of the rice milling industry that possess low moisture absorption properties suitable for use as a natural filler. Rice husk filler when added to recycled HDPE showed an increase in tensile strength by up to 10% at 70% filler concentration due to the reinforcement properties of the filler within the matrix. Past the 70% filler mark, agglomerates consisting of excess rice husk filler decrease the tensile strength along with lowered reinforcement properties. Similarly, the addition of rice husk fibers improved the flexural strength of the recycled HDPE by up to 28% at 80% filler concentration, imparted by the reinforcement of the polymer matrix. Filler loading in the rHDPE matrix slightly decreased the overall impact strength as crack propagation occurred at the filler aggregates, directly related to the brittleness of the rice husk filler. When compared to rHDPE, the addition of rice husk fillers improves the toughness at low filler loading [67, 68]. As such, the overall mechanical performance of rice hull fillers in composites provide specified advantages as a natural filler.

By contrast, man-made fillers can be added to polymer matrices with the intention of reutilizing waste products and potentially improving mechanical properties. Fly ash (FA) is a waste powder byproduct of the coal production process that is typically found as a fine powder containing silicon, iron, magnesium and calcium oxide. Reintegration of fly ash into the overall system provides an avenue for providing a use-case for a material currently categorized as a waste byproduct, furthering the model of a circular economy. Fly ash has been integrated within a multitude of polymer composites with varied mechanical and physical property changes. Fly ash when extruded with polyolefin elastomer and polypropylene drastically altered the mechanical properties of the resulting composites. The increase in tensile, flexural, and impact strength when compared to non-fly ash containing composites is a result of the dispersion and integration of FA as a filler. Additionally, most of the thermal characteristics of the composite's constituents remain unchanged with the exception of thermal stability which improves with FA integration [69, 70]. The dispersion of FA within the matrix was quantified through scanning electron microscopy images and showed the importance of a well-dispersed filler in the matrix. A well-dispersed filler without forming aggregates provides uniform mechanical properties. Increasing FA content within the composite yielded a balance between strength and flexibility of the overall composite. Similarly, FA and PP composites were produced with varying degrees of thermal and mechanical property alteration. The composites made imparted decreased thermal conductivity with fly ash addition and decreased the tensile and compressive strength of the overall composite [71]. Though the mechanical property decrease is problematic, the addition of fly with PP provides a niche application as an insulation material. In the production of polymer mortar based on PET resin, fly ash can be used as an integrative filler. The addition of FA to PET polymer mortar yielded minimal thermal property changes as both the glass transition and degradation temperatures remained unchanged. Mechanically, addition of FA improved the tensile strength of the composite, more specifically its peak tensile strength and ultimate tensile strain [72]. Fly ash is primarily used within construction applications as a filler, but integrated within a polymer mortar, both PET and FA can improve the mechanical properties and provide unique construction uses. Newer recycled HDPE composites containing FA provide an alternative method of utilizing both recycled

polymers as well as waste byproduct fillers. Mechanical properties, more specifically, flexural modulus and hardness, increased due to well-dispersed FA within the polymer matrix. Through the use of Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA), the thermal stability of the composites was quantified and showed improvement through the addition of FA [73]. Through further optimization and the addition of a compatibilizer, a balance in the thermal and mechanical property improvements was struck. As such, fly ash, as a filler, provides a cost-effective alternative to natural fillers in polymer composites yielding improved mechanical and thermal properties.

Similarly, processing aids, either in conjunction with or as is, can provide improved overall properties. Additives can alleviate some of the typical issues caused by fillers in polymer composites such as the adhesion between fiber and polymer matrix or lack of uniform filler dispersion. Using rPE and rPP as the polymer matrix and mica flakes and glass fibers as the filler, the influence of additives was quantified by AlMaaded, Madi et al by way of TGA and DSC. Overall, the impact of additives was slowed thermal degradation of recycled polymers as well as improved thermal stability overall [74]. The additives with rPE and rPP also improved the adhesion of glass fiber fillers within the matrix addressing one of the major pitfalls of using fillers within polymer composites. Further understanding of the combined impact of alternative fillers in recycled polymers can improve the landscape for recycled and sustainable polymers as a whole.

Future of Polymer Recycling and Conclusions

With the current reliance on petrochemical polymers and its effects on the environment, polymer recycling in its various forms and methods provides an avenue for minimizing the adverse effects of everyday polymers. As newer techniques for polymer recycling such as STRAP, radiation, and bacterial recycling methods are developed and integrated commercially, the impact on the environment as well as the degradation potential of petrochemical polymers are reduced. With the integration of not just fillers but also biobased composites, the future of polymer recycling research is constantly evolving. The overall aim with recycled polymers remains to improve functional properties so they are comparable to that of virgin polymers. With further research and constant integration of polymer recycling methods, the economic and environmental impact of petrochemical polymers can be reduced.

References

1. Barnes, S.J., *Understanding plastics pollution: The role of economic development and technological research*. Environmental Pollution, 2019. **249**: p. 812-821.
2. Geyer, R., J.R. Jambeck, and K.L. Law, *Production, use, and fate of all plastics ever made*. Science Advances, 2017. **3**(7): p. e1700782.
3. Lebreton, L. and A. Andrady, *Future scenarios of global plastic waste generation and disposal*. Palgrave Communications, 2019. **5**(1): p. 6.
4. Swift, G., *Degradable Polymers and Plastics in Landfill Sites*. Encyclopedia of Polymer Science and Technology, 2015: p. 1-13.
5. Stein, R.S., *Polymer recycling: Thermodynamics and economics*. Macromolecular Symposia, 1998. **135**(1): p. 295-314.
6. Turner, A., *Foamed Polystyrene in the Marine Environment: Sources, Additives, Transport, Behavior, and Impacts*. Environmental Science & Technology, 2020. **54**(17): p. 10411-10420.
7. Ioakeimidis, C., et al., *The degradation potential of PET bottles in the marine environment: An ATR-FTIR based approach*. Scientific Reports, 2016. **6**(1): p. 23501.
8. Al-Salem, S.M., P. Lettieri, and J. Baeyens, *The valorization of plastic solid waste (PSW) by primary to quaternary routes: From re-use to energy and chemicals*. Progress in Energy and Combustion Science, 2010. **36**(1): p. 103-129.
9. Jiun, Y.L., et al., *Effects of Recycling Cycle on Used Thermoplastic Polymer and Thermoplastic Elastomer Polymer*. Polymers and Polymer Composites, 2016. **24**(9): p. 735-740.
10. Hugo, A.M., et al., *Development of recycled polymer composites for structural applications*. Plastics, Rubber and Composites, 2011. **40**(6-7): p. 317-323.
11. Achilias, D.S., et al., *Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP)*. Journal of Hazardous Materials, 2007. **149**(3): p. 536-542.
12. Aumnate, C., N. Rudolph, and M. Sarmadi, *Recycling of Polypropylene/Polyethylene Blends: Effect of Chain Structure on the Crystallization Behaviors*. Polymers (Basel), 2019. **11**(9): p. 1456.
13. Anthony, L.A. and A.N. Mike, *Applications and societal benefits of plastics*. Philos Trans R Soc Lond B Biol Sci, 2009. **364**(1526): p. 1977-1984.
14. Foundation, E.M., *Towards a Circular Economy: Business rationale for an accelerated transition*. 2015, Ellen MacArthur Foundation: Ellen MacArthur Foundation. p. 98.
15. Gewert, B., M.M. Plassmann, and M. MacLeod, *Pathways for degradation of plastic polymers floating in the marine environment*. Environmental Science: Processes & Impacts, 2015. **17**(9): p. 1513-1521.
16. Leejarkpai, T., T. Mungcharoen, and U. Suwanmanee, *Comparative assessment of global warming impact and eco-efficiency of PS (polystyrene), PET (polyethylene terephthalate) and PLA (polylactic acid) boxes*. Journal of Cleaner Production, 2016. **125**: p. 95-107.
17. Tollner, E.W., P.A. Annis, and K.C. Das, *Evaluation of Strength Properties of Polypropylene-Based Polymers in Simulated Landfill and Oven Conditions*. Journal of Environmental Engineering, 2011. **137**(4): p. 291-296.
18. Ragaert, K., L. Delva, and K. Van Geem, *Mechanical and chemical recycling of solid plastic waste*. Waste Management, 2017. **69**: p. 24-58.
19. Li, J., et al., *Environmentally-friendly technology for rapid on-line recycling of acrylonitrile-butadiene-styrene, polystyrene and polypropylene using near-infrared spectroscopy*. Journal of Cleaner Production, 2019. **213**: p. 838-844.
20. Cecon, V.S., et al., *The challenges in recycling post-consumer polyolefins for food contact applications: A review*. Resources, Conservation and Recycling, 2021. **167**: p. 105422.

21. Kiran, N., E. Ekinçi, and C.E. Snape, *Recycling of plastic wastes via pyrolysis*. Resources, Conservation and Recycling, 2000. **29**(4): p. 273-283.
22. Donaj, P.J., et al., *Pyrolysis of polyolefins for increasing the yield of monomers' recovery*. Waste Management, 2012. **32**(5): p. 840-846.
23. Kunwar, B., et al., *Catalytic and thermal depolymerization of low value post-consumer high density polyethylene plastic*. Energy, 2016. **111**: p. 884-892.
24. Baliga, S. and W.T. Wong, *Depolymerization of poly(ethylene terephthalate) recycled from post-consumer soft-drink bottles*. Journal of Polymer Science Part A: Polymer Chemistry, 1989. **27**(6): p. 2071-2082.
25. Paszun, D. and T. Spychaj, *Chemical Recycling of Poly(ethylene terephthalate)*. Industrial & Engineering Chemistry Research, 1997. **36**(4): p. 1373-1383.
26. Balema, V.P., et al., *Depolymerization of polystyrene under ambient conditions*. New Journal of Chemistry, 2021. **45**(6): p. 2935-2938.
27. Dement'ev, K., et al., *Thermal depolymerization of polystyrene in highly aromatic hydrocarbon medium*. Journal Of Analytical And Applied Pyrolysis, 2019. **142**.
28. Alberti, C., et al., *Chemical Recycling of End-of-Life Polyamide 6 via Ring Closing Depolymerization*. ChemistrySelect, 2019. **4**(43): p. 12638-12642.
29. Kumar, A., et al., *Hydrogenative Depolymerization of Nylons*. Journal of the American Chemical Society, 2020. **142**(33): p. 14267-14275.
30. Drain, K.F., W.R. Murphy, and M.S. Otterburn, *A solvent technique for the recycling of polypropylene — degradation on recycling*. Conservation & Recycling, 1983. **6**(3): p. 123-137.
31. Cella, R.F., et al., *Polystyrene recycling processes by dissolution in ethyl acetate*. Journal of Applied Polymer Science, 2018. **135**(18): p. 46208.
32. Walker, T.W., et al., *Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation*. Science Advances, 2020. **6**(47): p. eaba7599.
33. Mumladze, T., et al., *Sustainable approach to recycling of multilayer flexible packaging using switchable hydrophilicity solvents*. Green Chemistry, 2018. **20**(15): p. 3604-3618.
34. Shin, C., *A new recycling method for expanded polystyrene*. Packaging Technology and Science, 2005. **18**(6): p. 331-335.
35. Burillo, G., et al., *Polymer recycling: potential application of radiation technology*. Radiation Physics and Chemistry, 2002. **64**(1): p. 41-51.
36. Bonhomme, S., et al., *Environmental biodegradation of polyethylene*. Polymer Degradation and Stability, 2003. **81**(3): p. 441-452.
37. Yoshida, S., et al., *A bacterium that degrades and assimilates poly(ethylene terephthalate)*. Science, 2016. **351**(6278): p. 1196.
38. Yousif, E. and R. Haddad, *Photodegradation and photostabilization of polymers, especially polystyrene: review*. SpringerPlus, 2013. **2**(1): p. 398.
39. Pandey, J.K., et al., *An overview on the degradability of polymer nanocomposites*. Polymer Degradation and Stability, 2005. **88**(2): p. 234-250.
40. Ray, S. and R.P. Cooney, *Chapter 9 - Thermal Degradation of Polymer and Polymer Composites*, in *Handbook of Environmental Degradation of Materials (Third Edition)*, M. Kutz, Editor. 2018, William Andrew Publishing. p. 185-206.
41. Aboulkas, A., K. El harfi, and A. El Bouadili, *Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms*. Energy Conversion and Management, 2010. **51**(7): p. 1363-1369.
42. Minguez, R., et al., *A simple approach to understand the physical aging in polymers*. EJP, 2018. **40**(1): p. 15502.

43. Curtzwiler, G.W., et al., *Certification markers for empirical quantification of post-consumer recycled content in extruded polyethylene film*. *Polymer Testing*, 2018. **65**: p. 103-110.
44. Rouillon, C., et al., *Is carbonyl index a quantitative probe to monitor polypropylene photodegradation?* *Polymer Degradation and Stability*, 2016. **128**: p. 200-208.
45. San-Gil-León, A. and B. A. Stradi-Granados, *Determination of thermal and mechanical properties of HDPE-based polymer blends for use in traffic signs*. *AIMS materials science*, 2016. **3**(3): p. 722-736.
46. Kukaleva, N., G.P. Simon, and E. Kosior, *Modification of recycled high-density polyethylene by low-density and linear-low-density polyethylenes*. *Polymer Engineering & Science*, 2003. **43**(1): p. 26-39.
47. Maleki, M., M. Farzin, and P. Mosaddegh, *Investigation of mechanical, thermal and recycled characteristics of reinforced ternary blends of LDPE/LLDPE/HDPE by ANOVA*. *MRX*, 2018. **5**(6): p. 65305.
48. Momanyi, J., M. Herzog, and P. Muchiri, *Analysis of Thermomechanical Properties of Selected Class of Recycled Thermoplastic Materials Based on Their Applications*. *Recycling*, 2019. **4**(3).
49. Al-Jarrah, M.M.F., S.R. Salman, and S.A. Hammo, *Effect of thermal ageing on the optical properties of recycled high impact polystyrene*. *Polymer Degradation and Stability*, 1989. **23**(1): p. 75-81.
50. Kozderka, M., et al., *High impact polypropylene (HIPP) recycling – Mechanical resistance and Lifecycle Assessment (LCA) case study with improved efficiency by preliminary sensitivity analysis*. *Journal of Cleaner Production*, 2016. **137**: p. 1004-1017.
51. Curtzwiler, G.W., et al., *Mixed post-consumer recycled polyolefins as a property tuning material for virgin polypropylene*. *Journal of Cleaner Production*, 2019. **239**: p. 117978.
52. Bahlouli, N., et al., *Recycling effects on the rheological and thermomechanical properties of polypropylene-based composites*. *Materials & Design*, 2012. **33**: p. 451-458.
53. De Santis, F. and R. Pantani, *Optical Properties of Polypropylene upon Recycling*. *The Scientific World Journal*, 2013. **2013**: p. 354093.
54. Curtzwiler, G., et al., *Effect of recycled poly(ethylene terephthalate) content on properties of extruded poly(ethylene terephthalate) sheets*. *Journal of Plastic Film & Sheeting*, 2011. **27**(1-2): p. 65-86.
55. Alvarado Chacon, F., M.T. Brouwer, and E.U. Thoden van Velzen, *Effect of recycled content and rPET quality on the properties of PET bottles, part I: Optical and mechanical properties*. *Packaging Technology and Science*, 2020. **33**(9): p. 347-357.
56. Khoramnejadian, S., *Enhance mechanical and thermal properties of recycled Poly ethylene terephthalat (PET) from used bottle*. *Advances in environmental biology.*, 2011. **5**(13): p. 3826.
57. Jiang, Z., et al., *Preparation and properties of bottle-recycled polyethylene terephthalate (PET) filaments*. *Textile Research Journal*, 2018. **89**(7): p. 1207-1214.
58. Lee, J.H., et al., *Properties of recycled and virgin poly(ethylene terephthalate) blend fibers*. *Journal of Applied Polymer Science*, 2013. **128**(2): p. 1250-1256.
59. Su, K.-H., J.-H. Lin, and C.-C. Lin, *Influence of reprocessing on the mechanical properties and structure of polyamide 6*. *Journal of Materials Processing Technology*, 2007. **192-193**: p. 532-538.
60. Lozano-González, M.J., et al., *Physical–mechanical properties and morphological study on nylon-6 recycling by injection molding*. *Journal of Applied Polymer Science*, 2000. **76**(6): p. 851-858.
61. Meyabadi, T.F., M.R. Mohaddes Mojtahedi, and S.A. Mousavi Shoushtari, *Melt spinning of reused nylon 6: structure and physical properties of as-spun, drawn, and textured filaments*. *The Journal of The Textile Institute*, 2010. **101**(6): p. 527-537.

62. Vallés-Lluch, A., et al., *Influence of water on the viscoelastic behavior of recycled nylon 6,6*. Journal of Applied Polymer Science, 2002. **85**(10): p. 2211-2218.
63. Li, T., et al., *Mechanical properties of commingled plastic from recycled polyethylene and polystyrene*. Journal of Applied Polymer Science, 1994. **52**(2): p. 315-327.
64. Valente, M., et al., *Hybrid recycled glass fiber/wood flour thermoplastic composites: Manufacturing and mechanical characterization*. Composites Part A: Applied Science and Manufacturing, 2011. **42**(6): p. 649-657.
65. Joshi, S.V., et al., *Are natural fiber composites environmentally superior to glass fiber reinforced composites?* Composites Part A: Applied Science and Manufacturing, 2004. **35**(3): p. 371-376.
66. La Mantia, F.P. and M. Morreale, *Mechanical properties of recycled polyethylene ecocomposites filled with natural organic fillers*. Polymer Engineering & Science, 2006. **46**(9): p. 1131-1139.
67. Chen, R.S., S. Ahmad, and S. Gan, *Rice husk bio-filler reinforced polymer blends of recycled HDPE/PET: Three-dimensional stability under water immersion and mechanical performance*. Polymer Composites, 2018. **39**(8): p. 2695-2704.
68. Tong, J.Y., et al., *Study of the Mechanical and Morphology Properties of Recycled HDPE Composite Using Rice Husk Filler*. Advances in Materials Science and Engineering, 2014. **2014**: p. 938961.
69. Ajorloo, M., M. Ghodrat, and W.-H. Kang, *Incorporation of Recycled Polypropylene and Fly Ash in Polypropylene-Based Composites for Automotive Applications*. Journal of Polymers and the Environment, 2021. **29**(4): p. 1298-1309.
70. Yao, W., et al., *Effect of fly ash on the structure and properties of polyolefin elastomer/fly ash/polypropylene composites*. Materials Research Express, 2018. **6**(2): p. 025308.
71. Bicer, A., *Effect of production temperature on thermal and mechanical properties of polystyrene–fly ash composites*. Advanced Composites Letters, 2020. **29**: p. 2633366X20917988.
72. Rebeiz Karim, S., S. Banko Amy, and P. Craft Andrew, *Thermal Properties of Polymer Mortar Using Recycled PET and Fly Ash*. Journal of Materials in Civil Engineering, 1995. **7**(2): p. 129-133.
73. Satapathy, S. and R.V.S. Kothapalli, *Influence of fly ash cenospheres on performance of coir fiber-reinforced recycled high-density polyethylene biocomposites*. Journal of Applied Polymer Science, 2015. **132**(28).
74. AlMaaded, M.A., et al., *Influence of additives on recycled polymer blends*. Journal of Thermal Analysis and Calorimetry, 2014. **115**(1): p. 811-821.