Recycling of multilayer plastic packaging materials by solvent-targeted recovery and precipitation

by

Kevin L. Sánchez-Rivera

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This dissertation is approved by the following members of the Final Oral Committee:

George W. Huber, Professor, Chemical and Biological Engineering

Reid C. Van Lehn, Associate Professor, Chemistry

Victor M. Zavala, Professor, Chemical and Biological Engineering

David M. Lynn, Professor, Chemical and Biological Engineering

Abstract

One of the largest sectors for single-use plastics is the packaging industry, where many plastic materials are manufactured in the form of multilayer films. These materials are composites of distinct polymer layers and traditional recycling methods like mechanical recycling cannot process them due to the chemical incompatibility of its components. Further development is needed for a more efficient collection, sorting, separation, and recycling of these multilayer packaging articles. Dissolution-based methods have been considered a viable option for the recycling of multilayer plastics, in which solvents are employed to separate polymers of interest within a plastic waste stream. We have developed a new strategy called Solvent-Targeted Recovery And Precipitation (STRAP) to deconstruct multilayer films into their constituent resins with a series of solvent washes that are guided by thermodynamic calculations of polymer solubility. The STRAP process has been shown with rigid multilayer films, printed multilayer films, disposable facemasks, and mixed plastic waste. Our work has led to the development of the STRAP technology at the laboratory scale, accurate polymer solubility predictions with various computational tools, assessments of potential environmental and economic benefits, an understanding of impurity buildup in solvents and their removal, and a demonstration of recycling STRAP polymers back into film applications. One of the main objectives of STRAP is to convey the scientific principles underlying selective polymer dissolution, while understanding important process design parameters to ultimately have a positive impact in the recycling rates of current complex plastic waste feedstocks.

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Chapter 1. Introduction

1.1 Circularity challenges in the plastic packaging industry

Most of the plastic waste generated globally from 1950 to 2015 has been discarded and is accumulating in landfills or in the environment [1, 2]. Only 9% of this plastic waste has been recycled. Through the improvement of existing recycling technologies and the development of new ones, recycling rates of different plastic materials could be increased. One of the largest sectors for single-use plastics is the packaging industry, which accounted for over 35% of the plastics produced in 2015 [3]. These plastics can come in the form of multilayer films which are composites of distinct polymer layers that are combined to achieve specific properties that cannot be provided by single plastics alone [4]. Each layer gives the final bulk plastic a property advantage that is desirable for food packaging, medical packaging, and other applications. It is the different layers that can provide sealing properties, oxygen and water barriers, and rigidity [4] . Flexible plastic packaging has the advantages of protecting enclosed products from breakages or contamination, extending shelf life, providing an attractive appearance and reducing packaging size and weight [5]. In most cases, these materials are intended for single use and there is no technology available for their economical recycling, since traditional recycling technologies like mechanical recycling cannot be used for the separation of these multilayer materials [5, 6]. The presence of other polymers can be detrimental to the mechanical properties and ideally, a clean, single material stream is preferred [7]. In addition to this, these materials can consist of 3 up to 12 layers of different polymers, which makes it challenging to recover all of the components [8]. The recycling rates of flexible packaging has been less than 1%, while for rigid packaging has been around 40 % [5]. Further development is needed for a more efficient collection, sorting, separation and recycling of these multilayer packaging materials, considering the growing concern that is the increase in post-consumer (PCW) and post-industrial plastic waste (PIW) in the environment.

1.2 Plastic recycling technologies

Plastic waste can be converted to useful products via different technologies. These processes will depend on the type of plastic waste, desired products, potential economic and environmental impacts, and scale up challenges. Figure 1.1 shows various ways plastic waste can be recycled [7]. One of the most common ways of processing plastics is via mechanical recycling, in which the plastic is sorted, washed, shredded, and melted to produce new plastic products without breaking down the polymer chains [9]. Mechanical recycling has several disadvantages, particularly causing degradation of the polymer properties during processing and requiring plastic waste streams with high purity since mixed plastics cannot be efficiently processed [7, 10]. One advantage of mechanical recycling is that its energy requirements are much lower than other recycling approaches. The second type of technology, purification or dissolution-based recycling, use solvents to selectively separate and recover target materials [2]. This is considered a viable way of separating dissimilar polymers, removing impurities, color, odor, and plastic additives [11-16]. Mixed and multilayer plastics can be processed via dissolution methods, and it can have less impactful energy requirements than chemical recycling, which deconstructs polymer chains to produce monomers or other molecules that can be further converted to valuable products [17]. Chemical recycling can be divided between depolymerization and conversion technologies. In a depolymerization reaction, the polymer is broken down into its constituent monomers which can be used to produce new polymers (Figure 1.1). Examples of depolymerization reactions include glycolysis, hydrolysis, and enzymatic depolymerization and normally condensation polymers like PET have been efficiently depolymerized [18]. In conversion processes, the polymers are reacted to produce other molecules that could be used to as fuels or specialty chemicals. Examples of conversion processes are pyrolysis, in which plastics are thermally degraded in the absence of oxygen to form gases, plastic oils, and waxes; liquefaction, in which plastics are converted in the liquid phase; gasification, where plastics are reacted to produce syngas; and hydrogenolysis, in which the polymers are reacted to produce hydrocarbons or monomers, depending on the starting material [19-22].

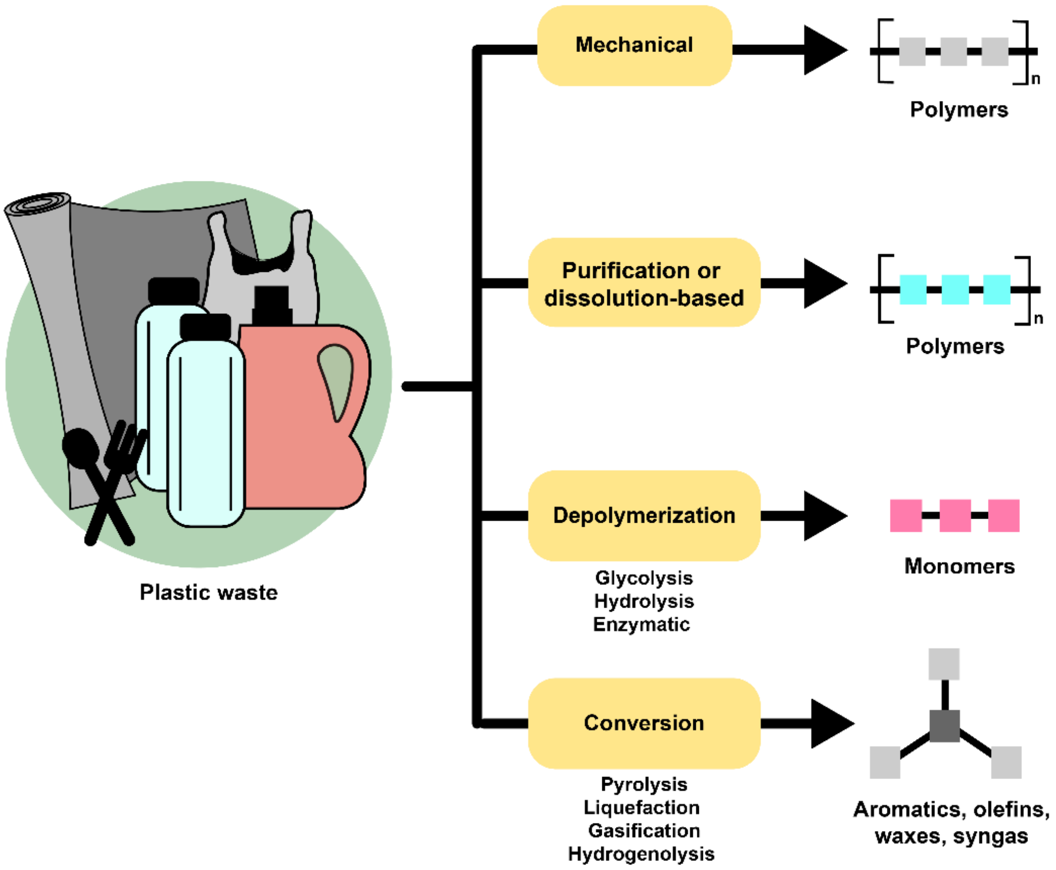

Figure 1.1 Summary of recycling technologies for different plastic materials [7, 17].

1.3 Dissolution-based plastic recycling

The use of solvents for the recycling of plastics is of great interest, primarily because it has advantages over current recycling processes like mechanical recycling for certain plastic structures like multilayer plastic films. These approaches employ solvents to selectively dissolve and separate the target materials. Polymer dissolution is also of great interest in other areas, including drug delivery, microlithography, and devices [23]. The dissolution kinetics of polymeric materials has been studied in the literature using transport models and analytical techniques like Fourier transform infrared spectroscopy (FTIR) imaging, optical microscopy, differential refractometry, gravimetry, and ellipsometry [23]. In general, polymer dissolution involves two transport processes which are solvent diffusion and chain disentanglement. Typically, in normal dissolution, the solvent penetrates the polymer, the polymer swells, it dissolves and then it diffuses into the solvent [2]. It is known that the polymer dissolution is affected by the types of polymers and solvents, the polymer size, the polymer molecular weight, dissolution temperature, dissolution time, and concentration [2, 24, 25]. For the polymer dissolution to occur, suitable solvents need to be used. A number of factors should be considered when selecting a solvent, which can be the viscosity, toxicity, cost, and time required for the dissolution [2].

Currently, there are various dissolution-based processes being commercialized: APK's Newcycling process, the Unilever/Fraunhofer Institute CreaSolv process, PureCycle Technologies process, and Polystyvert, among others [26-29]. APK AG is commercializing a solvent-based recycling scheme called Newcycling and has built a 8,000 ton/year plant in Germany to produce polyamide (PA) and polyethylene (PE) from PIW multilayer plastics [5, 27, 29]. APK's technology is based on dissolving a plastic using a solvent mixture from a group of alkanes, isooctane or cycloalkanes [30]. After the chemical dissolution of the polymers, the polymers are recovered from solution and then are pelletized by extrusion [5, 29]. Centrifuges separate the solids from the polymer solution and solvent [31]. APK AG claims that polypropylene (PP), polystyrene (PS), polylactic acid (PLA), PET and aluminum could also be recovered with this process in the future [5]. The Fraunhofer Institute introduced a multilayer film recycling process called CreaSolv and the solvent-based process produces plastics with comparable properties to virgin materials, effectively removing contaminants and additives [28]. The process is likely based on the dissolution of a target plastic, mainly polyolefins, using a solvent with a Hansen parameter δ_H

between 0.0 to 3.0 MPa$^{1/2}$, selected from a group of aliphatic hydrocarbons. An antisolvent made out of mono/polyhydroxy hydrocarbons, like 1-propanol or 1,3-propanediol, with a δ_H between 4.0 and 38.0 MPa$^{1/2}$ is then used to precipitate the polyolefin from the mixture [32]. The institute has also studied the separation of PS, [33] and are researching the recycling of multilayer food packaging that can consist of PET, PE, PP, EVOH, PA and metalized layers [34]. Currently, Unilever is implementing the CreaSolv process in a 1,100 ton/year demonstration plant in Indonesia to recover PE from multilayer sachets [26, 35]. Another company with efforts in using solvent systems is PureCycle Technologies which is building a 54,000 ton/yr facility that uses solvents to produce polypropylene (PP) [36, 37]. The method consists of contacting the plastic waste with a proprietary solvent at elevated temperatures and pressures to obtain the purified PP [36]. The process removes impurities, undesired colors and odors and produces PP with comparable properties to the virgin resin [37]. In terms of recycling printed plastics, Cadel Deinking is a technical company that currently removes inks from plastic surfaces using a deinking solution and also has a delamination process for multilayer plastics [38]. They claim that their deinking process can be applicable to all kinds of plastics and can work with any type of ink, water-based, solvent-based, UV inks and electron beam. Cadel deinking licenses the technologies to companies looking for a way to remove inks from plastics. The use of non-ionic, cationic and anionic surfactants for the ink removal in polymer surfaces has been disclosed in the literature [39]. Solvents, cleaning solutions and solutions of glycol ether have also been used to remove inks from polymer substrates [40-42].

We have demonstrated a dissolution-based recycling approach called Solvent-Targeted Recovery And Precipitation (STRAP) [43]. This process was initially demonstrated with a commercially available post-industrial, rigid multilayer film manufactured by Amcor called the

Amcor Evolution film into its three main polymer components with 100% recovery (Figure 1.2). [43, 44]. This multilayer film consisted primarily of polyethylene (PE), ethylene vinyl alcohol (EVOH) and polyethylene terephthalate (PET) with various tie layers that include ethylene vinyl acetate (EVA). In this process the film is dissolved in two different hot solvents, each of which solubilizes an individual polymer. The final resin is then precipitated by adding an antisolvent which renders the polymer insoluble.

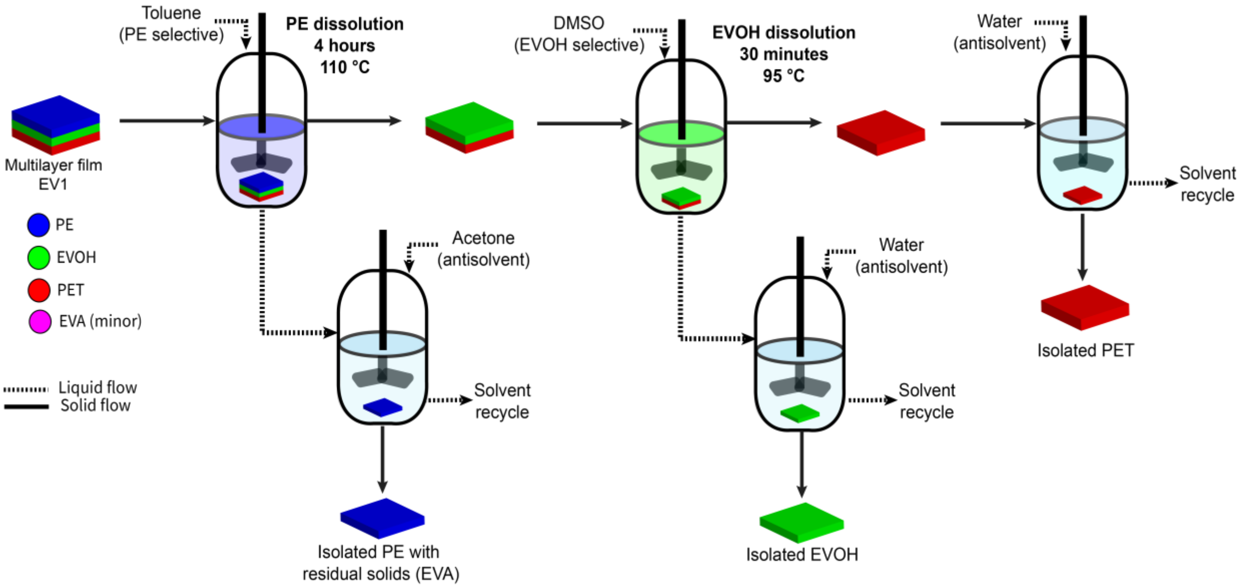

Figure 1.2 STRAP process with a post-industrial multilayer plastic film composed of PE, EVOH, EVA, and PET [44].

The solvent selection for STRAP is based on quantifying polymer-solvent thermodynamic properties using three computational methods of increasing accuracy and complexity: Hansen Solubility Parameters (HSPs), molecular dynamics (MD) simulations, and a combined quantum chemical and statistical mechanical approach called the COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS) [45, 46]. In general terms, HSP are used for the screening of solvents suitable for the selective dissolution of specific polymers, COSMO-RS enables predictions of polymer solubility as a function of both the temperature and the composition of the liquid phase, and MD simulations provide detailed calculations of polymer structures and conformations [47-52]. These methods together can efficiently select initial solvent compositions and temperatures for the STRAP process.

1.4 Overview of dissertation

The Solvent-Targeted Recovery And Precipitation (STRAP) process has been developed from various areas. After the initial experimental demonstration and economic analysis for the recycling of a multilayer film by STRAP, we looked at how the process could be improved economically and how it could be applied to different types of plastic waste.

In Chapter 2, the use of antisolvents in the STRAP process was reduced and solvent mixtures were considered to enable the temperature-controlled dissolution and precipitation of the target polymers in multilayer films. This was considered as a means to further improve the STRAP process and its estimated costs. Two STRAP approaches were compared based on different polymer precipitation techniques: precipitation by the addition of an antisolvent (STRAP-A) and precipitation by decreasing the solvent temperature (STRAP-B). Both approaches were able to separate the constituent polymers in a post-industrial film composed primarily of polyethylene (PE), ethylene vinyl alcohol (EVOH) and polyethylene terephthalate (PET) with near 100% material efficiency. A technoeconomic analysis indicated that the minimum selling price (MSP) of the recycled resins with STRAP-B is 21.0% lower than that achieved with STRAP-A. This provides evidence that thermally-driven polymer precipitation is an option to reduce the use of antisolvents, making the STRAP process more economically and environmentally attractive. A third process, STRAP-C, was demonstrated with another post-industrial multilayer film of a different composition. The results demonstrate that this process can also recover polymers at similar costs to those of virgin resins, indicating that the STRAP technology is flexible and can remain economically competitive as the plastic feed complexity is increased.

In Chapter 3, to broaden the applicability of STRAP, the process was demonstrated with a flexible post-industrial printed multilayer plastic film used for food packaging. The material was a reverse printed film composed of polyethylene (PE), ethylene vinyl alcohol (EVOH), polyethylene terephthalate (PET), and polyurethane (PU)-based inks. Removal of all colors was observed with biomass-derived gamma-valerolactone (GVL) and the recovered polymers possessed comparable properties to the corresponding virgin resins. A technoeconomic analysis indicated that this STRAP process could be economically feasible at a processing capacity of 6,000 tons per year. Moreover, the production of plastic films with materials recovered by this STRAP process can have a lower climate change impact than the production of films from virgin polymers.

In Chapter 4, three different experimental methods were considered to recover a polyethylene (PE) resin from a printed multilayer film by STRAP. The methods consisted of: 1) a filter bag system, 2) a Soxhlet extraction, and 3) a jacketed dissolution vessel. Cast films were produced with the PE recovered from each method and were analyzed for color, mechanical properties, and number of impurities. High-quality recycled PE cast films can be produced by increasing the solvent to plastic ratio, including a filter pore size of 100 μm, and optimizing temperature control in STRAP. This study demonstrated that STRAP polymers can be recycled back into plastic films, enabling the potential circularity of these packaging materials.

In Chapter 5, the STRAP framework was applied to develop a series of steps to separate up to 10 polymers from a post-industrial mixed plastic waste (MPW) stream. The STRAP steps were initially demonstrated with a physical polymer mixture containing LDPE, HDPE, PS, PVC, EVOH, PET, PP, PA6, PA66, and PA 66/6, in which recoveries of 89% or higher were achieved for each polymer. It was found that the main components recovered by selective dissolution from the post-industrial MPW from packaging were LDPE, HDPE, and PET. This approach can provide an estimate composition of complex feedstocks like MPW that may contain multilayer films from packaging and serve as a pretreatment for other recycling technologies.

In Chapter 6, the post-STRAP solvents were analyzed to detect the buildup of impurities after polymer dissolution. It was found that different plasticizers, fluorinated substances, and oligomers remain in the solvent after STRAP with LDPE. Short-chain PE oligomers, in the concentration range of 6 to 106 ppm, can accumulate in the solvent after multiple LDPE dissolutions. A potential option for removing impurities from the solvent is via adsorption, and the removal of a diethylene glycol dibenzoate plasticizer from toluene was achieved with activated carbon and silica gel.

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Chapter 2. Solvent use reduction in STRAP: economic and environmental benefits

The contents in this chapter were adapted from the following references:

K.L. Sánchez-Rivera, P. Zhou, M.S. Kim, L.D. González Chávez, S. Grey, K. Nelson, S.C. Wang, I. Hermans, V.M. Zavala, R.C. Van Lehn, and G.W. Huber, Reducing Antisolvent Use in the STRAP Process by Enabling a Temperature-Controlled Polymer Dissolution and Precipitation for the Recycling of Multilayer Plastic Films, ChemSusChem, 14 (2021) 4317-4329

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2.1 Introduction

One of the largest sectors for single-use plastics is the packaging industry, which accounted for over 35% of the plastics produced in 2015 [1]. Flexible plastic packaging has the advantages of protecting enclosed products from breakages or contamination, extending shelf life, providing an attractive appearance and reducing packaging size and weight [2]. These plastic packaging materials can come in the form of multilayer films, which are composites of distinct polymers that are combined to achieve specific properties that cannot be provided by single plastic layers [3]. Each layer gives the final bulk plastic a property advantage that is desirable for food packaging, medical packaging, and other applications. It is the different layers that provide sealing properties, oxygen and water barriers, and structural rigidity [4]. In most cases, these multilayer materials are intended for single use, as there is currently no technology available for their widespread economical recycling. Specifically, traditional recycling methods such as mechanical recycling cannot process these materials [2, 5]; this is because the different polymers are not chemically compatible and will phase separate during mechanical recycling [6, 7]. Multilayer plastic materials can consist of more than 17 layers of different polymers, which makes it challenging to recover all of the components [8-10]. Further technology development is needed for the more efficient collection, sorting, separation, and recycling of these multilayer packaging materials, as they represent an increasing amount of post-consumer (PCW) and post-industrial plastic waste (PIW).

Our team has recently reported a new processing method for the recycling of multilayer plastic films into pure resins by selectively dissolving each polymer into a different solvent in an approach we call Solvent-Targeted Recovery And Precipitation (STRAP) [11]. Solvent-based plastic recycling approaches have been studied by several researchers and are currently being implemented by a number of companies[2, 12-17]. For example, APK AG's Newcycling process is being carried out at a capacity of 8,000 metric tons per year in Germany for the recycling of polyethylene (PE) and polyamides (PA) from multilayer films [18, 19]. Another process is the CreaSolv process developed by CreaCycle GmbH and the Fraunhofer Institute IVV, which targets thermoplastics from plastic packaging waste, electronic waste, and construction insulation foam [19, 20]. One of their plants has a capacity of 2,000-4,000 tons per year. Most of the solvent-based processes in the industry are in the early commercial or pilot stage of maturity, demonstrating that there is interest in implementing these technologies. In our case we used the STRAP process to convert a commercially available post-industrial rigid multilayer film (A1) manufactured by Amcor into its three main polymer components with 100% recovery. This multilayer film consisted primarily of PE, ethylene vinyl alcohol (EVOH) and polyethylene terephthalate (PET), with various tie layers that include ethylene vinyl acetate (EVA). In this process, the film is dissolved in two different solvents at a high temperature, each of which solubilizes an individual polymer. Antisolvents are then added to precipitate the dissolved polymer from the solvent. The solvent selection for STRAP is based on quantifying polymer and solvent thermodynamic properties using three computational methods of increasing accuracy and complexity: the calculation of Hansen Solubility Parameters (HSPs), molecular dynamics (MD) simulations, and a combined quantum chemical and statistical mechanical approach called the COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS). In general terms, HSPs are used for the rapid screening of solvents suitable for the selective dissolution of specific polymers, MD simulations provide detailed calculations of polymer structures and conformations, and COSMO-RS enables predictions of polymer solubility as a function of both the temperature and the liquid phase composition using the conformations from MD. A rigorous technoeconomic analysis (TEA) indicated that STRAP can produce the recycled resins at lower costs than the virgin resins when the process operates at a size greater than 3000 tons per year [11]. However, the TEA also showed that the largest costs were associated with the thermal separation (distillation) of the solvents and antisolvents, accounting for 33.6% and 79.3% of the capital and operating costs, respectively. It would thus be highly desirable to reduce the costs of the STRAP technology and it would be helpful to see if STRAP can be applied to other types of multilayer packaging materials.

The objective of this Chapter is to identify operating conditions that will reduce the amount of antisolvents used in the STRAP process and to demonstrate how STRAP can be applied to a more complex, industrial multilayer film (provided by Amcor). We combine thermodynamic computational tools, polymer characterization methods, and modern process design tools to develop a realistic near-term approach to design solvent systems to recycle multilayer plastics. The efficient utilization of these solvents requires a process that can recover and reuse the solvents, while minimizing the amount of solvents left as waste material. An approach to reduce the use of antisolvents is to use solvents or solvent mixtures that can enable the temperature-controlled dissolution and precipitation of the target polymers in a multilayer film. The use of solvent combinations has been considered as an option in dissolution/precipitation methods for certain polymers. Some studies have used solvent mixtures only for the dissolution of the target plastic to later add an antisolvent for precipitation. Hadi et al. studied mixtures of turpentine/petroleum ether (PetE) to dissolve polyolefins and later precipitate them using n-hexane and PetE [21]. Weeden et al. used mixtures of acetone/dichloromethane to dissolve electronic waste components [22]. Pure solvents and solvent combinations have also been used to dissolve various polymers at different temperatures, reducing the number of solvents needed to recover each polymer. Some patents disclosing this technique have relied on evaporating the solvent to obtain the final solid polymers [23, 24]. Precipitating the polymers through a solvent temperature change instead of evaporating the solvent or adding an antisolvent could be a way to make dissolution/precipitation methods more feasible [15].

In this chapter, we evaluate and compare the STRAP technology using two different polymer precipitation techniques: precipitation by the addition of an antisolvent (STRAP-A) and precipitation by decreasing the solvent temperature (STRAP-B). Two different post-industrial rigid multilayer films manufactured by Amcor (A1 and A2) were used to demonstrate the STRAP process. The multilayer film A1 was composed of PE, EVOH and PET with minor component EVA. Film A2 was composed of the same polymers with the addition of glycol-modified polyethylene terephthalate (PETG). Thermodynamic tools were used for solvent selection and the experimental results were used in a process model that allowed an estimation of the process costs and potential environmental benefits.

2.2 Methods

2.2.1 Computational methods

We assessed polymer solubility computationally to guide solvent selection for the STRAP process; our approach uses a combination of Hansen Solubility Parameters, molecular dynamics (MD) simulations, and the Conductor-like Screening Model for Real Solvents (COSMO-RS), following our previous work [11]. HSPs are empirical solvent parameters that are widely used to qualitatively identify solvents that are capable of dissolving target polymers [25]. Each compound (polymer or solvent) is assigned three parameters that account for dispersion, polar and hydrogen-bonding forces [26]. These three parameters are used as coordinates that locate the compounds in HSP space. Each polymer has an additional radius parameter, R_0, that defines a sphere in HSP space. Solvents with HSPs within this sphere are expected to dissolve the polymer, whereas solvents with HSPs outside of this sphere are not expected to dissolve the polymer. HSPs (and values of R_0) have been tabulated for a wide range of polymers and solvents based on solubility experiments in reference solvent systems that span the HSP space [25]. In this work, HSPs were obtained from the HSP handbook [26] and used for preliminary solvent selection, although these values do not provide quantitative predictions of solubility.

MD simulations and COSMO-RS are used for further quantitative solubility predictions utilizing an updated protocol compared to our previous work. Atomistic MD simulations for oligomers were performed to obtain input structures for COSMO-RS. MD simulations were first performed of a single oligomer in dilute solution in the isothermal-isobaric ensemble. Each MD simulation contained one oligomer molecule (EVOH or PETG) and 216 solvent molecules. EVOH was simulated in water and PETG in toluene. The EVOH oligomer molecule contained four vinyl alcohol repeat units and two ethylene repeat units. The PETG oligomer contained four ethylene glycol repeat units and two 1,4-cyclohexanedimethanol repeat units. The radius of gyration (R_g) and solvent accessible surface area (SASA) of the oligomer were then calculated as a function of simulation time from the MD trajectories to characterize the distribution of oligomer conformations. Representative oligomer conformations that span the R_g-SASA space were extracted from the MD trajectories and used as input to the COSMO-RS workflow detailed below.

A total of 22 conformers were taken from the EVOH trajectory and 18 conformers were taken from the PETG trajectory. MD simulations were performed using Gromacs 2016 [27]. All compounds were parameterized by using Antechamber and the Generalized AMBER force fields [28, 29].

COSMO-RS predicts the equilibrium properties of multicomponent systems based on quantum mechanical calculations and statistical thermodynamics methods [30]. It represents each molecule based on the screening charge density that arises at its molecular surface due to the polarization of the medium. The screening charge density is obtained from density functional theory (DFT) calculations and histogrammed to generate a σ-profile. We approximated the σ-profile of a polymer by generating σ-profiles for oligomer structures with deactivated terminal groups [31]. The screening charge density and resulting σ-profile depends on the specific molecular conformation; consequently, we generated a set of oligomer conformations using MD (as described above) to span a range of possible σ-profiles. Figure 2.1 provides an example of two conformers for different oligomers and their DFT calculation results of screening charge distributions. The chemical potential of a polymer is calculated based on the σ-profiles to enable predictions of polymer solubility via a solid-liquid equilibrium calculation. DFT calculations of screening charge distributions were performed by Gaussian 16 at the BVP86/TZVP/DGA1 level of theory [32]. COSMO-RS solubility calculations were performed by COSMOtherm 19 with the parameterization BP_TZVP_19 [30, 33].

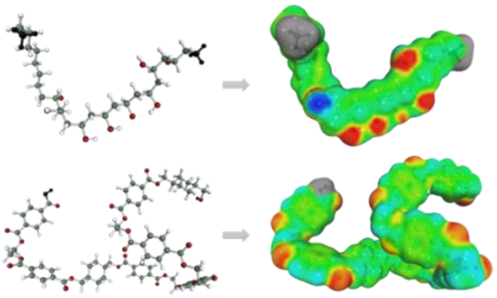

Figure 2.1 Molecular structures and corresponding COSMO-RS screening charge densities of an example EVOH oligomer (top) and PETG oligomer (bottom). Regions with negative screening charge densities are in blue, positive screening charge densities are in red, intermediate values are in green and teal, and deactivated groups (which do not contribute to the σ-profile) are in grey.

The main goal of the STRAP process is to separate the constituent polymers in a multilayer plastic film using a series of solvent washes. A model film manufactured by Amcor was used to develop and demonstrate the experimental procedure. The plastic film was an A1 film composed primarily of PE, PET, EVA and EVOH. Before a typical STRAP experiment, the multilayer film was cut into 1×1 cm^2 stamps. A 250 mL round bottom flask connected to a reflux condenser with a cold-water supply line was used. The round bottom flask, which would contain the corresponding solvent and the pieces of multilayer film in 40-gram batches, was partially submerged in a 1500 mL dish containing silicone oil as a heat transfer fluid. The system was heated to the desired dissolution temperature with an electric heat plate equipped with a magnetic stir drive and the stirring rate was adjusted to have a constant mixing. Based on the computational analysis for solvent selection, we experimentally assessed the recovery of each polymer in the multilayer film A1 by performing three processing steps: (1) selectively dissolving the PE fraction in toluene at 110 ℃ for four hours, then separating the solubilized fraction from the EVOH and PET via mechanical filtration; (2) selectively dissolving the EVOH fraction in DMSO at 95 ℃ for 30 minutes, then separating the solubilized fraction from the remaining PET via mechanical filtration; and (3) precipitating the solubilized PE and EVOH fractions with the addition of acetone or water, respectively. The precipitated PE and EVOH were then separated from the toluene-acetone and DMSO-water mixtures by filtration. The resulting solid fractions were dried in a vacuum oven overnight at 65 °C to remove residual solvents. This method was identified as STRAP-A, where the addition of antisolvents is required to precipitate the target polymers.

An alternative method for the precipitation of the dissolved polymers was considered. This consisted of lowering the temperature of the solvent and the dissolved polymer to 35 °C. For this method, labeled as STRAP-B, solvent mixtures were considered to both dissolve the target polymer at a high temperature and precipitate the polymer at a lower temperature, reducing the need for high amounts of antisolvents to be added after the dissolution to precipitate the polymer. In this case, a 60% DMSO-40% water (v/v) solvent mixture was used for EVOH and pure toluene was still used for PE, as it still allowed for a precipitation with a temperature change.

The same experimental set up was used for the multilayer film A2, which consisted of PETG, PE, EVOH, PET and EVA. Similarly to A1, the multilayer film was cut into 1×1 cm^2 stamps. We experimentally assessed the recovery of each polymer in the multilayer film A2 by performing four processing steps: (1) selectively dissolving the PETG fraction in a mixture of 60% DMF-40% THF (v/v) at 87 °C for four hours, then separating the solubilized fraction from the PE, EVOH, PET and EVA via mechanical filtration; (2) selectively dissolving the PE and EVA fraction in toluene at 110 °C for two hours, then separating the solubilized fraction from the EVOH and PET via mechanical filtration; (3) selectively dissolving the EVOH fraction in a mixture of 60% DMSO-40% water (v/v) at 95 °C for 30 minutes, then separating the solubilized fraction from the remaining PET via mechanical filtration; and (4) precipitating the solubilized PETG by adding 1-propanol as antisolvent and precipitating the PE and EVOH fractions by reducing the temperature of the solvents containing the dissolved polymers to 35 °C. The precipitated PETG, PE and EVOH solids were then separated from the corresponding solvents by filtration. The EVA was recovered by adding acetone as antisolvent to the toluene after removing the PE solids. The resulting five solid fractions were dried in a vacuum oven overnight at 65 ℃ to remove residual solvents. The process with multilayer film A2 was labeled as STRAP-C.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the separated polymer fractions from the STRAP process and compare their spectra to virgin resins. The instrument was a Bruker Vertex 70 with a liquid nitrogen-cooled MCT detector. The ATR cell used was a MIRacle single reflection cell equipped with a diamond crystal (Pike Technologies). In a typical measurement, 128 scans were averaged with a 4 cm^{-1} resolution and range from 4000-400 cm^{-1}.

2.2.3 Technoeconomic analysis (TEA)

Based on the experiment data and simulation results, the economic feasibilities of the proposed STRAP processes were analyzed using TEA. The major assumptions and parameters applied to the economic evaluation are listed in Table 2.1. As an economic evaluation method, the minimum selling price (MSP) of the recycled polymers were estimated [34]. The MSP is the sale price of the recycled polymer determined at the break-even point, where the total income and outcome are equal. The total income is the revenue generated from the polymer sales, whereas the outcome consists of the return on investment (ROI), tax, and operating cost (OPEX). The ROI, which depends on the contribution of capital cost (CAPEX), the interest rate (i), and the economic project life (r), is obtained by applying Eq. (1).

$$ROI = \frac{i \times (1+i)^r}{(i+1)^r} \times CAPEX \qquad (1)$$

where the CAPEX includes ISBL, OSBL, engineering cost and contingency costs. The value of ISBL can be calculated by multiplying the Lang factor (this study used factor of 3.63 which was suggested for both solid and liquid processes) by the major equipment purchase cost [35]. The value of OSBL can be obtained as being equal to 40% of ISBL. The engineering cost is assumed to be 30% of ISBL plus OSBL and the contingency cost is equal to 25% of ISBL plus OSBL [36]. Finally, the MSP can be calculated in terms of USD per kilogram ($/kg):

$$MSP = \frac{ROI + OPEX - (OPEX + DEP) \times TAX}{A_{polymer} \times (1 - TAX)} \tag{2}$$

where DEP and TAX are depreciation and tax rate, respectively, and $A_{polymer}$ is the amount of the recycled polymer per year. OPEX can be obtained through the energy and mass information and purchase price of the corresponding information. Table 2.2 shows the utility and material purchase prices for calculating the variable operating cost and the component for estimating the fixed operating cost [11]. In order to estimate labor costs, the labor cost was calculated for 2 operators per shift position and 3 shift position, for a total salary cost of $395,172 per year. The salary for one operator was estimated from a report by NREL [37]. The sizes and costs of the proposed process units were estimated using Aspen Process Economic Analyzer. The pre-process, including a shredder, floating tank, friction washer, dewatering machine, and a thermal dryer, was used to prepare the film. The equipment cost was estimated using an exponential scaling expression based on the previous work [11].

Table 2.1 Assumptions and parameters for the economic evaluation.

Lifetime [year]	20
Interest rate [%]	10
Income tax rate [%]	25
Depreciation method	Straight line
Plant operability per year [hours]	8,000

Table 2.2 Assumptions and parameters for calculating OPEX.

Variable operating cost	
Toluene purchase [\$/kg]	0.85
Acetone purchase [\$/kg]	0.70
DMSO purchase [\$/kg]	1.90
Water purchase [\$/kg]	0.065
THF purchase [\$/kg]	1.50
DMF purchase [\$/kg]	1.70
Propanol purchase [\$/kg]	0.90
Electricity purchase [\$/kWh]	0.07
High-pressure steam [\$/kJ]	2.50×10^{-6}
Medium-pressure steam [\$/kJ]	2.20×10^{-6}
Low-pressure steam [\$/kJ]	1.90×10^{-6}
Cooling water purchase [\$/kJ]	2.12×10^{-7}
Fixed operating cost	
Salaries [\$/each operator/year]	65,862
Benefits and overhead [% of Salaries]	90
Maintenance [% of CAPEX]	3
Insurance [% of CAPEX]	0.7
Rent of land [% of ISBL + OSBL]	1

2.2.4 Life cycle assessment (LCA)

This LCA study aims to quantify the environmental benefits (climate change, energy use, water use, and process toxicity) of the STRAP technology and of the production of multilayer plastic film from virgin resins. The study evaluates the impacts of a potential commercial plant of 3000 tonnes per year. The LCA study is performed by taking a product perspective (23), in which the STRAP process is seen as an alternative process that produces virgin-grade polymers (that can be used for multilayer films. Therefore, we compare the environmental impacts of producing multilayer films from virgin resins (from fossil sources) against producing multilayer films using

STRAP (which avoids using fossil sources). The factors to estimate the environmental impacts of the processes are obtained from the Ecoinvent and the Environmental Footprint databases. The Ecoinvent 3.6 cut-off by classification database (32) is used for the solvent impacts since it has all the necessary factors for the solvents utilized in STRAP processes. Similarly, the impacts related to the production of polymers are modeled based on the Environmental Footprint database (33) The software openLCA v1.10.3 (34) is used to perform the LCA calculations with the Environmental Footprint (EF 2.0) (35) impact assessment method, providing fair evaluation and comparison for all products within the system boundaries.

In the virgin resins alternative, the system boundaries include the extraction and transportation of raw materials (fossil sources), material processing (production of monomers, polymerization, and multilayer film extrusion), and consumption of process utilities (energy and water inputs). Any additives such as fillers (fibers), reinforcements, colorants (pigments), or functional additives (stabilizers, flame retardants, lubricants, foaming agents, flame retardants) (30) are not considered within the scope of the system boundaries. In the STRAP alternative, the multilayer films from post-industrial waste are treated through the recycling technology to isolate the constituent polymer layers. The resins are then extruded to produce an equivalent amount of multilayer plastic film. Thus, the STRAP system boundaries include the collection and transportation of multilayer film waste (considering a distance of 1000 km), the material inputs (solvents and utilities), the transportation of the process solvents, and the ML film extrusion to produce the new film from recovered polymers. The film treated in the STRAP process is assumed to be clean PIW; therefore, product use, and treatment (such as screening, sorting, grinding, and cleaning) are not within the scope of the system boundaries. The ability to use PIW is a key benefit compared to PCW.

2.3 Results

2.3.1 STRAP-A with multilayer film A1

The STRAP-A process followed the same procedure as in our previously published work and it was used as a benchmark to compare with the alternative processes in this study. Table 2.3 shows that an overall average mass balance of 102.58 wt% was obtained with a standard deviation of +/- 0.96 wt% for the recovery of PE, PET and EVOH from multilayer film A1. The overall mass balances exceeded 100 wt% possibly due to solvent uptake. Drying conditions will need to be adjusted to minimize entrained solvents. The values reported in Table 2.3 are consistent with our previously published results [11]. Figure 2.2 shows solvents, antisolvents, temperatures and dissolution times that were used in each process step for STRAP-A. Acetone and water were used as antisolvents for the precipitation of PE and EVOH, respectively.

Table 2.3. Yield of polymers from multilayer film A1 with the STRAP-A process.

Experiment	Initial Film Mass (g)	Polymer Yield (wt %)			Overall Mass Balance (%)
		PE[1]	EVOH	PET	
1	38.30	4.98%	2.61%	94.15%	101.74%
2	38.28	5.33%	3.26%	95.03%	103.62%
3	38.35	5.42%	3.14%	93.81%	102.37%
Average	38.31	5.24%	3.01%	94.33%	102.58%
STDEV	0.04	0.23%	0.34%	0.62%	0.96%

1. PE solids contain the EVA component.

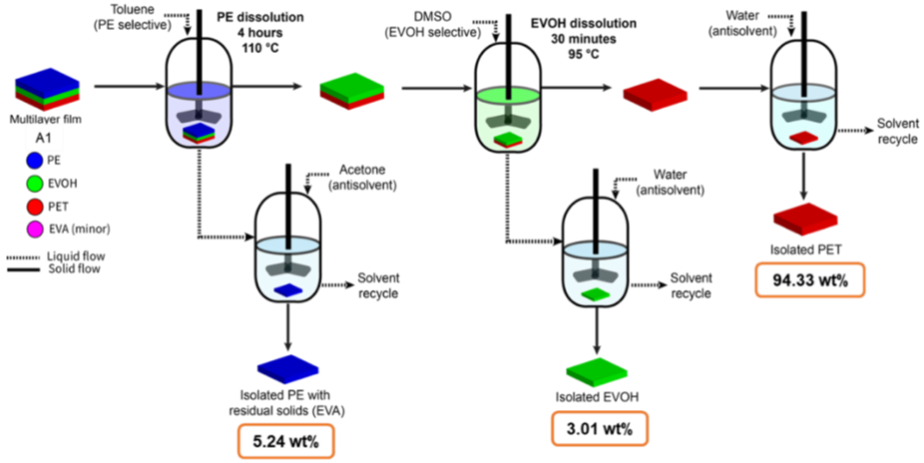

Figure 2.2 STRAP-A process schematic for the separation and recovery of the polymer components in a multilayer film A1 manufactured by Amcor.

The extensive use of antisolvents can be a concern at larger scales due to potential high costs and environmental and safety risks. It was determined that the energy required to separate the respective solvents and antisolvents used in STRAP-A accounted for 33.6% of the total capital costs and 79.3% of the total operating costs [11]. The distillation columns in STRAP-A were the main cost drivers in the process. An alternative to using antisolvents for polymer precipitation is to cool the solvent with the dissolved polymer to induce the precipitation. For this purpose, solvent mixtures were considered to both dissolve the target polymer at a high temperature and to easily precipitate the polymer as the temperature is decreased. In this way, we can have a constant solvent composition throughout the process that targets a specific polymer component in the multilayer film. The thermodynamic computational tools allowed us to quickly screen potential solvent compositions for the recovery of EVOH and PE using this approach.

2.3.2 Computational modeling results

COSMO-RS predictions were used to identify potential solvent compositions for the EVOH recovery, leveraging the ability of this method to capture temperature-dependent solubilities. Figure 3 shows COSMO-RS predictions of EVOH solubility as a function of temperature and DMSO-water compositions. For comparison, the predicted EVOH solubility in pure DMSO at 95°C is 22.77 wt%, which is similar to the experimentally measured solubility of 24.02 wt%. This comparison supports the validity of COSMO-RS to predict EVOH solubilities. The STRAP-A process dissolves EVOH in pure DMSO at 95°C. Water is then added as the antisolvent to achieve a final 20% DMSO-80% water (v/v) mixture at a lower temperature, reducing the EVOH solubility to trigger its precipitation. These steps are indicated by the labeled white arrow in Figure 3. This first process takes advantage of the large solubility difference (as predicted by COSMO-RS and measured experimentally) between the two states to achieve a high EVOH recovery.

Figure 2.3 indicates that the STRAP-B process could achieve the same decrease in solubility to precipitate the polymer by reducing the temperature without varying the solvent composition. The COSMO-RS solubility calculations indicate that EVOH recovery should be possible in pure DMSO, which is consistent with the inability of pure DMSO to dissolve EVOH at room temperature. However, the experimental recovery of EVOH upon cooling was low. Therefore, different mixture compositions were tested. A 60% DMSO-40% water mixture (v/v) was selected for EVOH recovery since it was predicted to have a satisfactory solubility (10.45 wt%) at 95°C and low solubility (1.72 wt%) at 35°C; the latter value is comparable to the predicted EVOH solubility for the final step of the STRAP-A process. Experimental values indicated a solubility of 7.17 wt% at 95 °C and 0.01 wt% at 35 °C, leading to a high EVOH recovery. We note that COSMO-RS overpredicts the experimental solubility, but general trends are correctly captured.

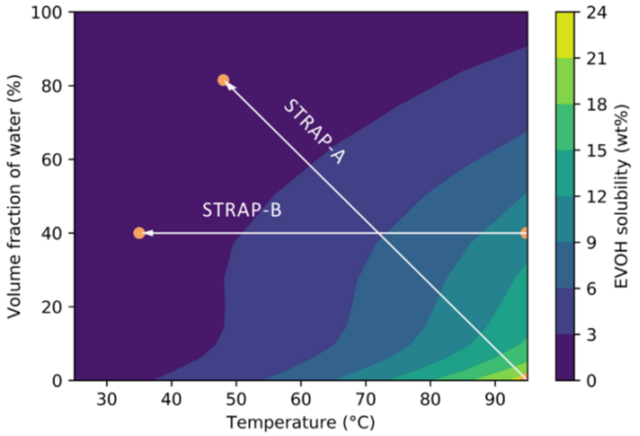

Figure 2.3 COSMO-RS solubility predictions for EVOH in DMSO-water mixtures. Two EVOH recovery processes are shown by arrows. The STRAP-A process dissolves EVOH in pure DMSO at 95°C (predicted solubility 22.77 wt%) and precipitates the EVOH in 81.5% water at 48°C (predicted solubility 1.23 wt%). The STRAP-B process dissolves EVOH in 40% water at 95°C (predicted solubility 10.45 wt%) and precipitates the EVOH by reducing the temperature to 35°C (predicted solubility 1.72 wt%).

Similar COSMO-RS solubility predictions were computed for PE in various toluene-acetone mixtures to identify if any mixtures were suitable for recovery. The experimental solubility of PE in pure toluene (14.56 wt% at 110 °C) was used as a reference input to the COSMO-RS calculations. The computational results indicate that PE solubility in 90% toluene-10% acetone (v/v) is 0.02 wt% at 55 °C. This result suggests that adding only a small fraction of acetone to toluene makes PE insoluble in the mixture, even at elevated temperatures; similar results were obtained for other volume fractions of acetone. This low solubility was verified experimentally, where none of the tested toluene-acetone mixtures could dissolve the PE. Therefore, pure toluene was still used in order to ensure initial PE dissolution. Pure toluene still allowed the PE precipitation to occur with a decrease in temperature.

2.3.3 STRAP-B with multilayer film A1

The STRAP-B process was completed with the solvent compositions allowing for a temperature induced precipitation of the EVOH and PE polymers using the thermodynamic insights from the former section. Table 2.4 shows that similar polymer yields to STRAP-A were obtained for PE, EVOH and PET with STRAP-B, demonstrating that temperature-controlled dissolution and precipitation for the polymer recovery is a promising approach that could reduce costs and make solvent-based recycling processes more attractive.

Table 2.4. Yield of polymers from multilayer film A1 with the STRAP-B process. Polymers were precipitated by reducing the solvent temperature. A DMSO 60%-water 40% solvent mixture was used for EVOH and toluene was used for PE.

Experiment	Initial Film Mass (g)	Polymer Yield (wt %)				Overall Mass Balance (%)
		PE	EVOH	EVA	PET	
1	38.272	4.02%	3.16%	1.06%	93.47%	101.86%
2	38.34	4.05%	3.27%	0.76%	93.81%	102.84%
3	38.26	4.53%	3.24%	0.78%	92.69%	102.02%
Average	38.29	4.20%	3.22%	0.91%	93.32%	102.24%
STDEV	0.04	0.28%	0.06%	0.17%	0.57%	0.53%

One of the major differences between the STRAP processes was in the PE yield achieved. The PE yield was higher with STRAP-A where acetone was used as an antisolvent to precipitate the polymer. This difference in yield is due to the presence of ethyl vinyl acetate (EVA), which is a minor component in the multilayer film A1. The EVA is soluble in toluene and can also precipitate when acetone is added, along with the PE. An NMP step was previously considered for the EVA removal from the PE but we found that this separation can be easily done by decreasing the temperature of the toluene to precipitate PE, as EVA still remains in the solvent. The EVA can then be precipitated with the addition of acetone as an antisolvent. Figure 2.4 shows the solvents, temperatures and dissolution times that were used in each process step for STRAP-B.

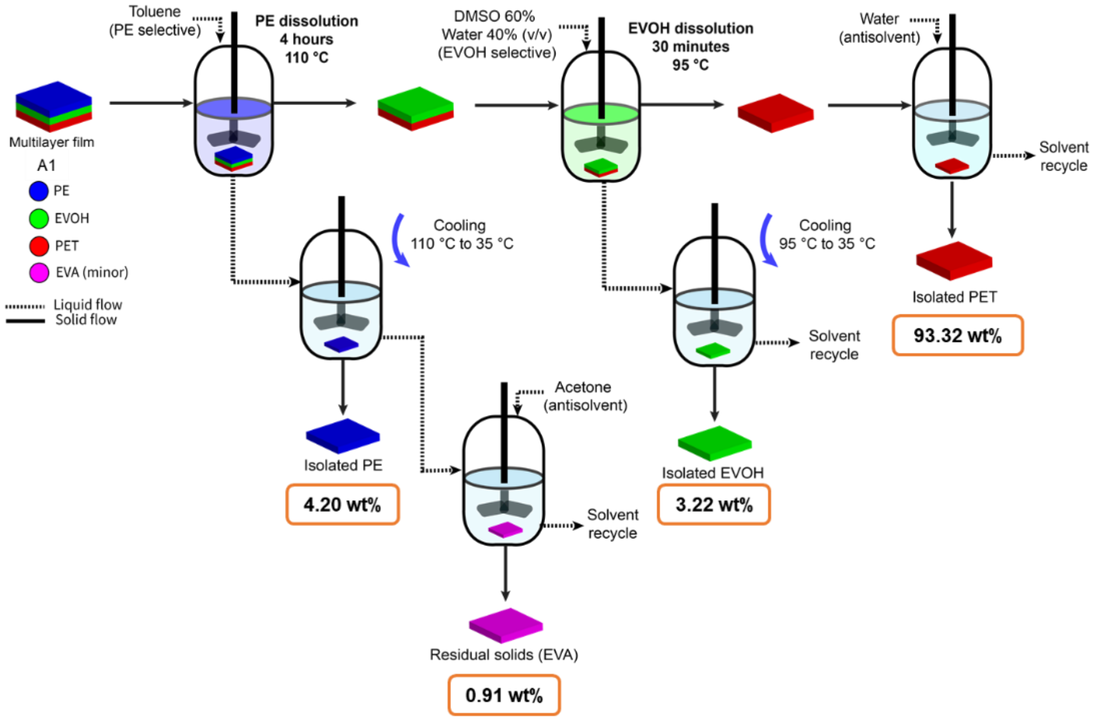

Figure 2.4 STRAP-B process schematic for the separation and recovery of the polymer components in a multilayer film A1 manufactured by Amcor.

2.3.4 Characterization of solids recovered with STRAP-A and STRAP-B

Previous FTIR results have shown that the PE, EVOH and PET recovered from physical mixtures of these components and from the multilayer film A1 using the STRAP-A process were indistinguishable from the corresponding virgin resins [11]. The FTIR spectra of the PE, EVOH and PET recovered with STRAP-A and STRAP-B were for the most part similar, indicating that pure polymers can be obtained using either precipitation method after selective dissolution (Figure 2.5). One of the major differences was observed in the PE spectra, where the polymer recovered through STRAP-A had extra peaks around 1736, 1240, 1097, and 1018 cm^{-1} (red spectrum in Figure 2.5(a)). These peaks were previously attributed to EVA. It was observed in the spectra of the PE recovered through STRAP-B that the EVA peaks were less prominent, confirming that through this process the EVA polymer can be separated from the PE. Further removal of the EVA from the solvent required the addition of acetone as antisolvent. The solids recovered from that additional step were characterized and the spectra confirmed mainly EVA peaks (Figure 2.6(b)). In the PET recovered from STRAP-A and B, there were low intensity peaks around 3000 cm^{-1} possibly coming from PE remnants in the PET (Figure 2.5(c)). The PET purification could be improved by changing solvent amounts and dissolution times of the other polymers. A quantitative measurement of the amount of PE present in the PET could be completed to determine if the PE is significant enough to affect the PET properties.

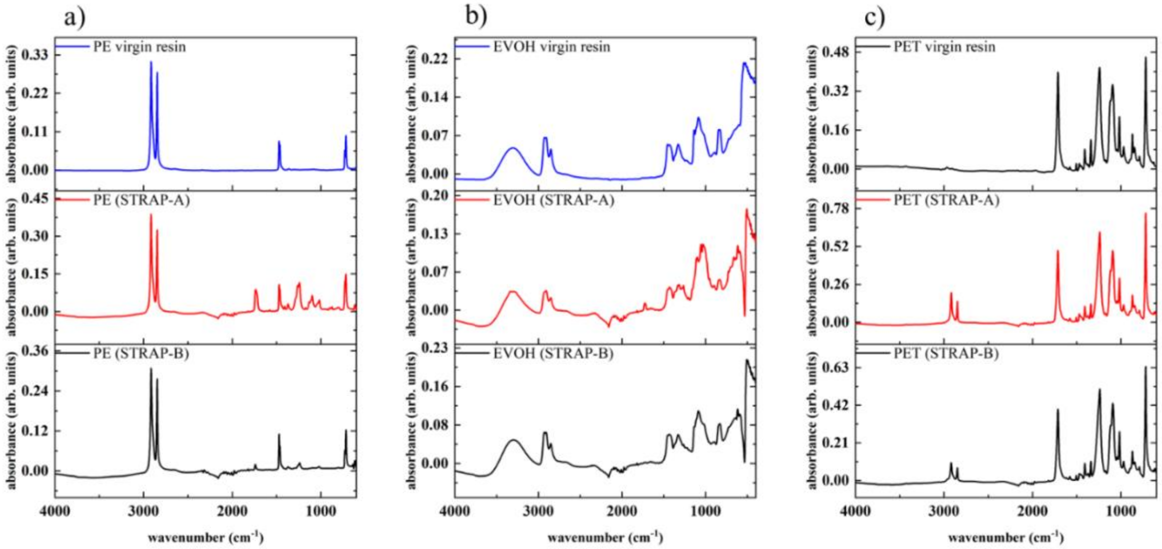

Figure 2.5 ATR-FTIR spectra of the virgin resins and polymers recovered from multilayer film A1 through STRAP-A and STRAP-B: a) PE, b) EVOH, c) PET.

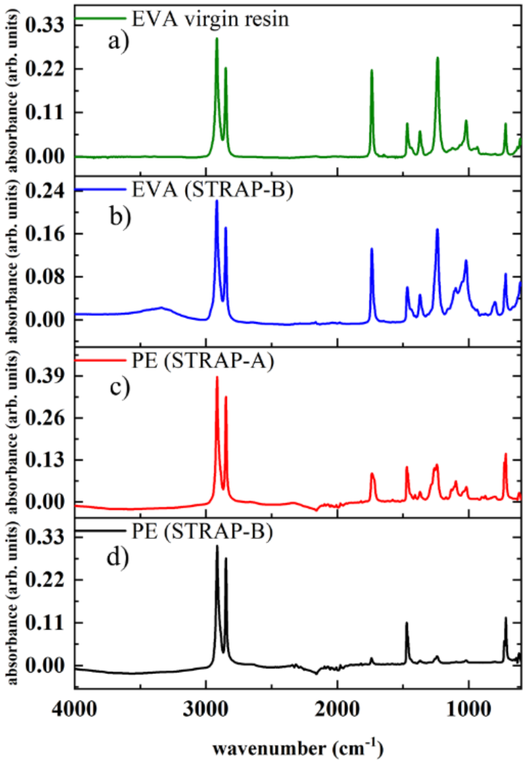

Figure 2.6 ATR-FTIR spectra: a) EVA virgin resin, b) EVA recovered through STRAP-B from multilayer film A1, c) PE recovered through STRAP-A from multilayer film A1, d) PE recovered through STRAP-B from multilayer film A1.

2.3.5 STRAP-C with multilayer film A2 and characterization of recovered solids

An A2 multilayer film, manufactured by Amcor, was used to demonstrate the STRAP process with a more complex feed composition. This film included PETG as an additional polymer component. If the same STRAP process developed for film A1 were applied to film A2, both PETG and PE would be dissolved by toluene. Therefore, we used the computational approach to identify alternative solvents capable of dissolving PETG to develop a new STRAP process (referred to as STRAP-C). We first obtained HSPs for 850 solvents and calculated each solvent's distance in HSP space (R_a) to the HSPs of PETG. Each value of R_a was then normalized by the radius of the PETG solubility sphere (R_0). Only solvents with values of R_a/R_0 less than 1 are expected to dissolve PETG. Table 2.5 includes HSP values for common, readily available solvents. Toluene, cyclohexanone, 1,4-dioxane and triethylamine are recognized as good candidates with

R_a/R_0 values less than 0.7. THF, 1,1-dichloroethane and ethyl acetate have R_a/R_0 values between 0.9 and 1, indicating probable dissolution. DMF and ethanol are identified as poor solvents with R_a/R_0 values greater than 2. However, PETG is a copolymer that is typically synthesized from terephthalic acid (TPA), ethylene glycol (EG) and 1,4-cyclohexanedimethanol (CHDM), with the ratio of EG:CHDM influencing its properties [38]. Unfortunately, available HSP values for PETG do not provide any information on its composition [26]; consequently, we also performed COSMO-RS solubility calculations, which consider both the structure and composition of this copolymer, to identify solvents capable of dissolving PETG. In this case, PETG was modeled as a random copolymer with a 2:1 molar ratio of EG:CHDM based on known information on the PETG component in film A2. Table 2.5 shows that the HSP and COSMO-RS results agree with each other for toluene, cyclohexanone, 1,4-dioxane, THF and ethanol; these solvents have large COSMO-RS predicted solubilities and low values of R_a/R_0. However, the COSMO-RS results also identify DMF as a potential good solvent. Based on these results, toluene, cyclohexanone, dioxane, DMF, and THF could all be good solvents for PETG dissolution. Toluene was eliminated as a possible solvent for PETG because it also dissolves PE. We also eliminated dioxane as a solvent due to potential health hazards and eliminated cyclohexanone because ketones can be unstable. We thus selected THF and DMF as possible solvents for further experimental investigation.

Table 2.5 COSMO-RS and HSP solubility predictions for PETG.

Solvent	COSMO-RS predicted solubility (wt%)	HSP values (R_a/R_0)	Boiling point (°C)	Temperature for COSMO-RS prediction (°C)
toluene	47.82	0.43	110.6	110
cyclohexanone	36.80	0.58	155.4	100
1,4-dioxane	35.80	0.69	101.2	100
DMF	14.41	2.17	152.8	100
THF	10.21	0.90	66	65
1,1-dichloroethane	1.43	0.96	56.3	55
1-propanol	1.02	2.42	97.2	96
triethylamine	0.19	0.66	88.8	85
ethanol	0.15	2.84	78.2	78
ethyl acetate	0.04	0.98	77.1	75

After the solvent selection for the PETG component, the STRAP-C process was applied experimentally to the A2 multilayer film. The PETG dissolution was done at 65 ℃ for 4 hours using THF, before any other polymer component. Separating the PETG entirely from the film using THF was difficult, as some polymer was left behind after the dissolution time was completed. This was not improved with different polymer/solvent ratios or a longer dissolution time. This separation inefficiency was attributed to the film strips being glued together possibly due to the presence of THF. This behavior was not observed whenever DMF was used for the PETG separation. Since DMF also dissolved the EVOH component, different THF/DMF mixtures were tested experimentally to decrease the EVOH solubility because THF is a poor solvent for EVOH (R_a/R_0 is 1.34 and the COSMO-RS predicted solubility is 1.78 wt%). A 40% THF-60% DMF (v/v) solvent mixture was determined to selectively dissolve PETG and not EVOH. This mixture was used for the actual film and the PETG yields improved from 15.28 to 20.83 wt%. 1-propanol was selected as an antisolvent to precipitate the PETG since it had a low solubility in that solvent, and it allowed for an easier solvent recycle after the recovery of PETG. Future work could consider solvent compositions to dissolve and precipitate the PETG component without the addition of an antisolvent. The STRAP-C results are presented in Table 2.6. For the remaining polymer components, which were PE, EVOH, PET, and EVA, the steps from STRAP-B were used, as shown in Figure 2.7.

Table 2.6 Yield of polymers from a multilayer film A2 with the STRAP-C process.

Experiment	Initial Film Mass (g)	Polymer yield (wt %) PETG	PE	EVOH	EVA	PET	Overall Mass Balance (%)
1	38.61	21.04%	3.74%	2.05%	0.0031%	73.11%	99.94%
2	38.53	21.00%	3.48%	1.93%	0.99%	73.25%	100.65%
3	38.66	20.44%	4.39%	1.55%	0.59%	72.39%	99.35%
Average	38.60	20.83%	3.87%	1.84%	0.79%	72.91%	99.98%
STDEV	0.07	0.34%	0.47%	0.26%	0.28%	0.46%	0.65%

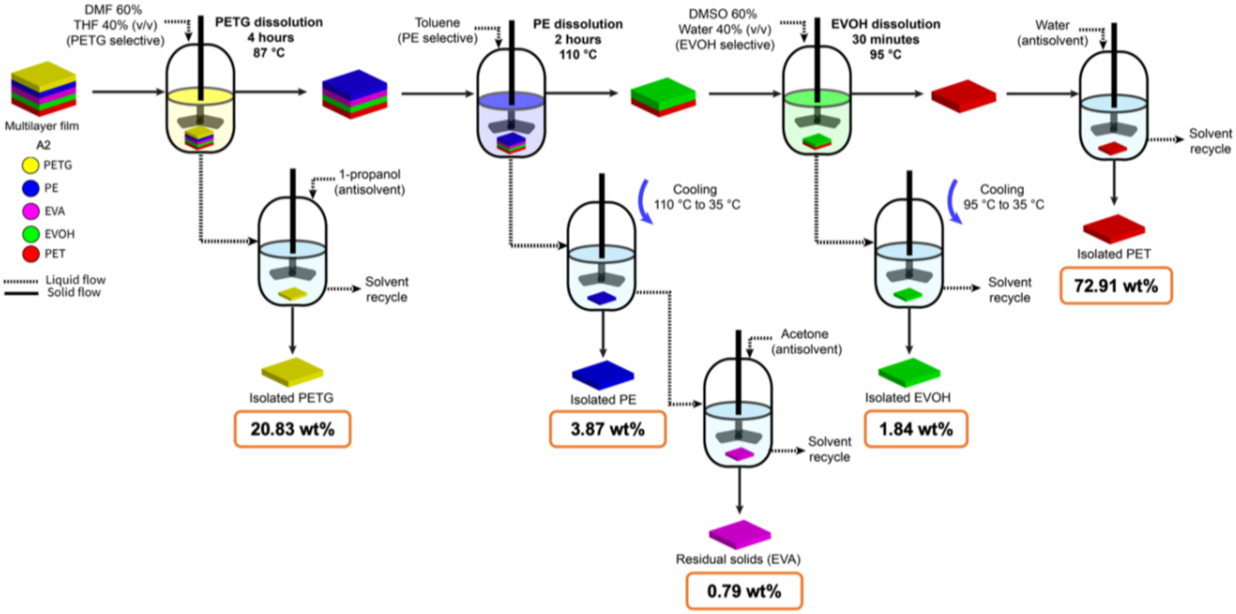

Figure 2.7 STRAP-C process schematic for the separation and recovery of the polymer components in a multilayer film A2 manufactured by Amcor.

The FTIR spectra of the PETG, EVOH, EVA and PET recovered using STRAP-C looked mostly similar to the corresponding virgin resins (Figure 2.8). Some notable differences were observed in the PE spectra, where additional peaks were present around 1740, 1370, 1240, and 1020 cm^{-1}. These could be due to PETG remnants that were not separated in the first dissolution step. A quantitative measurement would be needed to determine if the PETG amounts in the PE could affect its properties. Dissolution times and solvent amounts could be further adjusted to improve the purity of the PE and remove more of the PETG.

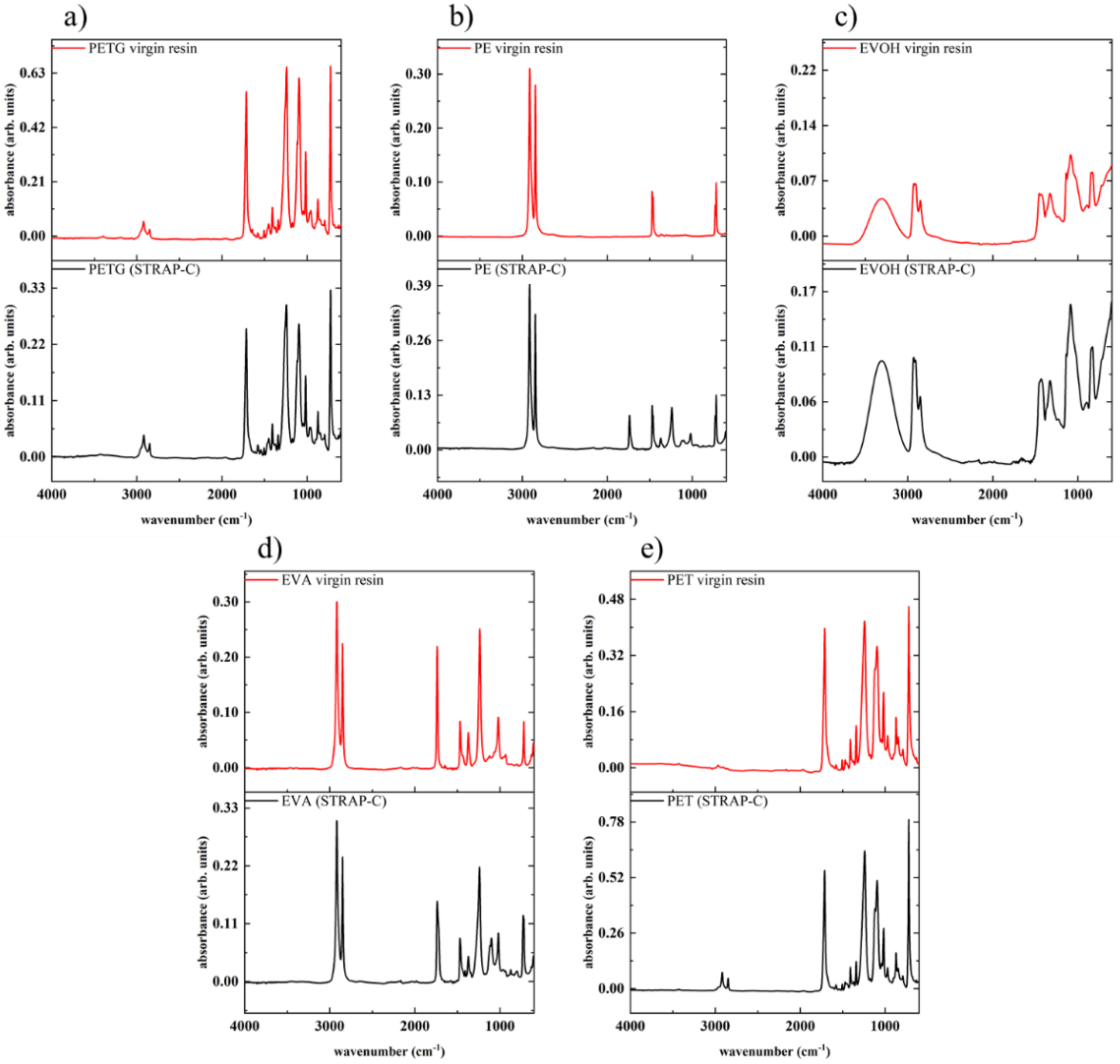

Figure 2.8 ATR-FTIR spectra of the virgin resins and polymers recovered from multilayer film A2 through STRAP-C: a) PETG, b) PE, c) EVOH, d) EVA and e) PET.

2.3.6 Technoeconomic analysis

A technoeconomic analysis (TEA) was completed to determine if it is possible to use any of the discussed STRAP processes to produce recycled polymers at a price that is comparable to the virgin resins. The minimum selling price (MSP) of the recycled resins was calculated for a process that operated continuously for 20 years with a 10% discount rate and a free input stream of the multilayer film (using a discounted cash flow analysis). We developed the STRAP process models in Aspen Plus (V11 Aspen Technology) based on our reported experimental mass balances. We estimated the size and cost of the required equipment in the three different STRAP processes with the multilayer films A1 and A2. The equipment purchase prices and variable operating costs of the distillation columns, pumps and heat exchangers were estimated using Aspen Process Economic Analyzer (V11 Aspen Technology), whereas the other equipment prices were estimated using engineering methods such as the proportional expression and the power law rules based on the cost data in our previous study [11].

We calculated the MSPs of the STRAP-A, STRAP-B, and STRAP-C processes based on the material balances and economic parameters given in Table 2.1 and Table 2.2 in the Methods Section. The total capital investment (in millions) was \$25.65 for STRAP-A, \$22.42 for STRAP-B and \$31.78 for STRAP-C. The MSPs of the STRAP-A and STRAP-B processes with the multilayer film A1 were calculated to be \$2.05 per kg and \$1.62 per kg, respectively, at a feed rate of 3,000 tonnes per year, as shown in Figure 2.9. According to our estimates, the MSP of the STRAP-B process was 21.0% lower than that of the STRAP-A process. This is because STRAP-B produced similar polymer yields to STRAP-A but without the distillation-based separation of the solvents and antisolvents. Even with the additional EVA recovery step in STRAP-B, it still has a lower MSP than STRAP-A. Furthermore, the MSP of STRAP-A is higher than that of the previous reported STRAP process [11] since the proposed STRAP processes in this paper include extruders for each of the recycled polymers. The extruder accounts for 55.22% of the total equipment purchase cost for STRAP-A.

The STRAP-C process was estimated to have a MSP of \$2.18 per kg at the feed rate of 3,000 tonnes per year with multilayer film A2. The higher MSP is explained by the fact that STRAP-C recovers an additional polymer, PETG, where DMF/THF and 1-propanol are used as the solvent/antisolvent pair and distillation steps are required to recover and recycle the solvents. In general, by selecting low-boiling solvents and minimizing the amount used, the utility cost of any required distillation columns can be decreased. As a result, even though STRAP-C requires higher capital investment, it operates at a lower variable operating cost.

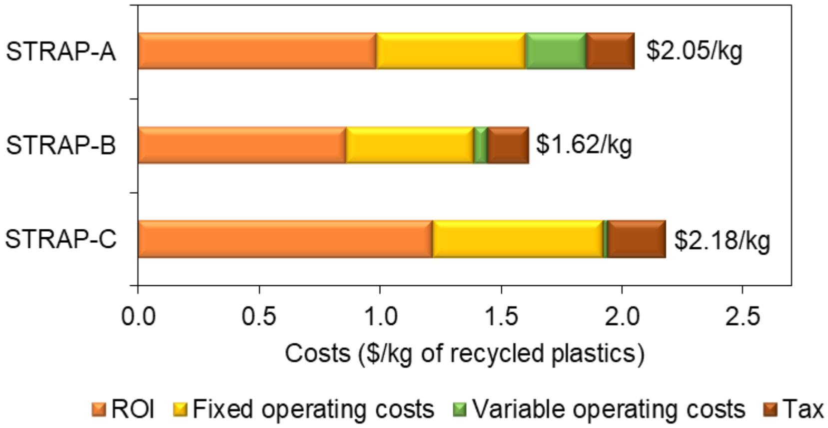

Figure 2.9 MSP and breakdown of revenue destinations for STRAP-A, STRAP-B and STRAP-C.

We also conducted a feed rate sensitivity analysis for the STRAP-B and STRAP-C processes in order to evaluate effects of economies of scale. The results, illustrated in Figure 2.10, indicate that, between 1,000 to 30,000 tonnes per year of feed, the capital investment appears to increase while the MSP begins to flatten out. The MSP of the STRAP-C process is lower than that of the STRAP-A counterpart as the feed capacity increases, especially after approximately 7,000 tonnes per year of feed [11]. This is because, at 3,000 tonnes per year, the annual capital investment of the STRAP-C process is 62.58% of the total required cost, whereas the annual capital investment accounts for 53.81% of the total required cost of the STRAP-A process. For example, at 7,000 tonnes per year of feed, the MSPs of the STRAP-A and STRAP-C processes are $1.43 per kg and $1.40 per kg, respectively. As the scale increases especially after 15,000 tones per year, the MSPs of the recycled polymers (STRAP-A:$1.07 per kg, STRAP-B: $0.78 per kg, STRAP-C:$0.95 per kg) are comparable to the average market values of the virgin resins which has been around

$0.9/kg-$1.2/kg [12, 39, 40]. These estimates show that the STRAP process could be implemented at a large scale to recover and recycle the components in different post-industrial multilayer films.

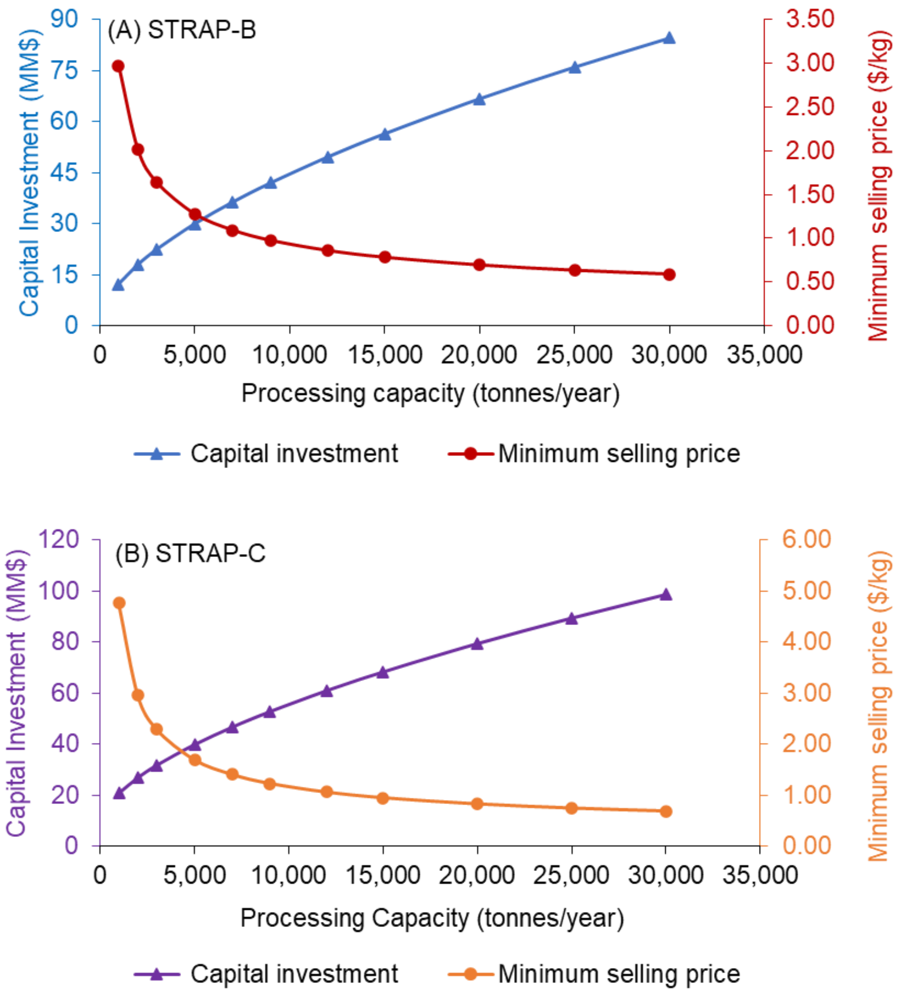

Figure 2.10 Total capital investment and MSP for (a) the STRAP-B process and (b) the STRAP-C process as a function of process feed capacity.

An economic analysis of the recycled polymers from the STRAP-C process was conducted by changing the polymer selling price from 0.8 to $3.0 per kg for three different feed capacities, as shown in Figure 2.11. As expected, the internal rate of return (IRR) of the STRAP-C process increases with increasing the selling price. At the polymer selling price of $3.0 per kg, the IRR of the STRAP-C process is estimated to be 16.63, 32.51, and 40.99% for 3,000, 9,000 and 15,000 tonnes per year, respectively. The economic feasibility of the STRAP process shows to be improved with the larger feed capacity due to the effect of economies of scale. Furthermore, to investigate the parameters which have impacts on the economics of the STRAP-C process, we conducted a sensitivity analysis by changing in ±30% of the selected parameters (Figure 2.12). The MSP of the STRAP-C is sensitive to the extruder equipment cost and the project lifetime. This is because the cost structure of the STRAP process is dominated by the capital investment. It is also observed that the solvent amounts to the polymer influences the MSP since the amount of solvents has an effect on the equipment sizes. Overall, the TEA results for STRAP-B and STRAP-C demonstrate that the STRAP process can remain economically viable as the plastic feed complexity increases. By using solvents that enable temperature-controlled dissolution and precipitation, the capital costs can be significantly reduced by decreasing the required number of separation equipment for solvent recovery.

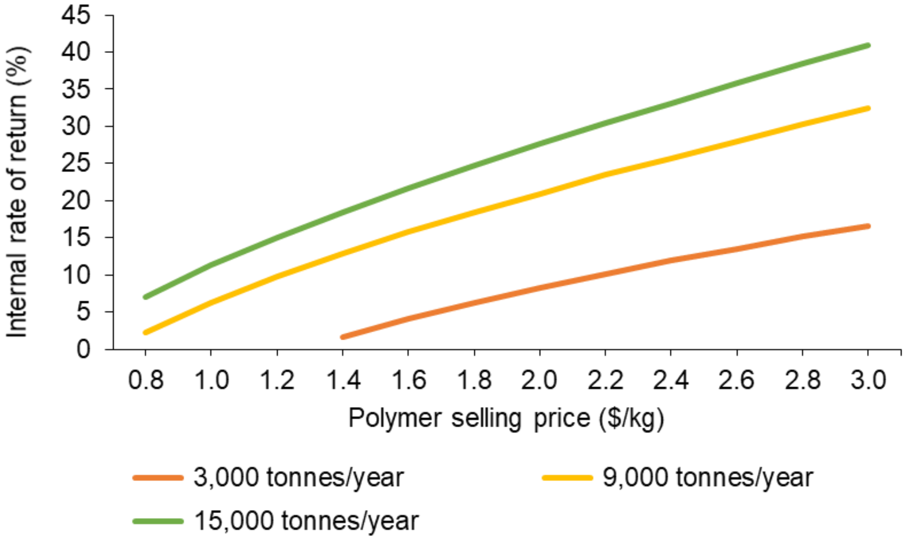

Figure 2.11 Internal rate of return for the STRAP-C process as function of polymer selling price for three different feed capacities.

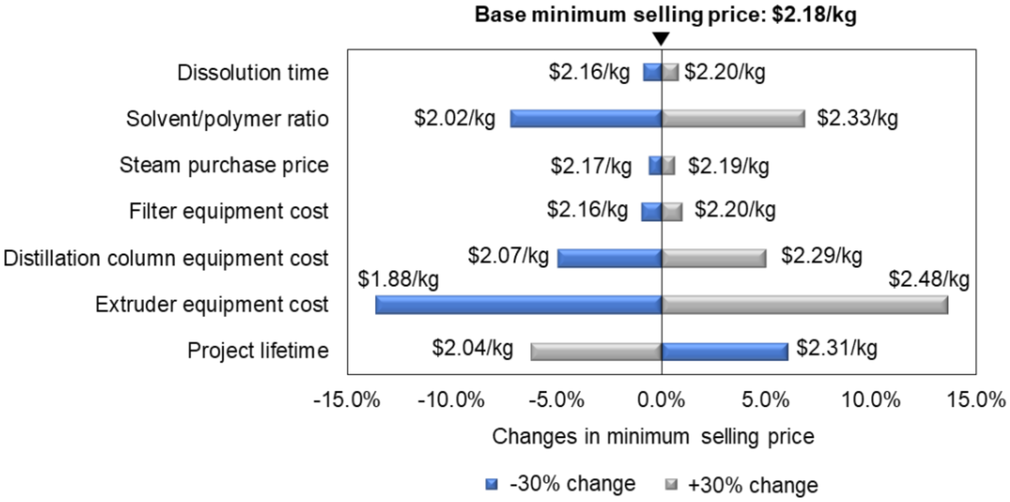

Figure 2.12 Sensitivity analysis (±30%) of the parameters fin the STRAP-C process.

2.3.7 Understanding environmental benefits of STRAP-A, B, and C

The environmental impacts of the STRAP-A, B, and C were estimated by comparing the climate change impacts of producing a multilayer film with materials recovered *via* the STRAP process against multilayer film production from virgin resins by process utilities. The impacts are expressed per functional unit: the production of 1 kg of a multilayer film. The STRAP-A and STRAP-B recover the components from multilayer film A1 and we compare their impacts in terms of CO_2 eq. emissions. Also, we compare the climate change impact of STRAP-C and the CO_2 eq. emissions related to the components of the A2 multilayer film. Figure 2.13 presents the climate change impacts of each method, considering production, transportation, and extrusion of the corresponding films.

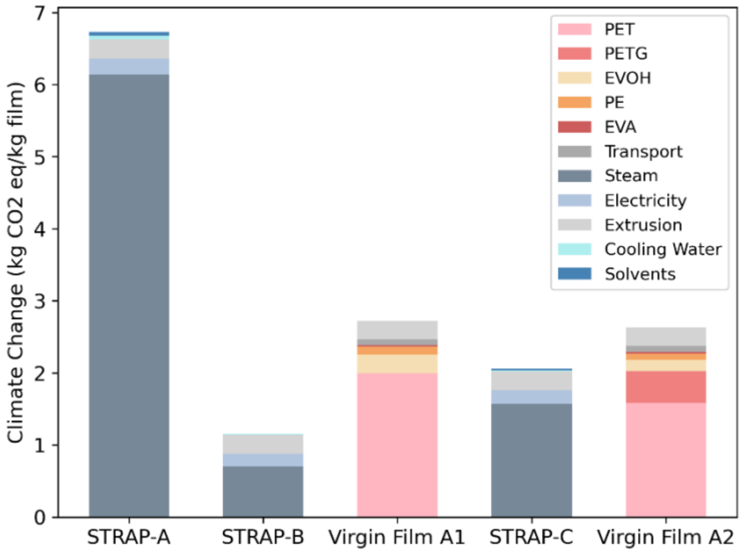

Figure 2.13 Impact on climate change with the production of 1 kg of A1 and A2 multilayer films through STRAP technology and through the production of virgin material (from virgin resins).

The STRAP-B and STRAP-C processes generate less CO_2 eq. emissions per kg of film than the virgin production of films A1 and A2. However, the STRAP-A process has a higher climate change impact, mainly due to the CO_2 eq. emissions associated with the required amount of steam used. This occurs because the precipitation method used in this approach (antisolvent addition) has high steam requirements (due to the use of distillation units). On the other hand, STRAP-B generates 54% fewer emissions than producing film A1 from virgin resins. These avoided impacts highlight the environmental benefits of the STRAP approach and the feasibility of using this process as an alternative for producing virgin-grade multilayer films. Since both STRAP-A and STRAP-B are used for film A1, we observe that the STRAP-B process is more promising to replace the production of this film from virgin resins. Regarding climate change impacts of producing film A2, we can see that the STRAP-C process had a lower GHG emission (by 18%) than the material virgin production. These environmental benefits show that STRAP-C is a suitable alternative to produce film A2 instead of producing it from virgin resins.

2.4 Conclusions

In this chapter, the STRAP technology was demonstrated to separate and recover the constituent polymers in two different rigid post-industrial multilayer plastic films manufactured by Amcor. The thermodynamic computational techniques permit initial predictions of polymer solubility in different solvents and solvent mixtures, reducing the number of experiments needed. It was previously determined that the main cost drivers in the STRAP process were the required distillation steps for the recycle of solvents and antisolvents. We show in this study that reducing the use of antisolvents and replacing them with solvents or solvent mixtures that enable a temperature-controlled polymer dissolution and precipitation is an alternative to make STRAP more economically and environmentally competitive. This was observed with our STRAP-B process which produced similar yields and was more efficient in the polymer separation than STRAP-A, while using less amounts of antisolvents. In addition to this, we have demonstrated that the STRAP process can remain economically competitive even as the plastic feed complexity increases, as was demonstrated in STRAP-C with multilayer film A2. STRAP also introduces environmental benefits when considering multilayer film production from the recovered materials instead of virgin polymers. For film A1, STRAP-B showed significant reduction in CO_2 emissions when compared to STRAP-A, since the latter relies on mixing solvents and antisolvents for polymer recovery. Solvent mixtures are of great importance in solvent-based recycling systems and tuning the solvent composition will be a valuable parameter to obtain the desired polymer yields. Further developing the computational tools to predict polymer solubilities in different solvents with varying compositions will support in implementing this approach for the recycling of multilayer plastic films. Dissolution times and solvent amounts can be further adjusted to improve the purity of some of the recovered polymers using STRAP. Quantitative measurements could be done to assess if some impurities in the recovered polymers would affect their properties. Future work will also focus on using STRAP to process multilayer films with polymers not reported in this chapter, like polyamides (PA), polystyrene (PS), polypropylene (PP) and polyvinyl chloride (PVC). Ideally, this would include finding solvents or solvent combinations that facilitate a thermally-driven dissolution and precipitation of each polymer. Moreover, we will consider the removal of additives like adhesives and inks which can also be present in plastic films. Our computational modeling framework will give us an understanding of the thermodynamic polymer-solvent properties and will allow for the design of solvent systems that can be used to efficiently separate and recover the polymer components in different multilayer plastic films.

2.5 References

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Chapter 3. Recovering plastic components from a post-industrial printed multilayer film

The contents in this chapter were adapted from the following reference:

K.L. Sánchez-Rivera, A.d.C. Munguía-López, P. Zhou, V.S. Cecon, J. Yu, K. Nelson, D. Miller, S. Grey, Z. Xu, E. Bar-Ziv, K.L. Vorst, G.W. Curtzwiler, R.C. Van Lehn, V.M. Zavala, and G.W. Huber. Recycling of a post-industrial printed multilayer plastic film containing polyurethane inks by solvent-targeted recovery and precipitation, Resources, Conservation and Recycling, 197 (2023) 107086.

3.1 Introduction

In the plastic packaging industry materials can be manufactured as monolayer or multilayer packaging articles. Typically, monolayer plastic films are used in stretch film applications and in agriculture and construction [1]. On the other hand, multilayer plastic films are composed of different polymeric or non-polymeric materials (like aluminum or paper) and these are combined to achieve desired properties for the overall packaging [2]. Typical polymers found in multilayer films include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS and high impact polystyrene, HIPS), polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), polyamides (PA) or nylons, ethylene vinyl alcohol (EVOH), ethylene-vinyl acetate (EVA) and other materials like papers, foils, inks, and additives [2, 3]. Each layer contributes unique attributes to the final properties of the film. For example, HDPE provides a moisture barrier, EVA provides sealability, polyamides provide mechanical integrity, and EVOH layers provide oxygen barrier properties [4].

Flexible packaging has benefits over other types of packaging, like less required material and energy for production than rigid containers, lighter weight for transportation, shelf-life extension of food products, visibility of contents, and the capability of providing necessary product information [4, 5]. In most cases, these materials are intended for single use and traditional recycling technologies like mechanical recycling cannot be used for their separation [4, 6]. Current recycling rates of flexible packaging have been around 1 to 2% in the United States, which has led to these being incinerated or landfilled [4, 7]. In a recent report, it was estimated that the global flexible packaging market was at 31.5 million tons in 2021 and it is expected for this market to grow annually at a rate of 3.4% to 37.5 million tons in 2026 [8]. Flexible plastic packaging has many benefits and are necessary to meet the needs of different sectors. Further technology development is required for more efficient collection, sorting, separation, and recycling of these flexible packaging materials to reduce the amount that end up in landfills or the environment, considering their expected production growth.

A method for recycling multilayer plastic films is the deconstruction of these materials via selective dissolution to separate their constituent polymers. This method has been studied by a number of researchers and it is currently being implemented by several companies [4, 9]. We have demonstrated this approach in what we call Solvent-Targeted Recovery And Precipitation (STRAP) [10, 11]. The STRAP process has been used to convert a commercially available post-industrial rigid multilayer film manufactured by Amcor into its three main polymer components with >99 wt% recovery. This multilayer film consisted primarily of polyethylene (PE), ethylene vinyl alcohol (EVOH) and polyethylene terephthalate (PET) with various tie layers that included ethylene vinyl acetate (EVA). In this process, the film is dissolved in two different solvents, each of which solubilizes an individual polymer. The final resin is then precipitated with the addition of an antisolvent or by cooling the solvent system. The solvent selection for STRAP is based on quantifying polymer-solvent thermodynamic properties using three computational methods of increasing accuracy and complexity: Hansen Solubility Parameters (HSPs), molecular dynamics (MD) simulations, and a combined quantum chemical and statistical mechanical approach called the COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS) [12]. In general terms, HSPs are used for the preliminary solvent screening for the selective dissolution of specific polymers, MD simulations provide structural information of polymer molecules in solution, and COSMO-RS enables predictions of polymer solubility as a function of both the temperature and the composition of the liquid phase [13-18].

Delamination is another approach for the recycling of multilayer plastic films. In this approach, the adhesive between polymer layers is selectively dissolved or reacted to achieve a separation of the different layers. Various media have been utilized for the delamination of multilayer plastic materials. For example, O'Rourke, et al. used glycolysis to target polyurethane (PU) adhesives for the separation of polyamide and polyolefin layers from a multilayer film [19]. In another example, Ügdüler et al. demonstrated the use of carboxylic acids for the delamination of PU adhesives in different multilayer plastic films. In that study, the authors determined that temperature and solvent to liquid ratios had significant effects on the delamination rates and fast delamination kinetics can be very beneficial in terms of potential reduction of CO_2 emissions when compared to incineration [20]. Berkane et al. studied the delamination of aluminum (Al) interlayers with and without performing microperforations to the multilayer material. They achieved the dissolution of the Al with a 10% sodium hydroxide (NaOH) solution [21]. Samorì, et al. developed a novel procedure with switchable hydrophilicity solvents to recycle multilayer materials containing PE and Al [22]. In their work, the plastic and metal components were recovered by adjusting the polarity of N,N-dimethylcyclohexylamine (DMCHA) via CO_2 addition. Other studies have been done with mixed textile waste where elastane can be recovered via selective dissolution with solvents like tetrahydrofurfuryl alcohol (THFA), gamma-valerolactone (GVL), cyrene, dimethylacetamide (DMCA), n-methylpyrrolidone (NMP) or dimethylformamide (DMF), depending on the other materials present in the waste stream [23]. Polymers recovered by the dissolution-precipitation method can be repurposed for alternative applications. For example, Cavalcante, Hardian, and Szekely recently demonstrated the dissolution of PP from disposable face masks using a green solvent, p-cymene. In their study, the recovered PP was used for the fabrication of membranes for organic solvent nanofiltration [24]. Other green solvents like α-pinene and D-limonene were demonstrated for the dissolution of polyolefins that can be used in similar membrane applications [25]. All these recent academic efforts demonstrate the interest in solvent-based recycling technologies and their potential for the recovery of various components commonly found in different plastic waste streams.

Flexible packaging films are printed to help market the product and provide product information [2]. There is significant interest in the removal of colorants from plastics since these are considered impurities that can lead to colored plastic streams which can limit applications when being recycled [26]. Color removal can be a difficult task since inks can be water-borne or solvent-borne and their compositions vary with each color and ink manufacturer. Inks can contain insoluble organic and inorganic pigments, binders, solvents, and additives like dispersing agents, stabilizers, slip agents, biocides, optical brighteners, among others [27]. These inks can be printed on polymeric substrates via different methods, one of them being reverse printing, which is a method where the printed ink is located as a trapped layer within the packaging material. This provides ink protection and avoids direct product or human contact [28, 29]. On the contrary, in surface printing, the printed ink is not buried in between layers of packaging materials and can be optionally coated with an overprint or lacquer [28]. For reverse printed films, color removal is more challenging since the ink is buried between different plastic layers.

In this chapter, STRAP was applied to a printed flexible multilayer plastic film to show the potential of this approach to recover and produce clear polymer resins. This was demonstrated with a post-industrial oriented polyester film (OPET) that comprises PE, EVOH, and PET, with polyurethane (PU) inks (Figure 3.1). A challenge with this specific plastic waste feedstock is how and at what stage of the process should the ink components be removed. Different surfactant solutions and PU-selective solvents were considered to achieve the recovery of the polymer fractions without coloration.

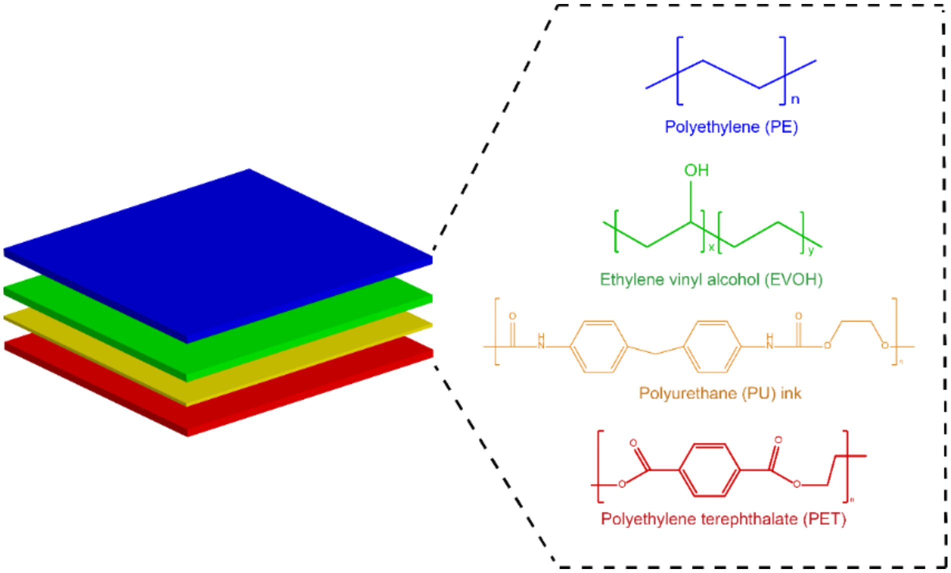

Figure 3.1 Simplified structure of an OPET multilayer printed film composed of PE, EVOH, PET, and PU-based inks, manufactured by Amcor.

3.2 Methods

3.2.1 Computational Modeling

Following our previous work, we used a combination of Hansen Solubility Parameters (HSPs) and the Conductor-like Screening Model for Real Solvents (COSMO-RS) to identify solvents for STRAP [10-12]. HSPs are three parameters associated with each compound (polymer or solvent) that account for dispersion, polar and hydrogen-bonding forces [18]. The values of these three parameters define the coordinates of a compound in HSP space. Each polymer has an additional radius parameter, R_0, that defines a sphere in HSP space, as shown in Figure 3.2(a). Only solvents with HSPs within this sphere (such that the distance in HSP space, R_a, between the polymer and solvent HSP values is less than R_0) are expected to dissolve the polymer. Tabulated, experimentally determined HSP values for polymers and solvents were obtained from literature sources [18, 30, 31]. COSMO-RS uses statistical thermodynamic methods to compute the equilibrium properties of multicomponent systems based on the screening charge density that arises at each compound's molecular surface due to the polarization of the medium [32]. Screening charge density profiles were obtained from density functional theory (DFT) calculations performed using Gaussian 16 at the BVP86/TZVP/DGA1 level of theory [33-35]. Screening charge densities were then used to predict polymer solubilities via a solid-liquid equilibrium calculation using the *COSMOtherm 19* software with the BP_TZVP_19 parameterization [12, 36, 37]. This solubility calculation requires the polymer melting temperature and an experimentally measured solubility in a reference solvent as input, which were obtained using data from our previous work [12, 38].

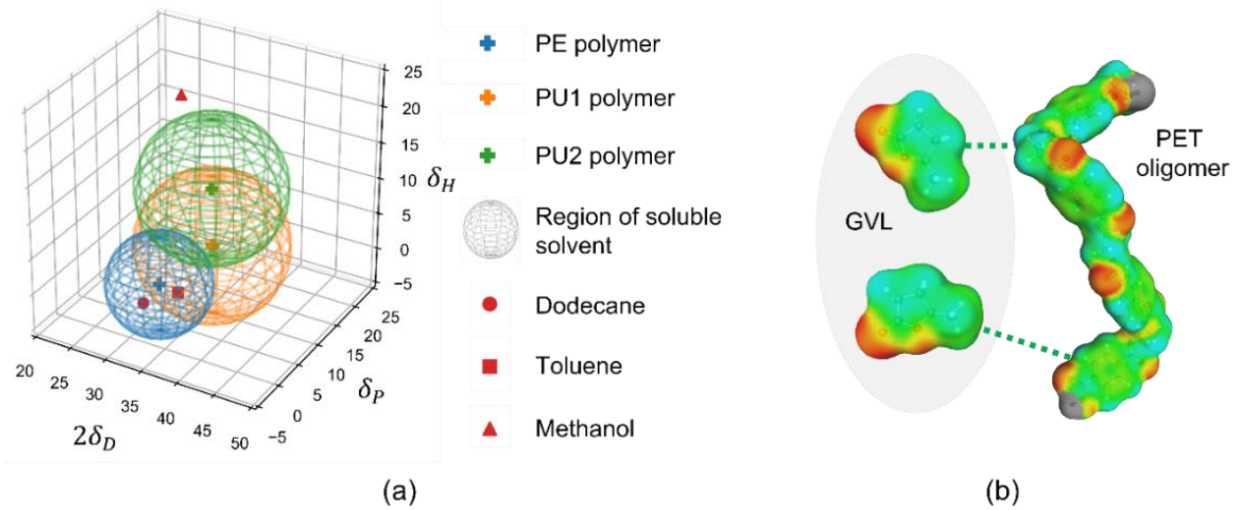

Figure 3.2 Computational methods used in this work. (a) Screening of PE-selective solvents in the presence of PU-based inks using HSPs. The HSPs for the PE polymer, two representative PU polymers, and 3 example solvents are indicated as points in HSP space, with t the soluble regions for each polymer drawn as spheres centered on the corresponding polymer HSPs. Dodecane lies within the PE sphere but outside of the PU spheres and is thus predicted to be a selective solvent for PE. (b) COSMO-RS screening charge distributions (colored surfaces) of GVL and a PET oligomer. Oligomer molecules with end groups neglected (gray surface) are used to represent the chemical properties of longer polymer chains. The intermolecular interactions between polymers and solvents are quantified by the interaction of screening charges, as schematically indicated by dashed lines.

3.2.2 Experimental procedure

A 250 mL round bottom flask connected to a reflux condenser with a cold-water supply line was used for the STRAP experiments. The round bottom flask, which would contain the corresponding solvent and shredded multilayer film with a ratio of 10:1 (by mass), was partially submerged in a 1500 mL dish containing silicone oil as a heat transfer fluid. The system was heated to the desired dissolution temperature with an electric heat plate equipped with a magnetic stir drive and the stirring rate was adjusted to have constant mixing. Based on the computational analysis for solvent selection, we experimentally assessed the recovery of each polymer in the printed multilayer film by performing three processing steps: (1) selectively dissolving the PE fraction in dodecane at 95°C for 30 minutes, then separating the solubilized fraction from the EVOH and PET via mechanical filtration; (2) selectively dissolving the EVOH fraction in a 60% DMSO-40% water (v/v) mixture at 95°C for 60 minutes, then separating the solubilized fraction from the remaining PET and ink via mechanical filtration; and (3) removing ink from PET using GVL at 125°C for 60 minutes. The PE and EVOH fractions were precipitated by reducing the respective solvent temperatures to 35 °C and then the solvents were separated via filtration. Similarly, the PET was separated from the GVL and ink via mechanical filtration. The resulting PE and EVOH solid fractions were dried in a vacuum oven for 3 hours at 100°C and -1 bar to remove residual solvents. The PET fraction was dried for 3 hours at 150°C and -1 bar. Sequential PE-dissolution steps were required to recover most of the polymer and clean out the experimental system. For the deinking step, color removal improved with sequential steps under the same conditions, longer deinking times, and/or higher temperatures.

3.2.3 Characterization of recovered polymers

Samples obtained from STRAP were analyzed with ATR-FTIR (Bruker Vertex 70) to verify polymer purity. PE samples were analyzed with high-temperature GPC (Malvern Viscotek 350 HT-GPC) to obtain molecular weight information. Thermal properties of the samples were analyzed with DSC (TA Instruments Q2000 differential scanning calorimeter) and TGA (TA Instruments Q5000IR thermogravimetric analyzer). Final color of the recovered polymers was quantified with a spectrophotometer and measurements were converted to CIELAB color space values, L* (lightness), a* (red-green color component) and b* (blue-yellow color component), and YI (yellowness index) [39].

3.2.4 Technoeconomic analysis (TEA) and life cycle assessment (LCA)

The process design and TEA were performed in the open-source platform BioSTEAM [40]. This Python-based process simulator has been validated against proprietary software (SuperPro Designer and Aspen Plus). The collected experimental data was used to simulate the STRAP process in BioSTEAM. Here, mass and energy balances are used to determine the sizing and the energy required by the different process units (e.g., heat exchangers and distillation). The economic parameters considered for the analysis are presented in Table 3.1.

Table 3.1 General parameters for the technoeconomic analysis [41, 42].

Parameter	Value
Lifetime (years)	20
Interest rate (%)	10
Income tax rate (%)	25
Depreciation method	MACRS
Plant operability per year (hours)	8,000
Lang factor	3.63
ISBL costs	Lang Factor multiplied by the equipment purchase cost
Chemical Engineering Plant Cost Index	776.9

The impact of the STRAP process with the printed multilayer film on climate change (kg CO_2 eq) was evaluated using a life cycle assessment (LCA) methodology. The STRAP process was analyzed from a product perspective [43]. From this perspective, the STRAP technology is seen as an alternative process to produce virgin-grade multilayer films. The functional unit considered is the production of 1 kg of multilayer film. Thus, we compare the impacts of producing 1 kg of film from traditional pathways with producing 1 kg of film through the STRAP process. The LCA was performed using the open-source software openLCA v1.10.3 [44]. The solvent impacts were taken from the Ecoinvent 3.6 cut-off by classification database [45] using the Environmental Footprint impact assessment method [46]. The rest of the impacts were taken from the Environmental Footprint database [47].

3.3 Results

3.3.1 Ink removal from the printed multilayer film

Non-ionic, cationic, and anionic surfactant solutions have been used for efficient ink removal from plastic substrates [48, 49]. One common cationic surfactant is hexadecyltrimethylammonium bromide (CTAB) and solutions of this surfactant were prepared at different concentrations (0.1-10 wt%) for deinking of the printed multilayer film at different temperatures and pH. The solutions were above the critical micelle concentration (CMC) of CTAB, which is 0.0009 M in water [50]. The printed multilayer film had yellow, white, and black as the main colors, with traces of blue and red. The deinking step with CTAB was incorporated at the beginning of the STRAP experiments to target all colors, however, no ink removal was visible at various temperatures (25-65°C), mixing rates (100-400 RPM), and pH (8 and 13) for the tested CTAB solutions in water. A pressurized system was also used to conduct the deinking with CTAB at 175°C but no significant ink removal was observed. We believed this could be due to the surfactant not contacting the ink components in the multilayer plastic film structure since the film was manufactured using the reverse printing technique. Ink removal using surfactants consists of four steps: (1) absorption of surfactant on plastic surfaces, (2) solubilization of the ink binder in surfactant micelles, (3) release of ink particles from the surface, and (4) stabilization of the ink particles [51, 52]. Deinking may not occur if there is no contact between the surfactant and the printed surface, as it was observed with the tested printed multilayer film. For example, researchers at the Universidad de Alicante developed a technology in which the ink removal includes a step where the plastics are punctured. This was done for the deinking agent to reach the interlayer ink components [53]. The deinking step was also evaluated with CTAB after the first and second polymer dissolution steps but still no efficient ink removal was observed. A recently published study on different deinking treatments for printed plastics reported that CTAB solutions were not optimal for removing PU-based inks on monolayer plastic films, and high deinking efficiency of PU resin was observed with N,N-dimethylcyclohexylamine (DMCHA) or formic acid [54]. This gives further indication that CTAB solutions are not optimal for removing inks containing PU resins and other media need to be considered, along with potentially puncturing the plastics for deinking. In our study, since the selected CTAB surfactant solutions did not achieve any significant deinking, PU-selective solvents that could target the ink components were screened, using our computational modeling tools. After a deinking step, it would be preferred to have a physical ink/plastic separation so that both can be easily isolated. Dissolution-based ink separation could be more energy costly since the medium would have to be purified if a physical separation cannot be achieved, as it would be with some organic solvents. The selectivity for the polymer components in the film over PU was considered, building upon our experience with transparent multilayer plastic films.

3.3.2 Computational modeling results

In Chapter 2, we successfully recovered the main constituent polymers (PE, EVOH, and PET) from a transparent multilayer film through a STRAP process in which PE was first dissolved by toluene, EVOH was dissolved by a DMSO/water mixture, and PET was recovered as the only remaining resin [11]. The printed film considered in this work consists of the same three polymers with an additional PU-based ink. Therefore, we sought to modify the prior STRAP process by using computational tools to identify new solvents that remain selective to the target polymers in the presence of the ink, as no ink removal was observed with different surfactant solutions.

The first step is to find a selective solvent for the PE component of the printed film. Since the specific molecular structure of the PU-based ink is unknown, we cannot directly predict ink solubility with molecular-scale modeling. We first conducted quantitative solubility predictions using COSMO-RS for the three known polymers to identify potential selective solvents, then used qualitative HSP calculations to eliminate solvents likely to dissolve the PU-based ink. Table 3.2 shows the predicted solubilities for PE, EVOH, and PET in 30 common solvents at elevated temperatures. We define PE-selective solvents as solvents with a predicted PE solubility greater than 10 wt% and predicted EVOH and PET solubilities that are each less than 5 wt%. The solubility values are defined as the mass of polymer than can be dissolved in a known amount of solvent at a given temperature (g polymer/g solution). Four PE-selective solvents were identified: toluene, dodecane, heptane, and diphenyl ether.

Table 3.2 COSMO-RS solubility predictions for PE, EVOH and PET in 30 common solvents.

Solvent	T (°C)	EVOH solubility (wt%)	PE solubility (wt%)	PET solubility (wt%)
methanol	63.6	0.8	0.1	0.0
dichloromethane	39.0	0.0	0.1	0.8
ethylene glycol	120.0	10.6	0.9	0.0
acetone	55.0	0.2	0.3	0.7
isopropanol	81.3	1.4	1.6	0.0
1-propanol	96.2	4.1	4.2	0.1
toluene	109.6	0.3	22.6	2.5

chloroform	60.1	0.0	0.6	1.0
tetrahydrofuran	64.0	0.9	1.7	0.8
tetrahydropyran	87.0	1.1	7.3	0.8
cyclohexane	79.7	0.0	6.9	0.0
heptane	97.5	0.0	15.3	0.0
triethylamine	88.0	7.7	8.7	0.0
1,2-propanediol	120.0	12.4	3.2	0.0
dimethyl sulfoxide	120.0	35.3	5.3	8.3
hexane	67.7	0.0	3.1	0.0
acetylacetone	120.0	6.6	8.2	2.0
tert-butanol	81.4	0.9	2.1	0.0
ethyl acetate	76.1	0.3	1.6	0.5
isopropylamine	30.7	11.7	0.1	0.0
diphenyl ether	120.0	0.4	18.5	1.4
dodecane	120.0	0.0	32.5	0.0
N,N-dimethylformamide	120.0	30.8	16.2	18.4
2,3-dihydropyran	85.0	0.1	5.0	0.7
methylacetate	55.8	0.1	0.3	0.2
ethanol	77.2	1.8	0.9	0.0
cyclohexanol	120.0	7.7	22.1	0.3
2-butanone	78.5	0.8	2.3	1.4
water	99.0	0.0	0.0	0.0
benzene	79.0	0.0	3.1	0.9

Since information on the ink structure is limited, we collected HSP data for 11 different PU resins to determine the potential of these four solvents to dissolve the ink. Table 3.3 presents HSP data for these PU resins and the 4 solvents studied and Table 3.4 reports calculated values of R_a/R_0. Based on these data, toluene is predicted to dissolve ($R_a/R_0 < 1$) 4 of the 11 PU resins and diphenyl ether is predicted to dissolve 7, whereas dodecane and heptane are not predicted to dissolve any of the PU resins. Therefore, dodecane and heptane are possible computationally identified PE-selective solvents for the printed film. Dodecane was finally selected for experiments since it has a higher predicted PE solubility than heptane. The selectivity of this solvent was verified experimentally.

Table 3.3 HSP data for some solvents, PET, and 11 PU polymers [18, 30].

Compound	Dispersion	Polarity	Hydrogen bonding	R_0
toluene	18	1.4	2	\
dodecane	16	0	0	\
heptane	15.3	0	0	\
diphenyl ether	19.6	3.2	5.8	\
60% DMSO-	16.3	16.1	33.5	\

40% water (v/v)				
GVL	15.5	4.7	6.6	\
PET polymer	18.7	6.3	6.7	6.5
	18.1	9.3	4.5	9.7
	17.9	6.9	3.7	2.7
	17.7	10.6	11.6	9.5
	19.1	12.2	9.9	8
	21.54	14.94	12.28	16.78
PU polymers	16	13.1	9.2	11.4
	20.6	7.8	11.6	13.1
	19.4	7.4	6	9.8
	17.9	9.6	5.9	8.2
	18.7	9.6	9.9	8.2
	19.9	8.1	6	9.8

Table 3.4 HSP calculations for some solvents and 11 PU resins.

Solvent	toluene	dodecane	heptane	diphenyl ether	DMSO/water mixture
R_a/R_0 for 11 PU	0.85	1.15	1.21	0.71	3.09
	2.13	3.22	3.48	2.02	11.60
	1.40	1.69	1.73	1.07	2.39
	1.70	2.11	2.18	1.24	3.07
	1.10	1.33	1.37	0.83	1.41
	1.26	1.40	1.41	1.11	2.14
	0.97	1.28	1.34	0.59	1.90
	0.79	1.19	1.28	0.43	3.01
	1.11	1.45	1.51	0.88	3.47
	1.40	1.81	1.88	0.95	3.04
	0.89	1.30	1.39	0.50	3.01

The second step is to find an EVOH-selective solvent after PE dissolution. In our previous STRAP process, we used a mixture of 60 % DMSO-40 % water (v/v) to selectively dissolve EVOH but not PET [11]. We thus considered whether the ink would dissolve in this solvent system. HSP calculations were again performed for this solvent mixture and the 11 PU resins with results shown in Table 3.4. None of the 11 PU polymers are expected to dissolve in this solvent mixture. Therefore, the same 60 % DMSO-40 % water (v/v) solvent system was used in experiments and selective EVOH dissolution was observed.

The final step is to remove the PU-based ink from the remaining PET resin after PE and EVOH separation. We performed HSP calculations to identify solvents that could dissolve PU but not PET. Since the HSP data for the different PU resins varied substantially, we identified potential PU-selective solvents that are predicted to dissolve at least 5 of the 11 PU resins without dissolving PET. Table 3.5 shows HSP calculations for solvents that fit these criteria. Among these solvents, we noted gamma-Valerolactone (GVL) as an appealing, bioderived and biodegradable green solvent with low toxicity [55]. The R_a/R_0 value of GVL to PET (1.02) is very close to 1, which indicates that it may dissolve PET at elevated temperatures. We thus computed temperature-dependent PET solubilities in GVL using COSMO-RS, as shown in Figure 3.3. Using a 5 wt% solubility threshold to distinguish good and poor solvents, we predict that the temperature should be below 125°C to avoid substantial dissolution of PET in GVL. Experiments have verified that PET can dissolve in GVL above 165°C but not at 125°C, which aligns with our computational predictions.

Table 3.5 HSP calculations for solvents considered for ink removal from PET.

Solvent	R_a/R_0 to PET	R_a/R_0 to 11 PU										
acetone	1.17	0.61	2.52	0.67	1.00	0.83	0.32	0.88	0.86	0.61	0.86	0.93
DMSO	1.65	0.94	4.28	0.65	0.55	0.40	0.52	0.75	1.03	0.99	0.83	1.00
DMF	1.40	0.85	3.80	0.33	0.50	0.50	0.31	0.66	0.93	0.84	0.62	0.94
cyclohexanol	1.17	1.08	3.79	0.72	1.19	0.82	0.91	0.58	0.93	1.15	0.86	1.01
GVL	1.02	0.75	2.23	0.94	1.36	1.00	0.78	0.90	0.84	0.84	1.06	0.96

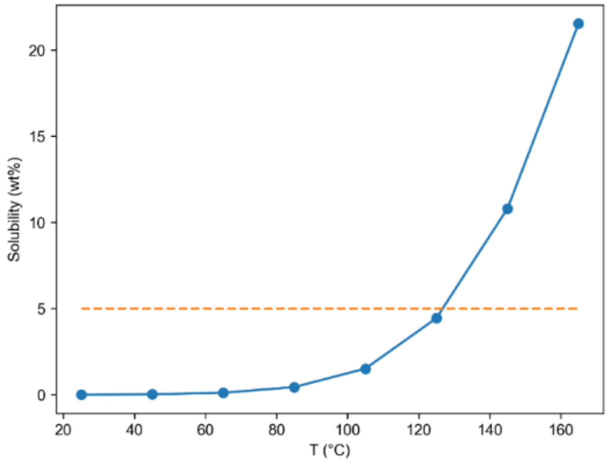

Figure 3.3 Temperature-dependent solubility prediction of PET in GVL. Dashed line is the dividing value to distinguish between a good solvent and a poor solvent (5 wt%).

3.3.3 Experimental demonstration of STRAP with the printed film

The flexible printed multilayer film composed of PE, EVOH, PET, and PU-based inks was processed through STRAP to recover all polymer components. Figure 3.4(a) shows solvents, temperatures, dissolution times, and polymer yields for each step. In our approach, the PE and EVOH are dissolved and recovered, leaving the PET and ink components behind. After this, the ink is removed from the PET component using GVL. Polymer precipitation was achieved by reducing the temperature of the respective solvents and not by the addition of antisolvents. In our previous work, this was demonstrated to be beneficial both economically and environmentally [11]. By visual inspection, the final recovered polymers after STRAP exhibited little to no coloration (Figure 3.4(b)). Due to the high percentage of PE in the printed film, an additional PE dissolution step was required to recover most of the polymer and clean out the experimental setup. This additional PE dissolution step was done in every experiment for this analysis, which allowed for an average PE yield of 61.78 ± 1.74 wt%. The average overall mass balance from the STRAP experiments was 88.66 ± 0.53 wt%. We found that the material that was not recovered after STRAP was left behind in our equipment, mostly in the round bottom flasks and filters. The overall mass balance improved when accounting for the material lost in the equipment which was around 8 wt% of the plastic feed. Furthermore, part of the ink (mostly yellow color) can be recovered via distillation of the GVL, around 3 wt% (Table 3.6). The overall mass balance can be >95 wt% of the starting material, considering the average recovery of PE, EVOH, and PET. This gives indication that when dealing with flexible plastics that have been shredded, material will be left behind in the equipment which should be considered when thinking about larger scale systems. Furthermore, it was challenging for us to predict and measure consistent amounts of material lost in the equipment since it depends on multiple factors like plastic size, stirring rates, and it is subject to how the material is handled by the person conducting the batch experiment.

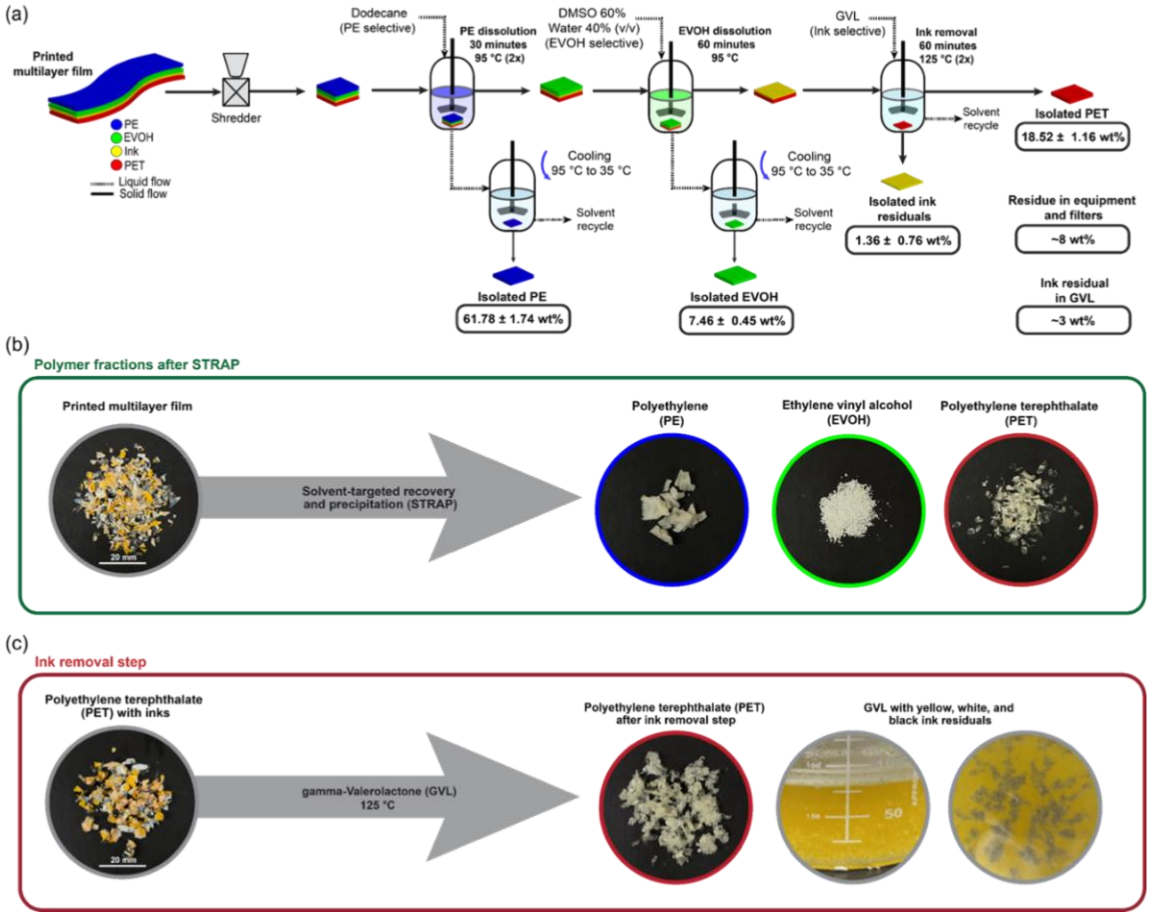

Figure 3.4 (a) Solvent-targeted recovery and precipitation (STRAP) of a printed multilayer film composed of PE, EVOH, PET, and PU-based inks, (b) Photos of each polymer after the STRAP process, (c) STRAP deinking step with gamma-Valerolactone (GVL) to separate white, black, and yellow ink from PET of a printed multilayer film.

Table 3.6 Amounts of the polymers and residues collected from equipment used in STRAP.

Initial Film Mass (g)	Component Yield (wt%)						Overall Mass Balance (%)
	PE	EVOH	PET	Black and White Ink Residue	Residue in Filters and Equipment	Yellow Ink Residue	
3.0006	57.47	9.31	17.3	1.76	7.86	3.14	96.82

The main colors in the PU inks were yellow, white, and black. PUs are commonly used as adhesives in multilayer packaging materials and as binders in printing inks for plastic substrates [27, 56]. The ink separation step uses GVL, which is a PU and PET-selective solvent, as it was determined by our computational predictions. The PET was not dissolved in the ink removal step since the temperature was 125°C and PET has a measured experimental solubility of 0.025 wt% at this temperature. Under these conditions, deinking was observed for all colors (Figure 3.4(c)). White and black ink components were dispersed in the GVL after the deinking time was completed, while the yellow component was dissolved. Deinking of the PET improved by modifying one of the following: adding another deinking step with new GVL under the same conditions, increasing the deinking time up to 2 hours, or increasing the GVL temperature to 135 °C. The final color of each polymer was quantified with CIELAB measurements, and all color values are presented in Table 3.7. The PE and EVOH had comparable L* values (lightness) to the corresponding virgin resins and did not have significant a* (red-green component) and b* values (blue-yellow component). The recovered PET samples had reduced L* values and higher b* values when compared to virgin PET. Out of the PET deinking conditions tested in Table 3.7, two sequential steps (or extractions) with GVL provided the lowest b* value. Extending the deinking time or incorporating additional sequential washes with GVL could further remove more of the yellow color from the PET. According to a recent study, PET swelling with GVL occurs at 120 °C [57] which could play a role in the release of white and black ink components since dissolution of those colors was not observed. The white and black pigment residues were recovered by filtration and the dissolved yellow ink residues were recovered by distillation of the GVL. In ink formulations, inorganic and/or organic pigments are used. For example, in white ink, titanium dioxide (TiO_2) pigment is commonly used. Researchers have disclosed the use of o-dichlorobenzene and o-xylene to remove TiO_2 from PE, but they were only able to remove 15% of the colorant [58]. Some of the solvents that have been used to target colors and pigments have been organic solvents and some have been chlorinated compounds, which raises concerns about toxicity, safe handling, and environmental impact [59, 60]. In this study, we demonstrated the use of a green solvent, GVL, to clean PET from black, white, and yellow PU-based ink; this by using a combination of dissolution and ink dispersion in the solvent.

Table 3.7 Color values for virgin resins and polymers recovered from a printed multilayer film by STRAP.

Name	Sample	L*	a*	b*	YI
LLDPE	1	93.98	1.66	-5.66	-9.51
	2	93.77	1.63	-5.56	-9.37
	3	93.81	1.71	-5.57	-9.32
EVOH	1	94.01	1.75	-5.81	-9.73
	2	93.77	1.78	-5.60	-9.33
	3	93.98	1.87	-5.86	-9.73
PET	1	93.87	1.79	-5.79	-9.68
	2	94.03	1.84	-5.79	-9.63
	3	93.52	1.73	-5.18	-8.59
STRAP PE	1	91.27	-0.10	-0.05	-0.17
	2	91.28	-0.29	0.45	0.65
	3	91.42	-0.39	0.61	0.88
STRAP EVOH	1	93.60	-0.52	-0.52	-1.40
	2	93.50	-0.53	-0.53	-1.42
	3	93.65	-0.26	-1.05	-2.20
STRAP PET1 (125 °C 1 hour)	1	68.19	-2.09	21.68	54.68
	2	70.02	-2.43	22.78	55.71
	3	70.01	-1.94	20.37	50.06
STRAP PET2 (135 °C 1 hour)	1	76.59	-1.42	17.04	38.47
	2	71.69	-0.99	19.38	47.37
	3	73.82	-1.80	19.97	46.65
STRAP PET3 (125 °C 2 hour)	1	73.43	-1.17	17.82	42.26
	2	74.84	-1.84	16.58	37.89
	3	74.29	-1.55	17.04	39.53
STRAP PET4 (125 °C 3 hour)	1	69.96	-0.53	18.41	46.52
	2	76.03	-1.03	15.12	34.61
	3	71.55	-0.60	15.66	38.54

STRAP PET5 (two extractions at 125 °C 1 hour)	1	76.90	-0.36	12.94	29.78
	2	75.89	-0.12	13.42	31.52
	3	77.14	-0.08	13.80	31.93

L* ≡ lightness value; black = 0; white = 100
a* ≡ red-green color value; a* > 0 is redder; a* < 0 is greener
b* ≡ yellow-blue color value; b* > 0 yellower; b* < 0 is bluer
YI ≡ Yellowness Index

3.3.4 Effect of plastic size on dissolution time

Previous STRAP experiments with transparent multilayer films were initially demonstrated with film sizes of 1x1 cm and this necessitated extensive dissolution times to recover the target polymers. We investigated the effects of film sizes over the dissolution time of the PE component in the printed multilayer film. This was tested in the PE-dissolution step using dodecane at 95°C and 500 RPM. Initial steps with a dissolution time of 30 minutes yielded 61.78 ± 1.74 wt% of PE when the film sizes were > 3 mm. This yield was calculated from the amount of extracted PE over the amount of plastic feed in a single experiment. Additional size reduction of the printed multilayer films to 3 mm and 1 mm showed improvement in the PE dissolution time. As seen in Figure 3.5, at a total PE dissolution time of 8 minutes, the PE recovery improves by reducing the size of the films to 3 mm. From 3 mm to 1 mm, a slight improvement in the PE yield was observed. The 8 minutes of dissolution time was divided in two steps, a 5-minute step and a 3-minute step. As explained in the experimental demonstration section, two steps were carried out to recover most of the dissolved PE due to its high concentration in the film, and this helped with cleaning out the experimental setup. From the above results, we concluded that by downsizing the plastic material to the proper size (1-3 mm) and having vigorous mixing and the required dissolution temperature, we were able to extract most of the PE with dodecane. In dissolution-based plastic recycling technologies, plastic sizes become important whenever short dissolution times are of interest.

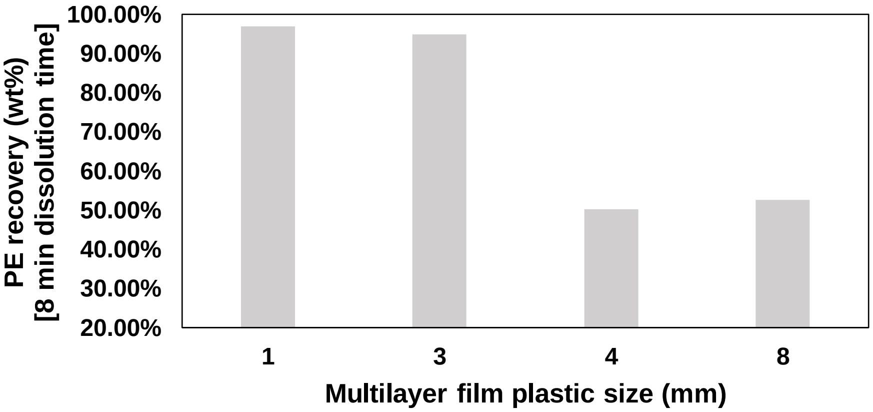

Figure 3.5 Polyethylene (PE) recovery after 8 minutes of dissolution time with different plastic sizes. The recovery is based on the maximum PE yield obtained experimentally after 30-minute steps, around 61.78 wt%.

3.3.5 Characterization of polymers recovered by STRAP from the printed multilayer film

In the STRAP process with the printed multilayer film, the polymers can be recovered, and the ink components can be efficiently removed. In Figure 3.6(a), the IR spectra of the PE STRAP and PE virgin resin are compared, displaying identical spectral bands with no trace of any other bands belonging to other resins, indicative to the purity of the extracted PE. Figure 3.6(b) and 3.6(c) show similar characteristics for EVOH and PET, respectively.

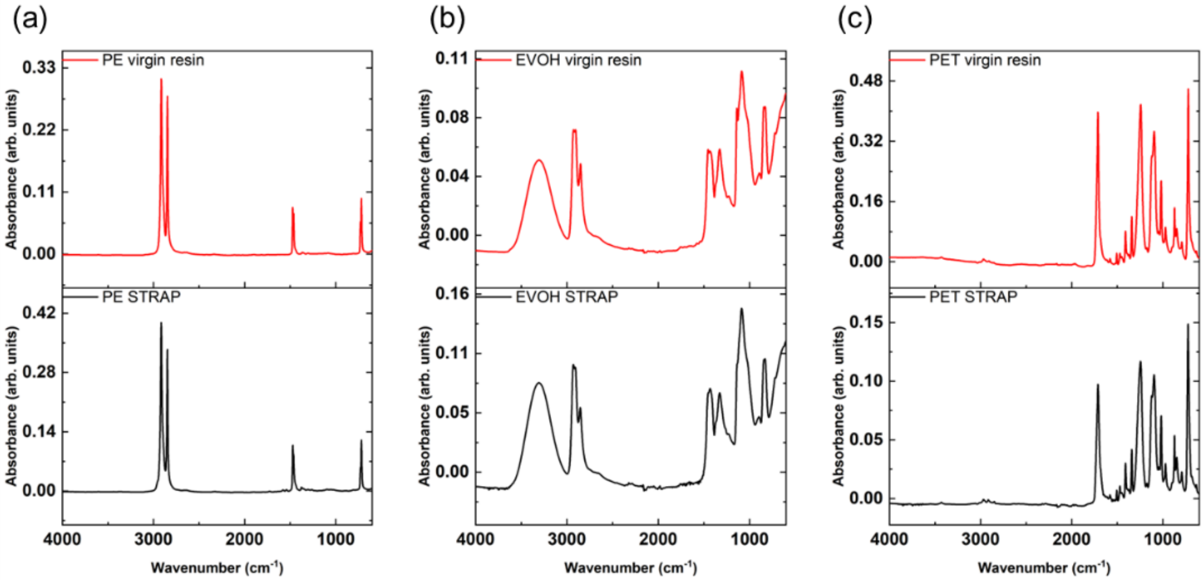

Figure 3.6 ATR-FTIR spectra of virgin resins and polymers recovered by STRAP from the printed multilayer: a) PE, b) EVOH, and c) PET.

The molecular weight values of the recovered PE from the printed multilayer film by STRAP were determined with high-temperature gel permeation chromatography (HT-GPC). As seen in Figure 3.7, the number-average molecular weight (M_n), weight-average molecular weight (M_w), and dispersity (D) of the STRAP PE were within values of virgin LDPE and LLDPE resins. The printed film itself was manufactured with both LDPE and LLDPE, and the produced PE from STRAP had molecular weight values that were within the range of the pure resins. This gives evidence that the molecular weight of the PE is not significantly affected after being treated with dodecane in the STRAP process.

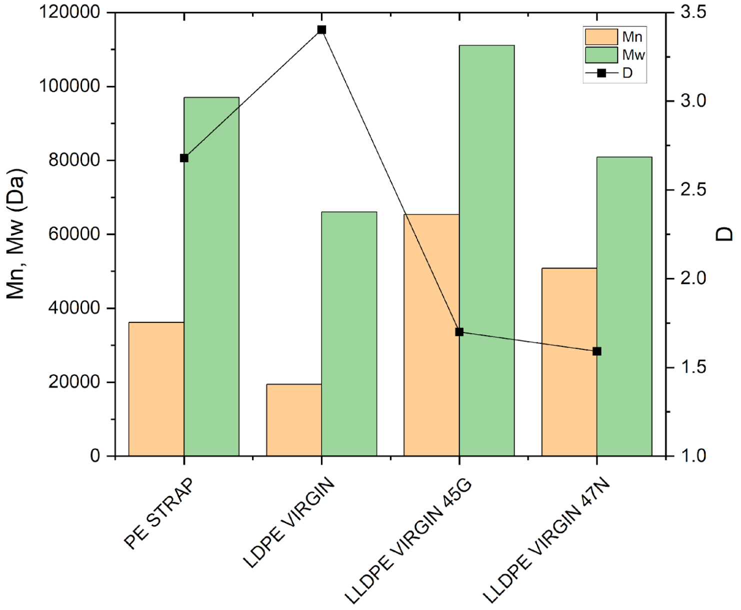

Figure 3.7 Comparison of the number-average molecular weight (Mn), weight-average molecular weight (Mw), and dispersity (D) of PE recovered from a multilayer printed film by STRAP and different PE virgin resins.

The recovered PE, EVOH, and PET for the most part had similar thermal properties to the corresponding pure virgin resins used in the starting material. For example, as seen in Table 3.8, the melt temperature ($T_{m,2}$) of the recovered polymers from the printed film by STRAP were comparable to the virgin resins. Similar results were obtained by Cecon, Curtzwiler and Vorst [61] for the PE resins recovered using STRAP, with the thermal properties within the ranges displayed by the virgin HDPE and LLDPE resins used in a rigid transparent multilayer film. However, differences were observed in some parameters of the PET STRAP samples, possibly due to residual polymers or ink components. This could be addressed by carrying out additional ink removal steps to ensure PET is free of any contaminants. After STRAP, decreases in the crystallinities were observed for the recovered EVOH and PET, which could also be an indication of contamination in the samples. The previous characterization study of STRAP recovered materials did not determine significant changes in the crystallinity but in the melt temperature of PET, which was associated with solvent retention in the polymer matrix as PET was the main layer in the film [61].

Table 3.8 Summary of thermal and molecular parameters for virgin resins and polymers recovered from the printed multilayer film by STRAP.

Resin	T_c (°C)	$T_{m,2}$ (°C)	ΔH_c (J/g)	$\Delta H_{m,2}$ (J/g)	Crystallinity
PE STRAP	105.0	119.7	76.0	82.3	28.38%
LDPE Virgin	98.3	112.0	84.8	86.1	29.69%
LLDPE Virgin 45G	106.1	122.4	83.3	85.5	29.48%
LLDPE Virgin 47N	107.0	122.2	70.2	73.3	25.28%
EVOH STRAP	150.4	175.7	41.8	37.4	17.17%
EVOH Virgin	147.8	176.4	54.2	54.3	24.93%
PET STRAP	209.6	246.0	41.7	22.7	16.21%
PET Virgin	169.2	244.6	30.0	38.5	27.50%

3.4 Economic and environmental impacts of STRAP with the printed multilayer film

The TEA and LCA of the STRAP process with the printed multilayer film were performed based on the collected experimental data. As described in the experimental demonstration section, part of the film could not be recovered and was left behind as residue in the equipment. Therefore, the material that could be recovered experimentally was normalized to close out the mass balance for the TEA and LCA. The sequential steps needed for PE and deinking of PET were considered in the amount of solvent and time required for those steps. Figure 3.8 shows the process flow diagram used for the economic and environmental analyses with the main equipment units for the recovery of the different polymers: PE, EVOH, and PET. The TEA and LCA were performed considering three different scenarios presented in Figure 3.8: (a) only PE recovery, (b) PE and EVOH recovery, and (c) PE, EVOH, and PET recovery. This allowed for an estimate of the economics and environmental impacts of the STRAP process as a function of the number of polymer recovery steps. All the input (multilayer film and solvents) and output (recovered polymers and ink) streams are considered for the analyses. The steps of the process can be summarized as follows: (1) the printed multilayer film is shredded and then mixed with dodecane (1:20 ratio) in the dissolution vessel, (2) the plastic/dodecane is filtered to separate the dissolved PE from the non-dissolved plastics, (3) the PE is precipitated and the mixture is filtered again to separate the dodecane from the solid PE, (4) the liquid dodecane stream is recycled and the solid PE stream is dried to remove residual dodecane, and (5) the dodecane stream in the gas phase is condensed and recycled. Similarly, the EVOH separation can be summarized with the following steps: (1) the insoluble solids recovered after the first filtration step (EVOH, PET, and ink) are heated and mixed with a DMSO/water mixture in a dissolution vessel (1:10 ratio), (2) the DMSO/water/plastic mixture stream is then filtered to separate the dissolved EVOH from the non-dissolved PET and ink, (3) the stream containing the dissolved EVOH is cooled and the steps from the PE separation are repeated. Finally, the insoluble solids obtained after the EVOH separation, PET and ink, are heated and mixed with GVL in a dissolution vessel (1:20 ratio). After a first filtration, the PET is dried and the GVL stream in the gas phase is condensed and recycled. The remaining mixture of liquid GVL and ink is cooled and sent to a precipitation vessel. After a second filtration, the black and white ink residues are recovered. Then, a fraction of the remaining ink (yellow) with GVL (10%) is sent to distillation and the rest of the mixture is directly recycled along with the GVL recovered from distillation and the condenser. Our process simulation indicated that 99.98% of solvent recovery for GVL and 99.9999% for the rest of the solvents (dodecane, DMSO, and water) is possible.

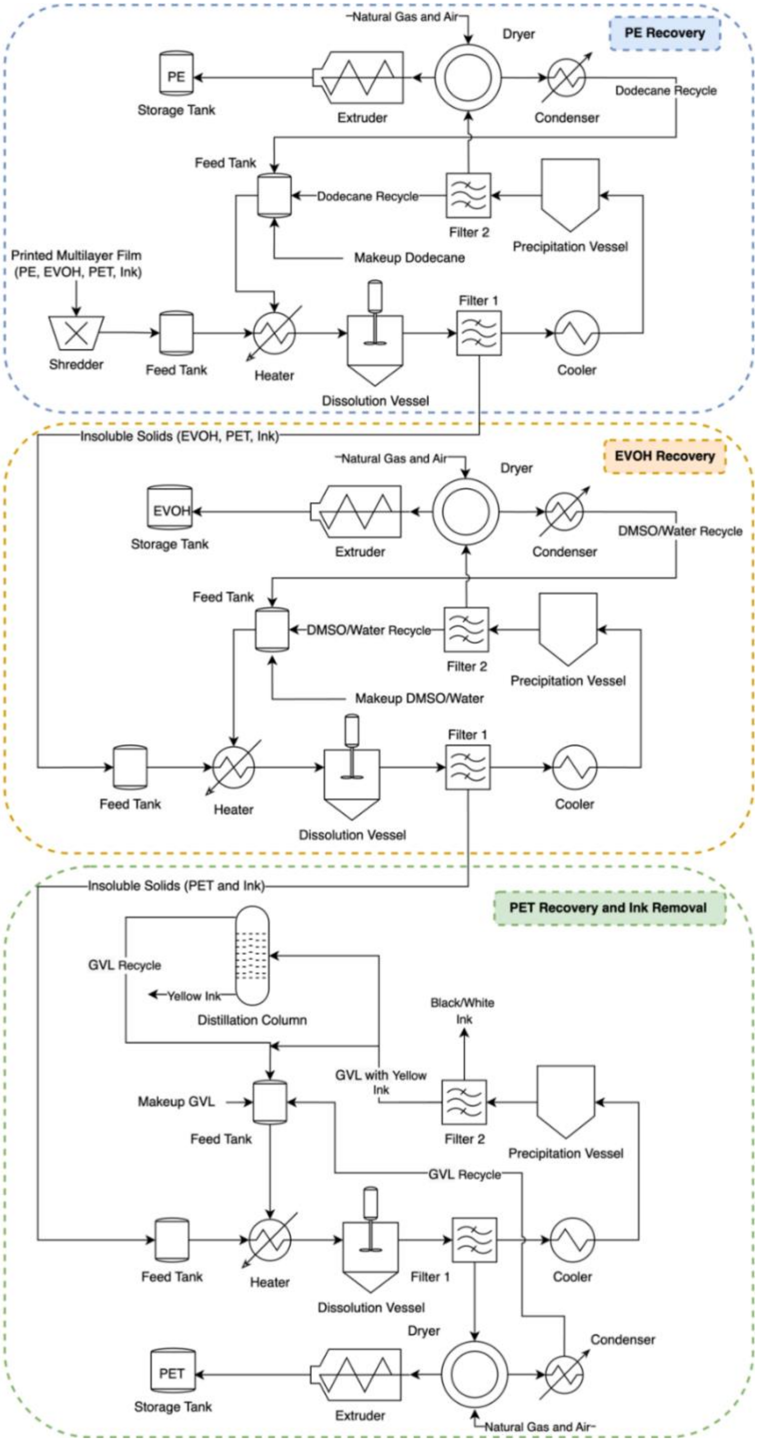

Figure 3.8 Process flow diagram of the recovery of the PE, EVOH, and PET from a printed multilayer film using the STRAP technology.

A summary of the economic and environmental impacts of the different scenarios considered for the STRAP process is shown in Figure 3.9. The analysis was performed for a plant capacity of 3,000 tons per year, and the economic performance of each scenario is compared using the minimum selling price (MSP), which is expressed in USD per kg of polymer sold. As expected, the PE recovery (around 62 wt% experimental yield) represented the lowest price, 1.96 USD/kg, and is the most attractive scenario economically because this value is within the average market values of the virgin and post-consumer recycled resins of 0.9-2.23 USD/kg [62]. When the remaining polymers (EVOH and PET) are recovered, the price increases because the complexity of the process increases. However, in the detailed economic analysis (**Section 3.6.1**), it was found that at larger plant capacities the EVOH and PET recoveries can be economically feasible. The environmental costs in Figure 3.9 were compared using the climate change impact (kg CO_2/kg of film) estimated using an LCA methodology. This metric refers to the generated emissions for the recovery of the different polymers via the STRAP process. The PE recovery also represented the lowest environmental impact, given that less consumption of resources is needed for one polymer recovery. In the detailed environmental analysis (**Section 3.6.2**), it was found that all the recovery scenarios have a lower impact than the alternative of producing films from virgin polymers.

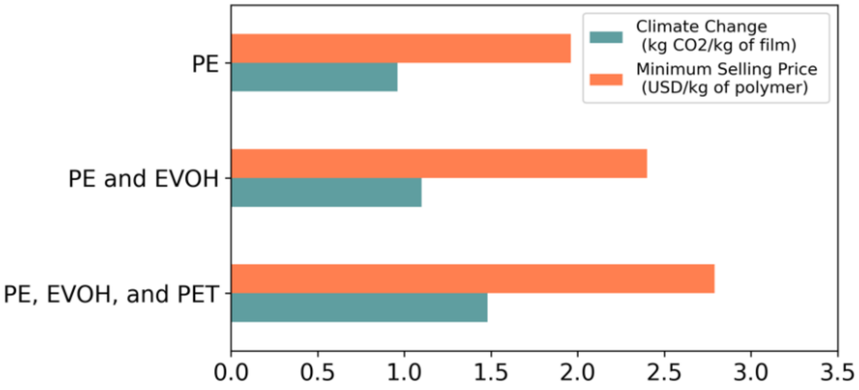

Figure 3.9 Economic and environmental costs of the STRAP process with the printed film for different scenarios: PE recovery, PE and EVOH recovery, and PE, EVOH, and PET recovery (including ink removal).

3.4.1 Economies of scale for the STRAP scenarios with the printed multilayer film

In the economic analysis it was assumed that the economic lifetime of the plant is 20 years, the interest rate is 10%, and the input stream of multilayer film does not have any cost since it is a post-industrial waste. The complete assumptions and parameters can be found in the Methods Section (Table 3.1). For the PE recovery step, it was determined that the total capital investment is 18.2 million USD and the operating costs are 1.24 million USD per year. The detailed capital and operating costs are reported in Table 3.9-Table 3.13. The equipment that accounted for most of the capital cost were the extruder, dryers, and filters (Table 3.9). The operating costs include the steam and electricity required by each piece of equipment as well as the required solvent (dodecane), cooling agent, and natural gas. The solvent recovery in the process is 99.999%. A sensitivity analysis was conducted for different processing capacities to evaluate the impact of the economies of scale on the process of the PE recovery step. These results are presented in Figure 3.10(a). We observe that after 3,000 tons per year, the MSP of recovered resins with the STRAP process is equal to average market values of the virgin resin and the price of post-consumer polymers (0.9-2.23 USD/kg) [62]. These results demonstrate that the STRAP process is economically feasible at capacities larger than 3,000 tons per year. This occurs due to the effect of economies of scale, which allows for a reduction of the cost per unit by increasing efficiency.

Table 3.9 Installed equipment cost for a 3,000 ton/year plant to produce PE from printed film *[40]*.

Equipment	Installed Cost (USD)
Shredder	160,720
Tanks	1,308,274
Vessels	728,196
Filters	1,894,146
Pumps	104,497
Extruder	4,232,107
Heat Exchangers	77,759
Dryers	1,847,427
Total installed equipment costs	10,353,127

Table 3.10 Capital cost (CAPEX) for a 3,000 ton/year plant to produce PE from printed film.

Category	Cost (USD)
ISBL costs (total installed equipment costs)	10,353,127
OSBL costs (30% of ISBL)	3,105,938
Engineering cost (15% of the ISBL plus OSBL)	2,018,860
Contingency cost (20% of the ISBL plus OSBL)	2,691,813
Total capital cost	18,169,738

Table 3.11 Fixed operating cost for a 3,000 ton/year plant to produce PE from printed film.

Category	Cost (USD/year)
Operator salaries	208,050
Benefits and overhead (50% of salary)	104,025
Maintenance (3% of CAPEX)	545,092
Insurance (0.7% of CAPEX)	127,188
Total fixed operating costs	984,355

Table 3.12 Variable operating costs for a 3,000 ton/year plant to produce PE from printed film.

Category	Unitary cost	Cost (USD/year)
Electricity	0.07 USD/kWh	112,240
Natural gas	0.016 USD/kWh	29,434
Low-pressure steam	1.79×10^{-6} USD/kJ	17,920
Cooling agent (chilled brine)	8.15×10^{-6} USD/kJ	51,680
Cooling agent (chilled water)	5×10^{-6} USD/kJ	39,440
Dodecane (99.999% of recovery)	2.17 USD/kg	862
Total variable operating costs		251,576

Table 3.13 Revenue for a 3,000 ton/year plant to produce PE from printed film.

PE production (kg/year)	Selling price (USD/kg) [62]	Revenue (USD/year)
2,040,640	2.23	4,550,627
Total revenue		4,550,627

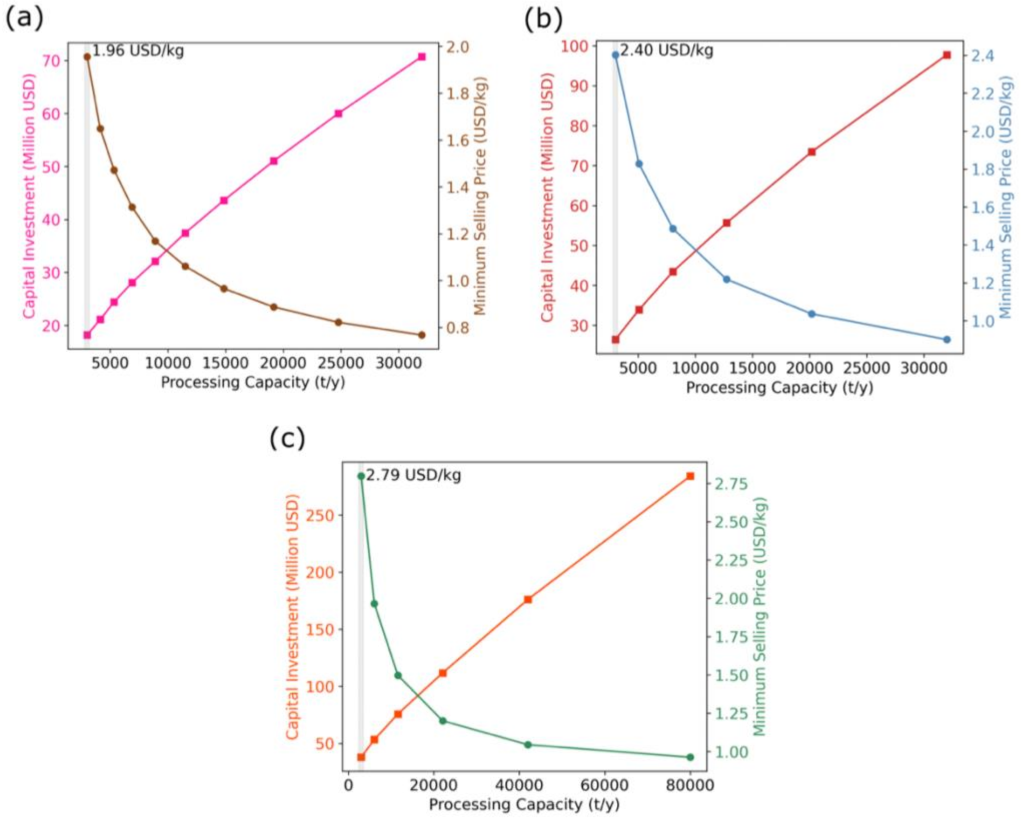

Figure 3.10 Sensitivity analysis for economies of scale for the different scenarios of the STRAP process: a) PE recovery, b) PE and EVOH recovery, c) PE, EVOH, and PET recovery (including ink removal). The minimum selling price at a plant capacity of 3,000 ton/year.

For the PE and EVOH recovery, at a processing capacity of 3,000 tons per year, we found that the MSP of the STRAP process is 2.4 USD/kg. This price is slightly higher than the average market values of the virgin resins and the price of post-consumer polymers (0.9-2.23 USD/kg) and higher than the MSP of just recovering the PE [62]. The total capital investment is 26.4 million USD, and the operating costs are 1.6 million USD per year. The detailed capital and operating costs are reported in Table 3.14-Table 3.18. The solvent recovery in the process is 99.999% (for the three solvents used: dodecane, water, and DMSO). The economic sensitivity analysis for different processing capacities of the PE and EVOH recovery steps is presented in Figure 3.10(b). We observe that after 4,000 tons per year, the MSP of the polymers recovered in the STRAP process is comparable to average market values of the virgin resins and the price of post-consumer polymers [62].

Table 3.14 Installed equipment cost for a 3,000 ton/year plant to produce PE and EVOH from printed film *[40]*.

Equipment	Installed Cost (USD)
Shredder	160,720
Tanks	1,905,908
Vessels	1,040,648
Filters	3,500,244
Pumps	174,817
Extruder PE	4,232,107
Extruder EVOH	1,338,199
Heat Exchangers	142,100
Dryers	2,562,774
Total installed equipment costs	15,057,518

Table 3.15 Capital cost (CAPEX) for a 3,000 ton/year plant to produce PE and EVOH from printed film.

Category	Cost (USD)
ISBL costs (total installed equipment costs)	15,057,518
OSBL costs (30% of ISBL)	4,517,255
Engineering cost (15% of the ISBL plus OSBL)	2,936,216
Contingency cost (20% of the ISBL plus OSBL)	3,914,955
Total capital cost	26,425,943

Table 3.16 Fixed operating cost for a 3,000 ton/year plant to produce PE and EVOH from printed film.

Category	Cost (USD/year)
Operator salaries	208,050
Benefits and overhead (50% of salary)	104,025
Maintenance (3% of CAPEX)	792,778
Insurance (0.7% of CAPEX)	184,982
Total fixed operating costs	1,289,835

Table 3.17 Variable operating costs for a 3,000 ton/year plant to produce PE and EVOH from printed film.

Category	Unitary cost	Cost (USD/year)
Electricity	0.07 USD/kWh	147,840
Natural gas	0.016 USD/kWh	33,434
Low-pressure steam	1.79×10^{-6} USD/kJ	25,600
Cooling agent (chilled brine)	8.15×10^{-6} USD/kJ	58,400
Cooling agent (chilled water)	5×10^{-6} USD/kJ	57,680
Dodecane (99.999% of recovery)	2.17 USD/kg	862
DMSO (99.999% of recovery)	1.9 USD/kg	103
Water (99.999% of recovery)	0.0065 USD/kg	0.23
Total variable operating costs		323,919

Table 3.18 Revenue for a 3,000 ton/year plant to produce PE and EVOH from printed film.

PE and EVOH production (kg/year)	Selling price (USD/kg) [62]	Revenue (USD/year)
2,340,080	2.23	5,218,378
Total revenue		5,218,378

Finally, we analyzed the economic feasibility of the PE, EVOH, and PET recovery steps (including the ink removal). For the processing capacity of 3,000 tons per year, we found that the MSP of the STRAP process is 2.79 USD/kg. This price is slightly higher than the average market values of the virgin resins and the price of post-consumer polymers (0.9-2.23 USD/kg) [62] and higher than the MSP of just recovering the PE and EVOH. The total capital investment is 37.8 million USD, and the operating costs are 2.24 million USD per year. The detailed capital and operating costs are reported in Table 3.19-Table 3.23. The solvent recovery for the dodecane, water, and DMSO is 99.999%, while the recovery for GVL is 99.98% (because this recovery requires distillation). The sensitivity analysis for economies of scale is shown in Figure 3.10(c). We observe that after 6,000 tons per year, the MSP of the resins produced in the STRAP process is comparable to average market values of the virgin resin and the price of post-consumer polymers [62]. These results show that the separation of the 3 polymers is economically feasible at large processing capacities. There are important parameters of the process that can vary and impact the MSP. A sensitivity analysis was performed for selected parameters (OSBL, interest rate, and economic lifetime) and it was determined that the MSP is sensitive to the interest rate in all the scenarios, which can be found in Figure 3.11.

Table 3.19 Installed equipment cost for a 3,000 ton/year plant to produce PE, EVOH, and PET from printed film [40].

Equipment	Installed Cost (USD)
Shredder	160,720
Tanks	2,611,375
Vessels	1,701,270
Filters	5,363,756
Pumps	245,538
Extruder PE	4,232,107
Extruder EVOH	1,338,199
Extruder PET	1,841,637
Heat Exchangers	217,889
Dryers	3,506,841
Distillation column	334,016
Total installed equipment costs	21,553,349

Table 3.20 Capital cost (CAPEX) for a 3,000 ton/year plant to produce PE, EVOH, and PET from printed film.

Category	Cost (USD)
ISBL costs (total installed equipment costs)	21,553,349
OSBL costs (30% of ISBL)	6,466,005
Engineering cost (15% of the ISBL plus OSBL)	4,202,903
Contingency cost (20% of the ISBL plus OSBL)	5,603,871
Total capital cost	37,826,127

Table 3.21 Fixed operating cost for a 3,000 ton/year plant to produce PE, EVOH, and PET from printed film.

Category	Cost (USD/year)
Operator salaries	208,050
Benefits and overhead (50% of salary)	104,025
Maintenance (3% of CAPEX)	1,134,784
Insurance (0.7% of CAPEX)	264,783
Total fixed operating costs	1,711,642

Table 3.22 Variable operating costs for a 3,000 ton/year plant to produce PE, EVOH, and PET from printed film.

Category	Unitary cost	Cost (USD/year)
Electricity	0.07 USD/kWh	201,680
Natural gas	0.016 USD/kWh	38,384
Low-pressure steam	1.79×10^{-6} USD/kJ	43,040
High-pressure steam	2.66×10^{-6} USD/kJ	15,920
Cooling agent (chilled brine)	8.15×10^{-6} USD/kJ	70,800
Cooling agent (chilled water)	5×10^{-6} USD/kJ	107,200
Cooling water	3.43×10^{-7} USD/kJ	1040
Dodecane (99.999% of recovery)	2.17 USD/kg	862
DMSO (99.999% of recovery)	1.9 USD/kg	103
Water (99.999% of recovery)	0.0065 USD/kg	0.23
GVL (99.98% of recovery)	3.88 USD/kg	45,303
Total variable operating costs		524,332

Table 3.23 Revenue for a 3,000 ton/year plant to produce PE, EVOH, and PET from printed film.

PE, EVOH, and PET production (kg/year)	Selling price (USD/kg) [62]	Revenue (USD/year)
2,850,000	2.23	6,355,500
Total revenue		6,355,500

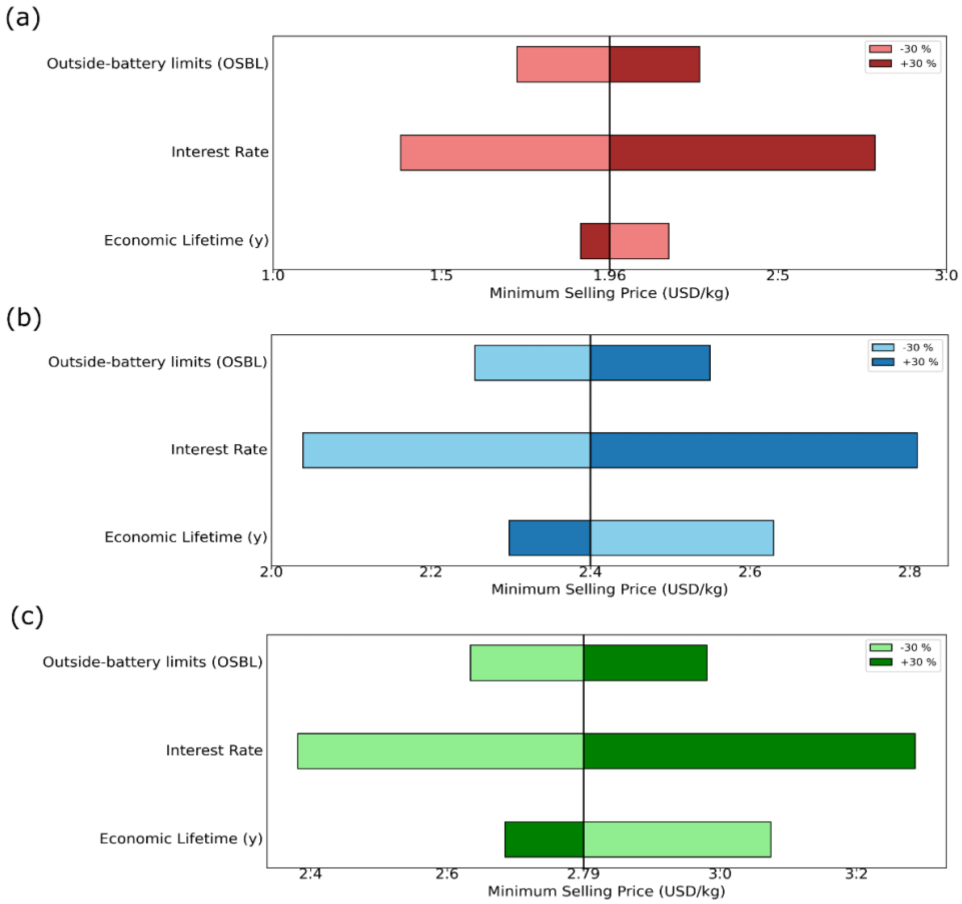

Figure 3.11 Sensitivity analysis for important parameters of the STRAP process considering different scenarios: a) PE recovery, b) PE and EVOH recovery, c) PE, EVOH, and PET recovery (including ink removal).

3.4.2 Comparison of STRAP environmental impacts to multilayer film production from virgin resins

The impact of the STRAP process with the printed multilayer film on climate change (kg CO_2 eq) was evaluated using a life cycle assessment (LCA) methodology. The STRAP technology was analyzed from a product perspective [43]. From this perspective, the STRAP approach is seen as an alternative process to the production of multilayer films from virgin-grade polymers. The functional unit considered is the production of 1 kg of multilayer film. Thus, we compare the impacts of producing 1 kg of film from traditional pathways with producing 1 kg of film through the recovery of the polymers via the STRAP process. The system boundaries of the production of multilayer film from fossil sources include the extraction and transportation of raw materials, material processing, and consumption of process utilities. In the STRAP process, the system boundaries include the material inputs (solvents and utilities), the transportation of the process solvents, and the material processing (extrusion) to produce the new multilayer films from recycled material. The film treated in the STRAP technology is assumed to be clean post-industrial waste. Therefore, the product use, waste collection, and treatment (e.g., sorting, grinding, and cleaning) are not within the system boundaries. The impacts for the solvents (DMSO and water) were taken from the Ecoinvent 3.6 cut-off by classification database [45] using the Environmental Footprint method [46]. Since the impacts of dodecane and GVL were not available, we considered an average value of organic solvents from the same database. The rest of the impacts, including the STRAP process utilities (steam, electricity, and cooling agents), the transportation of commodities, and the virgin production of polymers (PE, EVOH, and PET) were taken from the Environmental Footprint database [47].

The environmental impacts of each of the three STRAP scenarios with the printed film were compared to the production of 1 kg of film with the corresponding virgin resins. As seen in Figure 3.12(a), the total impacts of separating PE by the STRAP process (0.96 kg CO_2 eq./kg film) are lower than the impacts of a PE film produced with virgin resins (2.43 kg CO_2 eq./kg film). Specifically, around 60% fewer emissions are generated in the STRAP technology. Most of the emissions in the STRAP process are related to the use of steam and electricity. Figure 3.12(b) presents the generated emissions to produce a PE and EVOH film through the different alternatives. We can see how the impacts increase, but the STRAP approach keeps producing fewer emissions than virgin production despite including the impact related to solvents (DMSO and water). Finally, in Figure 3.12(c), the climate change impact of recovering all the constituent polymers (PE, EVOH, and PET) and producing 1 kg of virgin-grade multilayer film is presented. The generated emissions in the STRAP technology include the impacts related to the ink removal. The virgin film production generates around 51% more emissions (3 kg CO_2 eq./kg film) than the

STRAP process (1.48 kg CO_2 eq./kg film). Through this analysis, we conclude that the STRAP technology could help achieve the goals of a circular economy by reducing the environmental impacts related to resource consumption and providing environmental benefits over virgin film production. These results are consistent with our previously published analysis [63]. Furthermore, the STRAP process has similar economic and environmental performance as delamination [19].

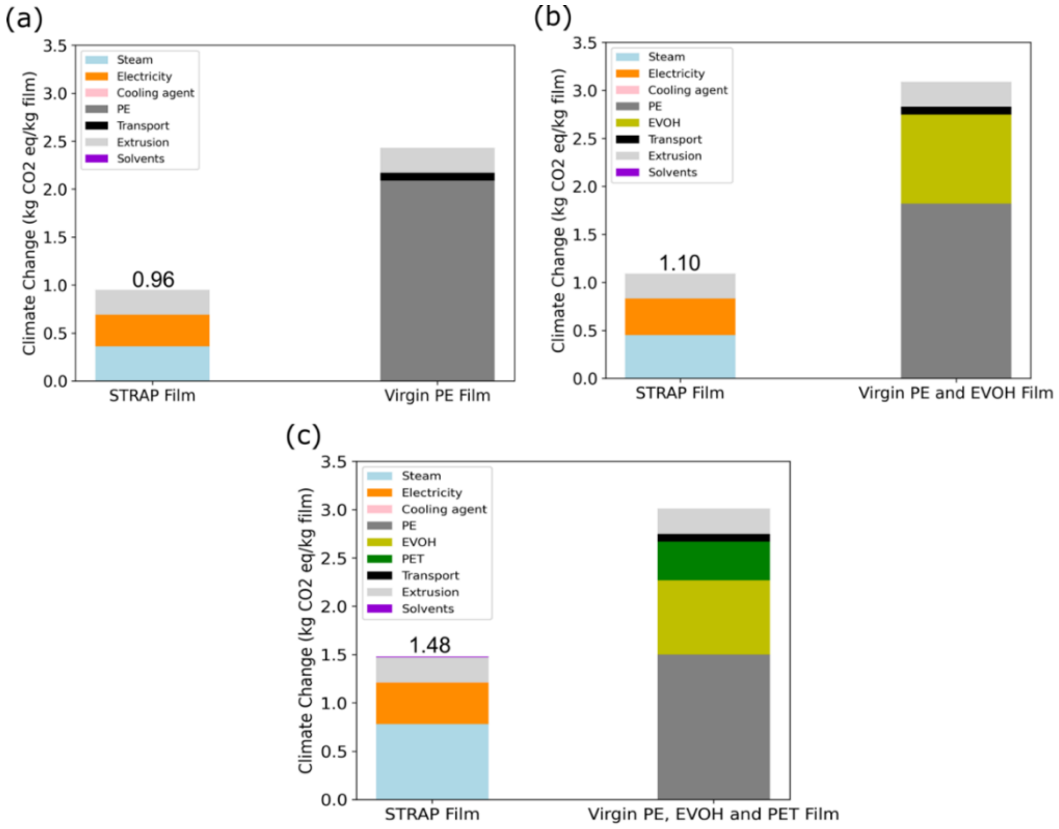

Figure 3.12 Climate change impact of producing 1 kg of film with polymers recovered through the STRAP process in comparison with producing a film with virgin resins. a) PE film, b) PE and EVOH film, c) PE, EVOH, and PET film.

3.5 Conclusions

The STRAP approach for recycling multilayer plastic films via selective polymer dissolution was applied to recover the constituent polymers of a printed flexible multilayer plastic film. A deinking step was included to remove all colors and obtain clear PE, EVOH, and PET that could be recycled for different applications. The computational modeling tools used in this study allowed for the selection of polymer-selective solvents in the presence of the inks and for the selection of solvents to develop an ink removal step. Out of the surfactant solutions and solvents tested, removal of all colors from the PET was observed with gamma-Valerolactone (GVL), after recovering the other polymer components. This demonstrated the use of a biomass-derived solvent to clean PET from black, white, and yellow ink components. After quantifying colors with CIELAB measurements, the only polymer that showed residual colors was the recovered PET, particularly of the yellow color. Further improvement in the deinking step would be needed to reduce the amount of residual color in the PET stream. Other characterization results showed that, for the most part, the recovered polymers had comparable properties to the corresponding pure resins. Some differences were observed in crystallinity values which could indicate sample contamination from other polymers or residual ink. The separation of the polymers from the printed multilayer film with STRAP could be economically feasible at a large scale and it could reduce environmental impacts when compared to the production of films from virgin polymers. These results demonstrate that the STRAP framework, which combines computational modeling for solvent selection, experimental demonstrations, and process design, can be used to develop a viable recycling approach for a printed multilayer plastic film. Future work will focus on demonstrating this recycling approach with other multilayer films that contain PU inks, mixed multilayer plastic waste, and films that contain other polymers like PP, PS, and nylons.

3.6 References

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Chapter 4. Exploring the potential applications of STRAP polymers in plastic film production

The contents in this chapter were adapted from the following reference:

K.L. Sánchez-Rivera, C. Granger, H. Appiah, K. Nelson, D. Sun, J.E. Estela-García, E. Chen, Z. Xu, T. Osswald, L. Turng, A.G. McDonald, R.C. Van Lehn, E. Bar-Ziv, and G.W. Huber. Cast film production with polyethylene recycled from a post-industrial printed multilayer film by solvent-targeted recovery and precipitation. *Submitted.*

4.1 Introduction

The packaging industry is one of the largest markets for single-use plastics, generating more global plastic waste than the transportation, textiles, healthcare, and construction industries [1, 2]. Currently, plastic packaging is mostly landfilled or incinerated in the United States and efforts are needed to improve the circularity of these materials by addressing recycling challenges [3]. Despite their end-of-life issues, flexible plastic packaging offers many benefits to consumers in food preservation. Flexible packaging has lower environmental impacts than other materials like glass, metals, or rigid plastic containers [4-6]. These flexible plastic materials can be manufactured as monolayer, coated monolayer, or multilayer films, with about 17% of all films produced being multilayer films containing multiple polymer components [7]. Typical polymers found in these structures include polyolefins like polyethylene (PE) or polypropylene (PP) for their moisture barrier properties, ethylene vinyl alcohol (EVOH) for its gas barrier properties, polyethylene terephthalate (PET) for its heat resistance and mechanical strength, modified ethylene vinyl acetate (EVA) or other tie layers for their ability to adhere dissimilar materials, among others [8, 9]. In most cases, these multilayer materials are intended for single use and their recycling is challenging due to difficulties in the separation of their complex structure [10, 11].

Solvent-Targeted Recovery And Precipitation (STRAP$^{\mathrm{TM}}$) recycles multilayer films by using a series of solvents to selectively recover the constituent resins of the material, guided by thermodynamic calculations of polymer solubility [12-15]. The STRAP process can enable a recycling pathway for rigid and flexible multilayer films by recovering polymers like polyethylene (PE), ethylene vinyl alcohol (EVOH), and polyethylene terephthalate (PET) with > 95 wt% material efficiency. This approach can produce polymers with comparable properties to pure resins, can be economically feasible, and can introduce environmental benefits when compared to film production from pure polymers [16, 17]. Dissolution-based recycling processes like STRAP have gained interest in recent years due to their potential for recovering valuable polymeric components from different types of plastic waste while removing plastic additives, adhesives, impurities, odor, and color [18-23]. Companies like Polystyvert, PureCycle, and APK are commercializing dissolution-based processes [24].

One important aspect to consider with a new recycling technology is the potential applications of the recycled materials after their processing. Previous studies have demonstrated some of these with materials that were recovered via dissolution-based approaches. For example, Ramírez-Martínez et al. fabricated membranes using polyolefins that were dissolved in bio-based solvents like D-limonene and α-pinene [25]. Saleem et al. produced thin films for oil-sorbent pouches with PP that was recovered from disposable face masks [26]. In another study, Phan et al. employed solvents to selectively dissolve elastane from different fiber mixtures, which could be incorporated back in other textiles [27]. Sriprom et al. produced foam/natural fiber composites with expanded polystyrene (EPS) that was recycled via a dissolution-based process using a mixture of thinner and acetone [28]. Polymer solutions can also find applications as paint additives and in glues for different materials like glass, paper, metals, and cloth. This was demonstrated with the dissolution of polyvinyl(butyral) (PVB) in 2-propanol and ethyl acetate, which also allowed for the removal of solid contaminants [29]. In general, a product that can be appropriate for the same or similar applications as the original waste would be preferred. This is considered an upcycling process and it is aligned with circular economy principles in which plastics maintain their value [30, 31]. On the other hand, in a downcycling process, the recycled materials do not possess the optimal qualities and must find applications in markets of lower value [32-34].

In this study, we aim to validate that polymers recovered by STRAP are suitable for re-use in film manufacturing. In the plastic packaging industry, polymers are converted to different formats depending on their intended use and properties. For example, these can be manufactured into monolayer or multilayer flexible, semi-rigid, or rigid films, along with bottles, trays, and jars [35]. Specifically for plastic films, these are normally manufactured by two techniques: blown and cast film extrusion [36]. In the blown film extrusion process, the polymer melt is inflated by air and chilled air is blown on the outside of the film to cool the polymer bubble [37]. After reaching the desired temperature, below the melting point of the polymer, the bubble is flattened, cut, and rolled [38]. In the cast film process, the polymer melt is extruded through a system of chilled rolls that produce the desired flattened film [35, 39]. In this chapter, the potential applications of STRAP polymers in plastic film production were explored. PE was recovered by STRAP from a post-industrial printed multilayer plastic film that was comprised of PE, EVOH, PET, polyurethane (PU) adhesives, and PU-based inks [17]. We have previously recovered PE, EVOH and PET from this material via three processing steps: (1) PE dissolution in n-dodecane, (2) EVOH dissolution in a DMSO and water mixture, and (3) ink removal with gamma-valerolactone. Three STRAP methods were considered to increase the production of PE and study the influence of experimental conditions like solvent selection, amount of solvent, and filtration on the film properties.

4.2 Materials and Methods

4.2.1 Materials

The printed flexible multilayer film was collected from an Amcor post-industrial waste stream. Average compositions of these materials can be 17 wt% PET, 8 wt% EVOH, 5 wt% inks and adhesives, and 70 wt% PEs. The materials were initially shredded to 3 mm in size through a 1/8" cross-cut shredder (Make: Allegheny 16-75CX) at Michigan Technological University. N-dodecane (ReagentPlus®, ≥99%) and heptane were received from Sigma-Aldrich. Dodecane, mixture of isomers, was received from Thermo Scientific Chemicals.

4.2.2 STRAP experimental procedure

The STRAP PE recovery step was carried out using three experimental methods with different heating setups and filter sizes. In these setups, 150 to 200 g of printed multilayer film was processed per experiment, with different amounts of a PE-selective solvent. During the polymer dissolution in each setup, the dissolved PE was separated from the non-dissolved contents. The first method utilized a filter bag with a pore size of 600 µm during the PE dissolution. N-dodecane and the plastic contents were mixed inside the bag with a high shear mixer at 1500 rpm and 95 °C for 2 hours. The second method consisted of a heated Soxhlet extraction system (96 °C) using heptane and a Nomex filter bag with a 1 µm pore size, 32 hours of extraction, and 4 siphonings per hour [40]. In the third method, the plastic contents were put in contact with dodecane isomers in a jacketed dissolution vessel at 95 °C for 1 hour. This system used silicone oil as a heat transfer fluid to achieve the desired temperature and allowed for pressurization during filtration. In our test with the dissolution tank, a filter size of 100 µm was used. The recovered PEs from each method were let to precipitate by lowering the temperature of the contents to room temperature. The PE solids were then separated from the solvent by vacuum filtration and later dried for up to 3 hours at 100 °C in a vacuum oven to remove residual solvents.

4.2.3 Extrusion of recovered polyethylene and cast film production

The recovered PE from the three STRAP methods was cryo-grinded with liquid nitrogen in a Thomas Model 4 Wiley Mill to a 3 mm powder before extrusion. The PE powder was extruded to 3 mm pellets using a Leistritz twin-screw extruder with a temperature range of 170-190 °C and a 19-rpm screw speed. After this, the PE pellets were extruded into a cast film at an average barrel temperature of 177 °C and die temperature of 193 °C with a Labtech Engineering cast film extruder.

4.2.4 Characterization of cast films

Tensile properties of the films were measured using an Instron testing machine following the ASTM Standard D882 – 1 [41]. Final color of the cast films was quantified with a spectrophotometer and measurements were converted to CIELAB color space values, L* (lightness), a* (red-green color component) and b* (blue-yellow color component), and YI (yellowness index) [42]. Optical properties were analyzed following the ASTM standard D1003-21 for haze and luminous transmittance of transparent plastics [43]. The defect analysis for determining the number of impurities in the cast films was performed with an Amcor internal method.

4.2.5 Characterization of STRAP solvents

The recovered solvents after STRAP were analyzed with gas chromatography-mass spectroscopy (GCMS) to detect species that accumulate in the solvents after STRAP. A Shimadzu GCMS-QP2010 with a DB-5 column (Agilent) at a maximum temperature of 310 °C was used, with helium as the carrier gas.

4.3 Results

4.3.1 Recovery of PE component from printed multilayer film and cast film production

In Chapter 3, a flexible printed multilayer film was processed through STRAP to recover PE, EVOH, and PET with minimized coloration [17]. Since polyolefins are extensively present in the packaging industry due to their clarity, toughness, inertness, and availability, we looked at increasing the recovery of the STRAP PE component to determine its suitability for film production [44]. In chapter 3, n-dodecane at 95 °C selectively dissolved the PE component in the presence of the other polymers and PU-based inks in the multilayer material (Figure 4.1). This solvent was initially selected after our computational modeling tools suggested alkane solvents, primarily heptane and dodecane, as selective PE solvents over the PU inks. This recovered PE was a mixture of LDPE and LLDPE and did not have significant coloration before extrusion and pelletization. The STRAP PE had similar thermal properties and molecular weight values as the corresponding virgin resins [17]. The PE yield in our previous work was 61.78 ± 1.74 wt%, and this required two sequential steps under the same conditions to recover most of the PE and clean the experimental setup.

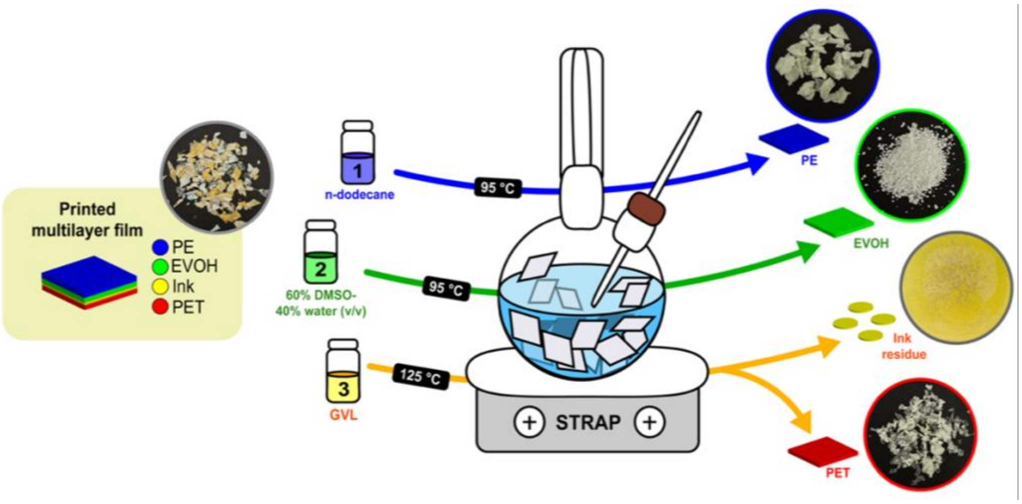

Figure 4.1 Recovery of polyethylene (PE), ethylene vinyl alcohol (EVOH) and polyethylene terephthalate (PET) from a post-industrial printed multilayer film via solvent-targeted recovery and precipitation (STRAP) [17].

The STRAP technology has been demonstrated mostly with post-industrial flexible and rigid multilayer plastic films that are used for food packaging. In our approach, we want to validate that the recovered polymers are suitable for applications in film manufacturing and plastic packaging. After the initial STRAP demonstrations, we looked at modifying our experimental setup to increase the amount of PE recovered per experiment. As presented in Figure 4.2, three different STRAP methods were considered for PE production after its dissolution from the printed multilayer film. The first method employed a filter bag with a pore size of 600 μm, in which all the plastic contents and dodecane were mixed under high shear with a solvent to plastic ratio of 10:1. In this system, heating occurred from the bottom part of the vessel and the remaining parts were insulated to avoid heat losses. After the dissolution time was completed, the filter bag was lifted to separate the undissolved contents from the dissolved PE. This resulted in an average PE yield of 30.0 ± 2.71 wt% (Table 4.1). It was observed that a significant amount of PE precipitated inside the filter bag as soon as it was removed from the solution, in part due to the low plastic-to-solvent ratio. Additionally, the solvent and dissolved PE would drip slowly out of the filter bag, even with a 600 μm pore size, most likely due to the high concentration of plastic contents inside the bag. A second step under the same experimental conditions was carried out to recover the PE residue that was left in the system and the yield was improved to 56.5 ± 1.70 wt%, which is closer to the target PE yields. This was an indication that premature PE precipitation should be avoided; either by including less plastic or more solvent in the feed, minimizing temperature gradients, having filter bags with larger pore sizes, or designing a pressurized filtration to achieve the desired separation. These adjustments were considered in the other STRAP methods.

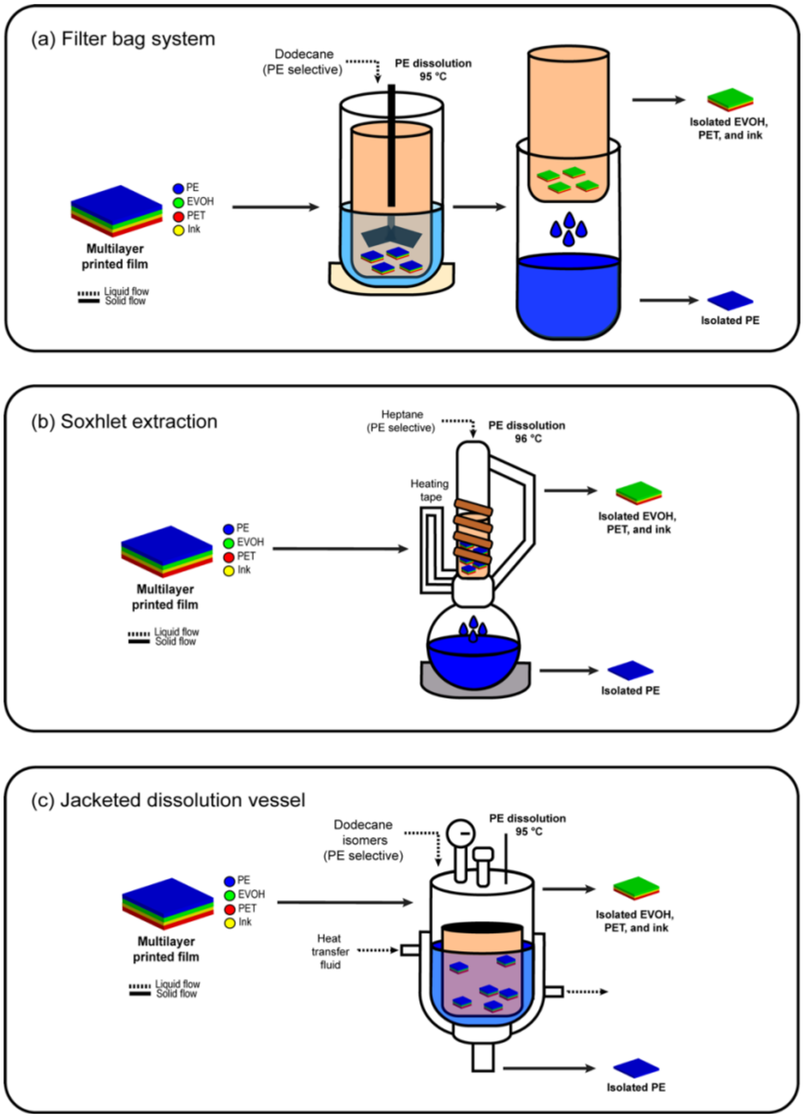

Figure 4.2 Recovery of polyethylene (PE) from a post-industrial printed multilayer film via three different solvent-targeted recovery and precipitation (STRAP) methods: (a) filter bag system, (b) Soxhlet extraction, and (c) jacketed dissolution vessel.

Table 4.1 Experimental parameters and PE yields from the three STRAP methods.

Method	Solvent	Feed (g)	Solvent volume (L)	Solvent to plastic ratio (g solvent/g plastic film)	Temperature (°C)	Time (hr)	PE yield (wt%)
1 - Filter bag system	n-dodecane	200	2.5	10.0	95	2	30.0 ± 2.71
2 - Soxhlet extraction	heptane	300	4.0	9.12	96	36	43.4 ± 0.65
3 – Jacketed vessel	dodecane isomers	135	3.6	20.8	95	1	63.8 ± 1.01

The second method was a Soxhlet extraction setup that included a filter with a pore size of 1 μm, as seen in Figure 4.2(b). The total time the solvent was kept in the system was 32 hours (in a 9.1:1 solvent to plastic ratio) to ensure most of the PE was recovered, with 4 siphonings per hour. However, the maximum PE yield obtained from this approach was only 43.4 ± 0.65 wt%. The extended time and low PE yield shows the disadvantages of this approach for producing the necessary amounts of the desired polymers with the STRAP approach. The third setup was a jacketed dissolution tank that had an inner filter with a pore size of 100 μm (Figure 4.2(c)). This design allowed for the inclusion of multiple filtration steps within the system, in case a more rigorous separation would be needed, along with the option for pressurization and optimized heating. Silicone oil was used as a heat transfer fluid in the main body of the dissolution tank. The solvent and plastics were added in a 20.8:1 ratio and an average PE yield of 63.8 ± 1.01 wt% was obtained, which was comparable to the target value [17]. This indicated that combining a higher solvent to plastic ratio and improved heating can allow for the optimal recovery of the PE component, even with a filter pore size of 100 μm.

After producing around 1-kg of PE from each method, the polymers were dried, cryo-ground, extruded, and pelletized before the cast film production (Figure 4.3). Property comparisons between the three different cast films and standard LLDPE/LDPE films were made, including color, tensile strength, and number of impurities present in the films. Images of the STRAP PE cast films are presented in Figure 4.3(c).

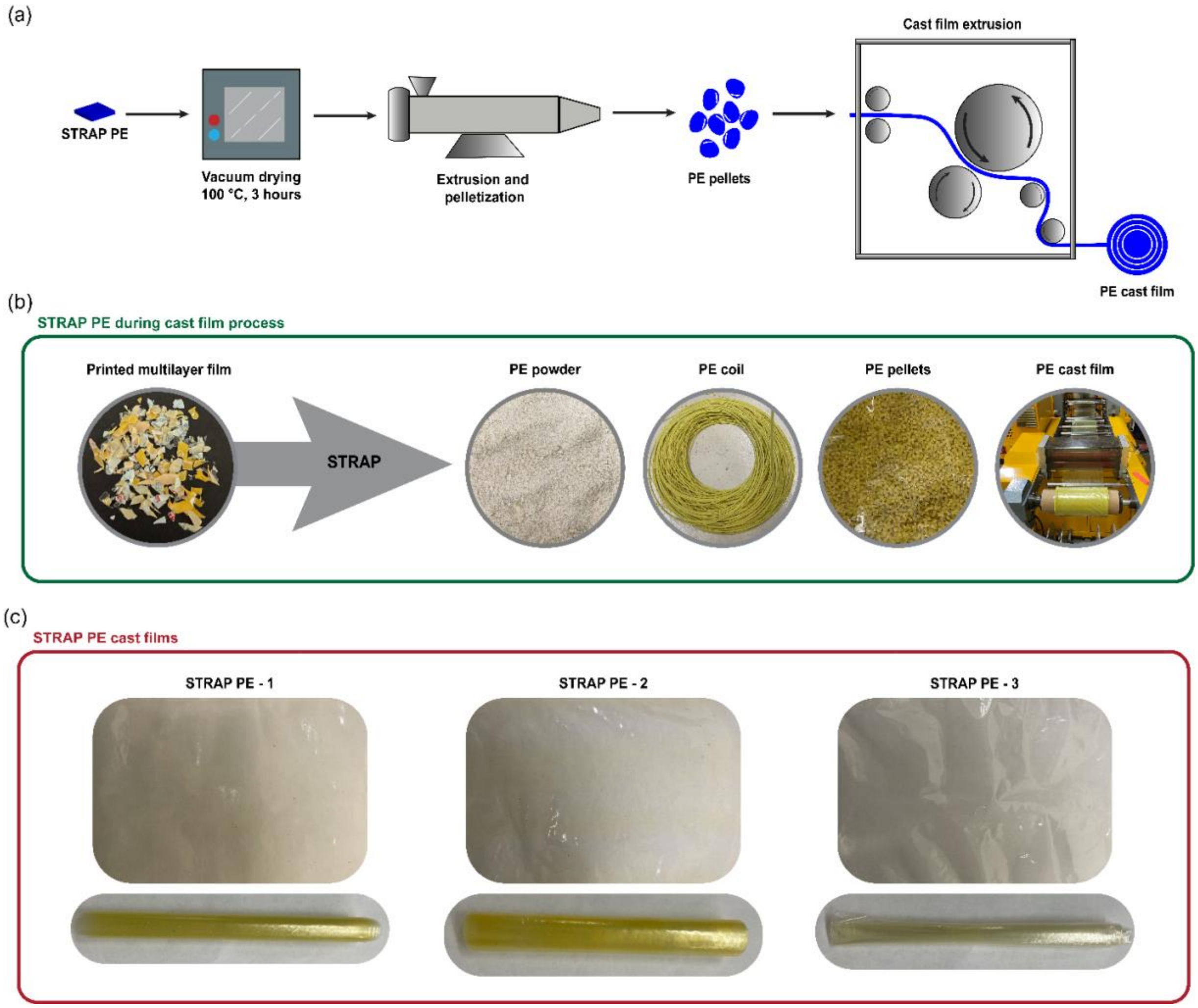

Figure 4.3 (a) Production of a cast film with polyethylene (PE) recovered from a post-industrial multilayer printed film by solvent-targeted recovery and precipitation (STRAP), (b) images of STRAP PE during the cast film production, and (c) images of the final STRAP PE cast films (each number correspond to the methods listed in Table 4.1).

4.3.2 Mechanical properties of cast films

Packaging films must meet different performance criteria according to their intended applications [45]. This assessment can be made by understanding their mechanical or tensile properties, which can determine how suitable the material is for packaging. Tensile properties will be dependent on the film manufacturing process, film structure, and testing parameters [46]. Regardless, we aimed for an initial analysis of the mechanical performance of the produced STRAP PE cast films. The tensile properties of the STRAP PE cast films; Young's modulus, stress at break, force at break, and elongation at break, were compared to two control films that contained LDPE, LLDPE, VLDPE, and EVA (C1 and C2 in Table 4.2) in both the machine and transverse directions. The machine direction is the direction in which the material comes out of the equipment and the transverse is the perpendicular direction. For flexible packaging, a low stiffness would be beneficial for optimal performance, as it reduces crackling sounds and crazing during processing and marketing [47]. The STRAP PE-1 film exhibited a stiff behavior, as it possessed the highest Young's modulus and lowest elongation at break out of all the samples, on both the machine and transverse directions. As will be discussed in the following section, the STRAP PE-1 had visibly more impurities than the other samples. These impurities were most likely the non-dissolved film components that were not efficiently separated, since a 600 μm pore size was used during STRAP. The presence of impurities has been observed to diminish the mechanical and barrier properties of plastic films, since it causes a disruption of the polymer matrix [48]. The STRAP PE-1 film also had the largest variability in the elongation at break, possibly further explaining the heterogeneity of the of the film as a result of the impurities. The STRAP PE-2 and 3 films had comparable Young's moduli to the control films, however, lower stresses and forces at break were observed, along with a lower elongation percentage (Table 4.2).

Table 4.2 Tensile strength properties of STRAP PE cast films.

Film sample	**Film thickness (µm)**	**Young's modulus (MPa)**	**Stress at break (MPa)**	**Force at break (N)**	**Elongation at break (%)**
			Machine direction		
C1[a]	79 ± 15.08	124 ± 4.49	32.2 ± 1.03	64.6 ± 6.85	719 ± 38.38 %
C2[b]	82 ± 14.36	112 ± 1.12	43.0 ± 0.64	90.3 ± 11.85	745 ± 42.43 %
STRAP PE – 1	124 ± 10.40	158 ± 4.35	14.5 ± 3.05	57.2 ± 11.53	494 ± 109.42 %
STRAP PE – 2	87 ± 5.76	108 ± 6.00	13.1 ± 0.74	27.6 ± 5.54	698 ± 29.53 %
STRAP PE – 3	84 ± 12.60	120 ± 5.73	21.4 ± 1.09	45.7 ± 4.62	592 ± 18.52 %
			Transverse direction		
C1[a]	82 ± 1.98	122 ± 4.85	24.6 ± 0.26	55.7 ± 1.69	854 ± 7.59 %
C2[b]	74 ± 3.00	119 ± 5.37	34.2 ± 2.02	71.0 ± 4.53	803 ± 16.87 %
STRAP PE – 1	127 ± 12.95	167 ± 16.10	12.1 ± 2.63	47.5 ± 5.83	568 ± 86.70 %
STRAP PE – 2	84 ± 4.93	103 ± 7.95	9.1 ± 0.15	22.0 ± 1.04	622 ± 26.95 %
STRAP PE – 3	81 ± 4.36	134 ± 7.10	18.8 ± 1.04	40.6 ± 3.40	685 ± 24.54 %

[a] C1 film has LDPE, LLDPE, and tie layers
[b] C2 film has VLDPE, LLDPE, and EVA

4.3.3 Quantification of cast film impurities

Impurities in the film were detected and counted from images taken in a sample area from the different films. The average number of impurities in the STRAP PE films correlated with the filter pore size used in the corresponding STRAP method (Table 4.3). Finer filter pore sizes reduced the presence of impurities in the final film. The STRAP PE-1 had the most impurities since a filter with a pore size of 600 µm was used during the STRAP process. These impurities were most likely non-dissolved components from the multilayer film.

Table 4.3 Comparison of impurities present in STRAP PE cast films.

Film sample	**STRAP filter pore size (µm)**	**Average number of impurities per 3600 mm^2**
C1[a]	-	457 ± 163
C2[b]	-	591 ± 266
STRAP PE - 1	600	2475 ± 378
STRAP PE - 2	1	798 ± 237
STRAP PE - 3	100	1273 ± 2544

[a] C1 film has LDPE, LLDPE, and tie layers
[b] C2 film has VLDPE, LLDPE, and EVA

4.3.4 Color tests

The STRAP PE cast films were compared in terms of color, clarity, and haze. As seen in Table 4.4, an improvement in clarity and haze was observed between the STRAP PE films, with the STRAP PE-3 film showing comparable clarity and haze to the control films C1 and C2. In the CIELAB color space, the STRAP PE-1 and 2 films had higher b* and a* values than the control films (Figure 4.4). This indicated the presence of colors in the yellow and green directions. A reduction in the b* value and increase in a* value was observed with the STRAP PE-3 film, having closer color values to the PE standard films.

Table 4.4 Clarity and haze comparison of the cast films. Values presented are an average from 5 separate measurements.

Film sample	Clarity	Haze %
C1[a]	87.8	7.9
C2[b]	94.4	4.7
STRAP PE - 1	59.0	30.9
STRAP PE - 2	83.4	26.7
STRAP PE - 3	86.9	8.1

[a] C1 film has LDPE, LLDPE, and tie layers

[b] C2 film has VLDPE, LLDPE, and EVA

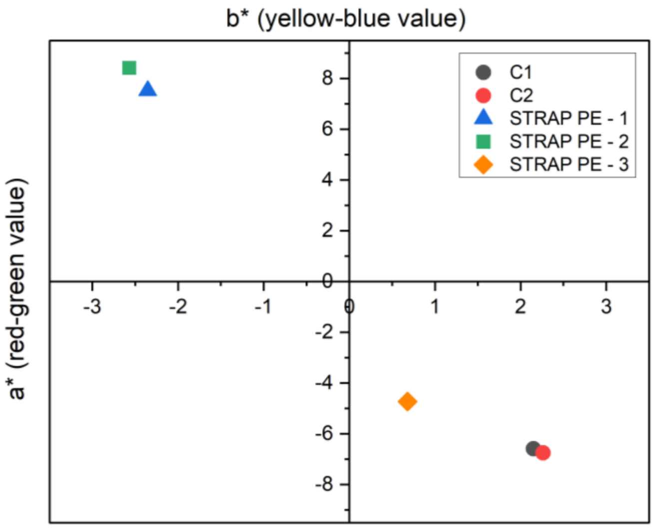

Figure 4.4 CIELAB color space values of the cast films: a* is the red-green color value (a* > 0 is redder, a* < 0 is greener), b* is the yellow-blue color value (b* > 0 yellower, b* < 0 is bluer).

The color improvement between the STRAP PE films was also observed in the yellowness index (YI), with the STRAP PE-3 cast film showing the lowest value among the STRAP films (Figure 4.5(a)). This reduction in yellow color was attributed to the amount of solvent used per experiment in the corresponding STRAP system (Figure 4.5(b)). Applying higher solvent to plastic ratios avoided the accumulation of color bodies in the solvent after each use. A more dilute system also aided in processing challenges in the filtration step for polymer-solvent separation, as it is more difficult to remove the solvent from the polymer in high concentrations.

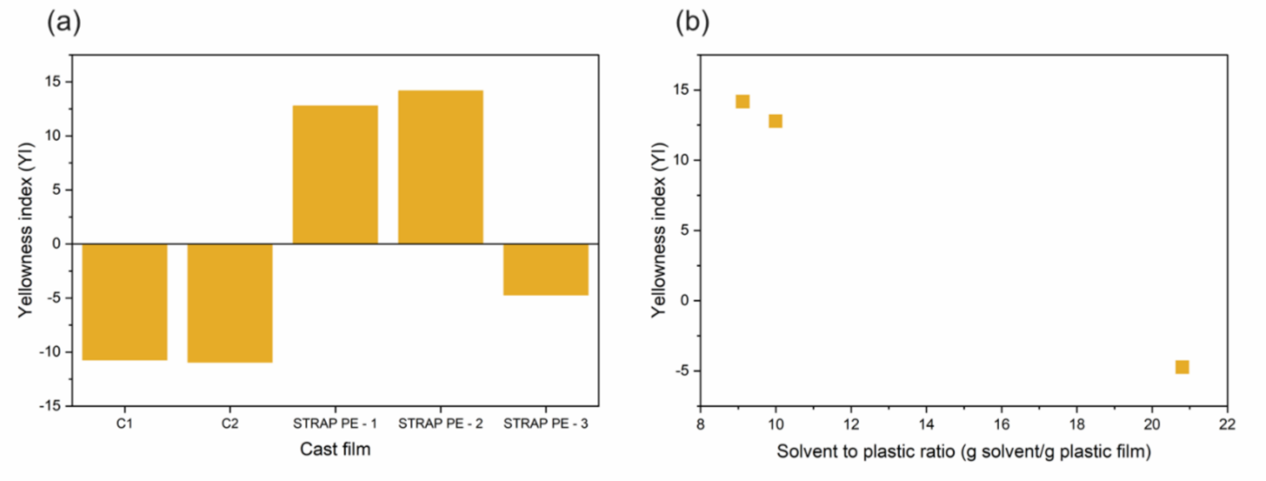

Figure 4.5 Color comparison of the cast films: (a) yellowness index (YI) of the cast films and (b) YI of the cast films with increasing solvent to plastic ratio in STRAP.

4.3.5 Solvent characterization

The solvents from the STRAP methods 1 and 3 were qualitatively analyzed with GCMS to characterize the accumulation of species after the PE dissolution and recovery. As seen in Figure 4.6(a), different plasticizers and slip agents were detected in the post-STRAP n-dodecane from the first method, along with short-chain PE oligomers. The dodecane isomers from the third method did not show significant accumulation of impurities after STRAP (Figure 4.6(b)). This is because, in the third method, a less concentrated system was used with a higher solvent to plastic ratio. Components related to color were not detected with this method. The buildup of different species in the STRAP solvents is more noticeable with lower plastic to solvent ratios during the polymer dissolution, as was observed with the filter bag method.

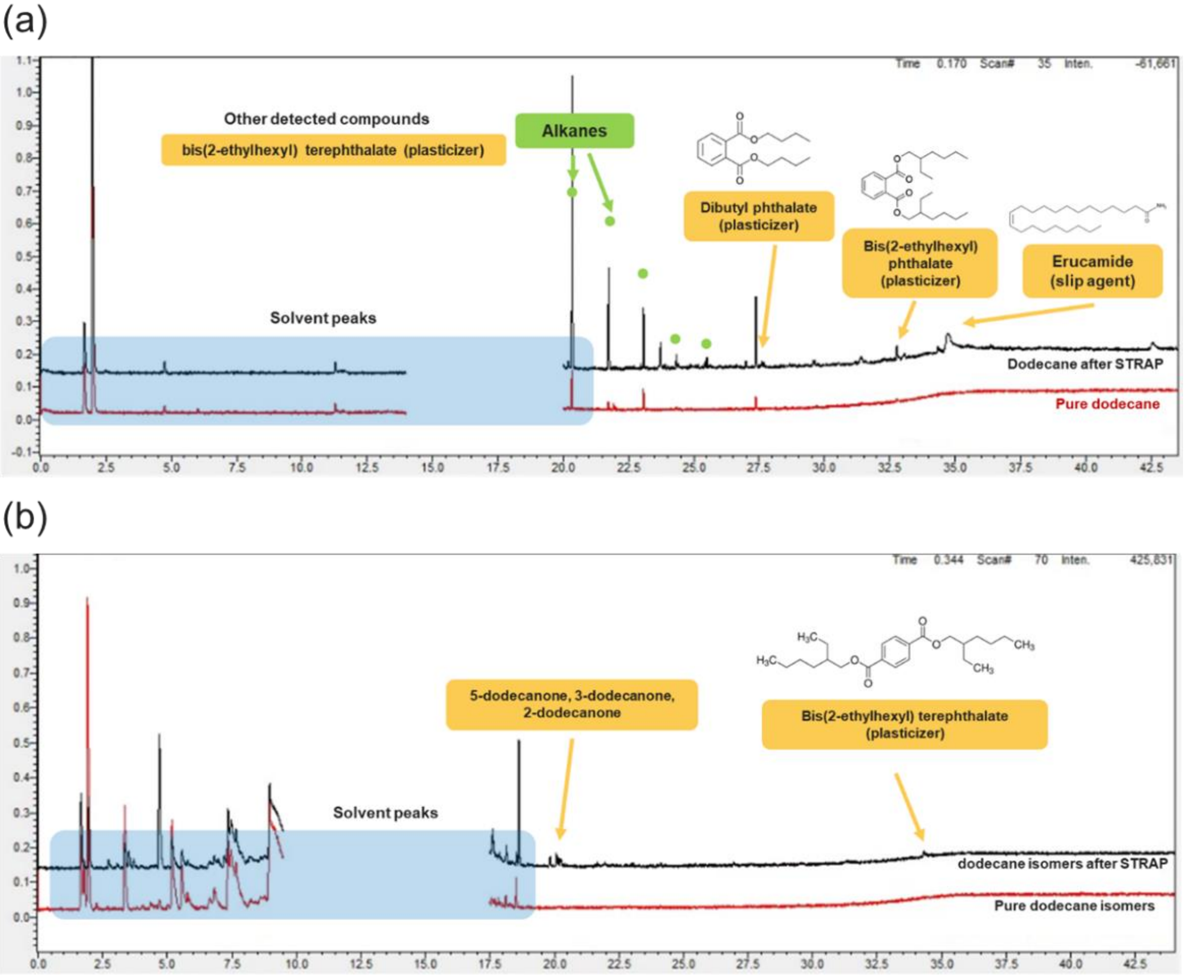

Figure 4.6 Chromatogram comparison of solvents before and after STRAP: (a) dodecane from the first method and (b) dodecane isomers from the third method. GC-MS: DB-5 column, 310 °C max temp, He (8.7 mL/min).

4.4 Conclusions

The STRAP process has been successfully demonstrated for the recovery of different polymeric components from flexible multilayer plastic packaging films. Three methods were considered for the recovery of PE from a post-industrial printed multilayer film: a filter bag system, a Soxhlet extraction setup, and a jacketed dissolution vessel. These different systems allowed us to understand how various processing parameters can influence the properties of the cast films produced from the recovered PE. The third method, the jacketed dissolution vessel, provided improvements in color and removal of impurities from the PE. The solvent to plastic ratio proved to be an important parameter, where higher ratios reduced the buildup of impurities like plasticizers, slip agents, and color components. This study demonstrates that STRAP polymers can be recycled back into plastic films, enabling the potential circularity of these packaging materials. Future work will focus on detailed studies on color removal with adsorption beds, quantification of color components in the solvents, and cast film production from other resins recovered by STRAP.

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Chapter 5. Recovery of plastic components from post-industrial mixed plastic waste

The contents in this chapter were adapted from the following references:

K.L. Sanchez-Rivera, P. Zhou, A. Sharma, R.C. Van Lehn, and G.W. Huber. A solvent-targeted recovery and precipitation scheme for the recycling of post-industrial mixed plastic waste. *In Preparation*.

5.1 Introduction

To address plastic recycling challenges, current and upcoming technologies should consider more complex feedstocks like mixed plastic waste (MPW) [1]. Proper sorting of plastic components from these streams can dictate the efficiency of the overall recycling process. Dissimilar plastics that are present in a MPW feedstock can have different properties and require different recycling approaches [2]. Another concern with mixed plastics is the presence of contaminants that could degrade at the processing conditions. This becomes a more significant concern with mechanical recycling, where the waste stream purity is an important factor [3]. In mechanical recycling, there are separation and sorting steps, bailing, washing, grinding, compounding, and pelletizing. The plastics can be separated in various ways by density, size, color, shape, or chemical composition [4]. One disadvantage with mechanical recycling is the degradation of the polymer properties, which means that the MPW is converted to less valuable products [5]. Compatibilization offers a solution to mechanically recycle multiple polymers, however, this becomes more challenging with complex polymer mixtures [6]. Other technologies don't require extensive sorting of plastic waste. For example, in a pyrolysis approach where plastics are processed at elevated temperatures in the absence of oxygen, different plastics can be included in the feed to produce valuable oils, waxes, and gases that can be converted to chemicals and fuels [5, 7, 8]. This recycling approach can be carried out with or without catalysts. Chattopadhyay et al. studied the catalytic co-pyrolysis of HDPE, PP, PET, and biomass with cobalt catalysts with alumina and ceria supports. In their observations, aromatics and olefins were produced when more plastic was present in the feed than biomass [9]. Das and Tiwari demonstrated the pyrolysis of a mixture consisting of HDPE, PP, and LDPE from plastics used for packaging, containers, and bottles. They produced mostly liquid and gaseous products at temperatures above 375 °C, with higher temperatures producing more middle (C_{12}-C_{20}) and heavy (C_{21}-C_{32}) products in the liquid phase [10]. In a different study, Martínez-Narro et al. pyrolyzed a mixture of PET, PP, LDPE, HDPE, and PS [7]. Similarly, Genuino et al. investigated the pyrolysis of post-consumer mixed plastic waste at 500 °C which included PET, PP, PS, and PE from films and rigid materials. The produced oils and waxes from the MPW were composed of aliphatic and aromatic compounds. A washing step before the pyrolysis was included and this did not significantly affect the overall yields of oils and waxes, however, this did aid in the removal of Cl from the feed, with 67% removed. This lead to less hydrochloric acid (HCl) formation in the gas phase during the pyrolysis but does not eliminate it completely [11]. In general, the Cl content needs to be monitored during the pyrolysis of MPW. Feedstocks that contain polyvinyl chloride (PVC) do become a concern with pyrolysis due to the release of HCl which is toxic and can corrode the processing units [1, 12, 13]. There are several ways chorine content can be removed from MPW, these include microwave irradiation, using solvents, or thermally, the last can achieve above 99% of Cl removed [14]. Overall, pyrolysis offers advantages since it can process mixtures of plastics, including multilayer packaging, which cannot be processed with mechanical recycling [15]. Disadvantages of thermally converting plastics are high energy requirements and potential for more environmental impacts than mechanical recycling [3, 16].

Other chemical conversion approaches for MPW have been disclosed in the literature. In a recent study, Sullivan et al. developed a scheme in which mixed plastics containing high-density polyethylene (HDPE), polystyrene (PS), and polyethylene terephthalate (PET) are converted to βketoadipate and polyhydroxyalkanoates in sequential chemical oxidation and bioconversion [17]. In another study, Rorrer et al. demonstrated the hydrogenolysis of a PP and PE mixture to produce branched and linear alkanes with a Ru/C catalyst [18]. Another alternative that is promising for complex plastic mixtures is gasification, which produces a mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4) in the presence of oxygen [19, 20]. Depolymerization is another alternative in which the polymer backbone is broken into its constituent monomers. Yang et al. presented the idea of a one-pot depolymerization, in which binary mixtures of polyester and polycarbonate materials were processed to produce monomers [21]. The mixtures considered were bisphenyl A polycarbonate (BPA-PC)/ polyethylene terephthalate (PET), polylactic acid (PLA)/ polybutylene succinate (PBS), and PLA/ polybutylene adipate terephthalate (PBAT). In more recent study, Spicer, Brandolese, and Dove, showed a three-step depolymerization of a mixture that consisted of PET, BPA-PC, and PLA, achieving 97% conversion or higher for each polymer [22]. The authors screened various single and dual catalysts to achieve the desired selectivity in each depolymerization step.

Dissolution-based recycling methods offer the recovery of single polymer components from plastic waste [23]. In this case, solvents are employed to selectively separate materials of interest from a single stream. Many solvents have been disclosed in the literature and in patents for most common polymers found in plastics produced today [24]. These dissolution-based processes do not break down the polymer chains and have shown advantages over chemical recycling in terms of energy requirements and potential environmental impacts [3, 16]. The Solvent-Targeted Recovery and Precipitation (STRAP) is one dissolution-based approach that can process different types of plastic waste, including plastic multilayer films and disposable facemasks, guided by thermodynamic calculations of polymer solubility [25-29]. The STRAP method has been demonstrated to recover up to 5 different polymeric components from a single, clean, post-industrial waste steam [26]. The materials contained polymers like polyethylene (PE), ethylene vinyl alcohol (EVOH), polyethylene terephthalate (PET), ethylene vinyl acetate (EVA), and glycol-modified polyethylene terephthalate (PETG). Polymer separation by dissolution can be an effective way of processing MPW, if selective solvents can be found for each polymer of interest.

In this chapter, STRAP was applied to recover different constituent polymeric materials from a post-industrial MPW stream. Our computational and experimental tools allowed us to develop a series of steps to selectively separate 10 different polymers by selective dissolution, both with physical mixtures and MPW. The polymers considered in this study were PVC, PS, LDPE, HDPE, PP, EVOH, PET, polyamide 6 (PA6), PA66, and PA6/66.

5.2 Materials and Methods

5.2.1 Materials

The resins used in this study were: LDPE 608A, EVOH EV3251, PET DAK 9921, PA6 B36, PA66 Zytel FG42A, and PA6/66 Ultramid C40L. The PP, HDPE, PS, and PVC were received from Sigma-Aldrich. The solvents in this study were also received from Sigma-Aldrich: toluene, DMSO, gamma-valerolactone, tetrahydrofuran (THF), 1,2-propanediol, formic acid, and o-xylene

5.2.2 Experimental procedure

A 250 mL round bottom flask connected to a reflux condenser with a cold-water supply line was used for the STRAP experiments. The round bottom flask, which would contain the corresponding solvent and solids, was partially submerged in a 1500 mL dish containing silicone oil as a heat transfer fluid. The system was heated to the desired dissolution temperature with an electric heat plate equipped with a magnetic stir drive and the stirring rate was adjusted to have constant mixing. We experimentally assessed the recovery of each polymer from the feed by performing the following processing steps: (1) dissolving the specific polymer in the selected solvent, then separating the solubilized polymer from the rest of the polymers via mechanical filtration, (2) reducing the solvent temperature and/or adding an antisolvent to precipitate the dissolved polymer, and (3) separating the precipitated polymer from the solvent via mechanical filtration. These steps were repeated for each of the targeted polymers in the mixed plastic waste (MPW). The recovered polymers were dried in a vacuum oven for 1 hour at 100 ℃ to remove residual solvents.

5.2.3 Computational methods

We evaluated polymer solubility computationally to help the solvent screening and temperature selection of the STRAP process. Following our previous work, we used conductor-like screening model for realistic solvents (COSMO-RS), a combined quantum chemical and statistical mechanical approach to calculate temperature-dependent polymer solubilities in various solvent systems [30-33]. As shown in Figure 5.1, COSMO-RS represents each molecule based on the screening charge density that arises at molecular surfaces due to polarization of the medium. Such screening charge density profiles were obtained from density functional theory calculations of our previous work [31]. We approximated the profiles of polymer molecules by oligomer structures with deactivated terminal groups [34]. The workflow established in our previous work can be easily adapted by using different reference inputs, so that resin-specific polymer properties can be addressed with minimum number of calculations.

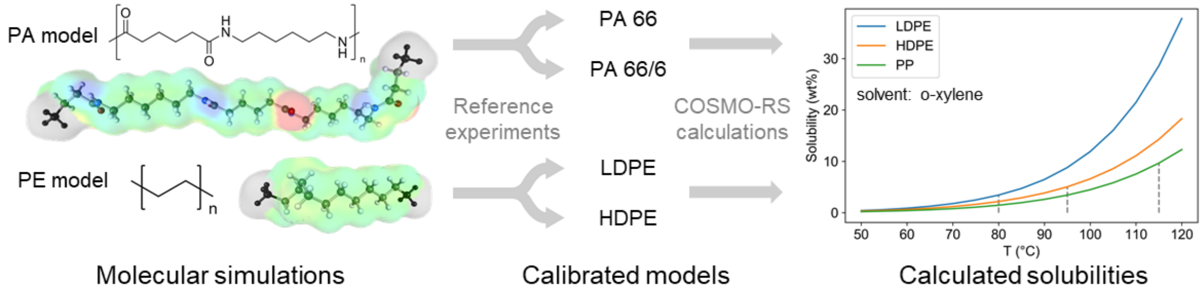


Figure 5.1 Computational methods for polymer solubility prediction. Left: example COSMO-RS screening charge distributions (colored surface) of PE and nylon models. Oligomer molecules with end groups neglected (gray surface) are used to represent longer polymer chains. Middle: the same molecular model can be calibrated with different reference experimental data to represent different materials (e.g. PE model for LDPE and HDPE, PA model for PA 6 and PA 66). Right: example calculation results of temperature-dependent solubilities of LDPE, HDPE, and PP in o-xylene. Dashed lines refer to selected temperatures in experiments.

COSMO-RS solubility calculations were performed by COSMOtherm 19 with the parameterization BP_TZVP_19 [30, 35]. In this work, HDPE calculations use the PE molecular model with a reference input of 16.2 wt% in dodecane at 120 °C. PA 66/6 calculations use the PA 66 model with a reference input of 9.1 wt% in DMSO at 135 °C. Note that PA 66/6 is a random copolymer with typical composition of 90% PA 66 and 10% PA 6, thus we employed the PA 66 model as an approximation [36]. Calculations of all other polymers use the same parameters as our previous work [31].

5.2.4 Characterization methods

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize the MPW feedstock and the separated polymer fractions from the STRAP process and compare their spectra to virgin resins. The instrument was a Nicolet TM iS50 spectrometer with a liquid nitrogen cooled MCT detector. In a typical measurement, 128 scans were averaged with a 4 cm^{-1} resolution and range from 4000-400 cm^{-1}. The thermal properties of the recovered polymer fractions were analyzed with a TA instruments Q100 differential scanning calorimeter (DSC).

5.3 Results

5.3.1 Characterization of the mixed plastic waste (MPW) feed

The MPW in this study was collected and shredded from different plastic packaging manufacturers. By visual inspection, there were plastic, metal, and carboard components in the feed (Figure 5.2(a)). To understand which polymers were present in the post-industrial MPW, an initial analysis was done with infrared spectroscopy (FTIR). As seen in Figure 5.2(b-d), the feedstock contained possibly PE, PET, and polyamides (PA) from three separate measurements. Since the MPW was collected from multiple manufacturers in the packaging industry, the presence of multilayer films was considered. Optical microscopy images were taken of the plastic components within the MPW, and this provided evidence of multilayer films (Figure 5.2(e)). This gave indication that some of the components might not be separated by just mechanical methods, and thus an alternative would be needed for their recovery and recycling. The recovery of the plastic components within the MPW could be achieved by selective polymer dissolution. Since the actual composition of the MPW was unknown, a model physical mixture containing 10 common packaging polymers was used to develop each STRAP step. The polymers in the physical mixture were LDPE, HDPE, EVOH, PA 6, PA6/6, PA 6/66, PP, PET, PS, and PVC. Our computational tools allowed us to predict solubility values for each polymer in solvents of interest, solvents that were already disclosed in the literature for each polymer were also considered [24].

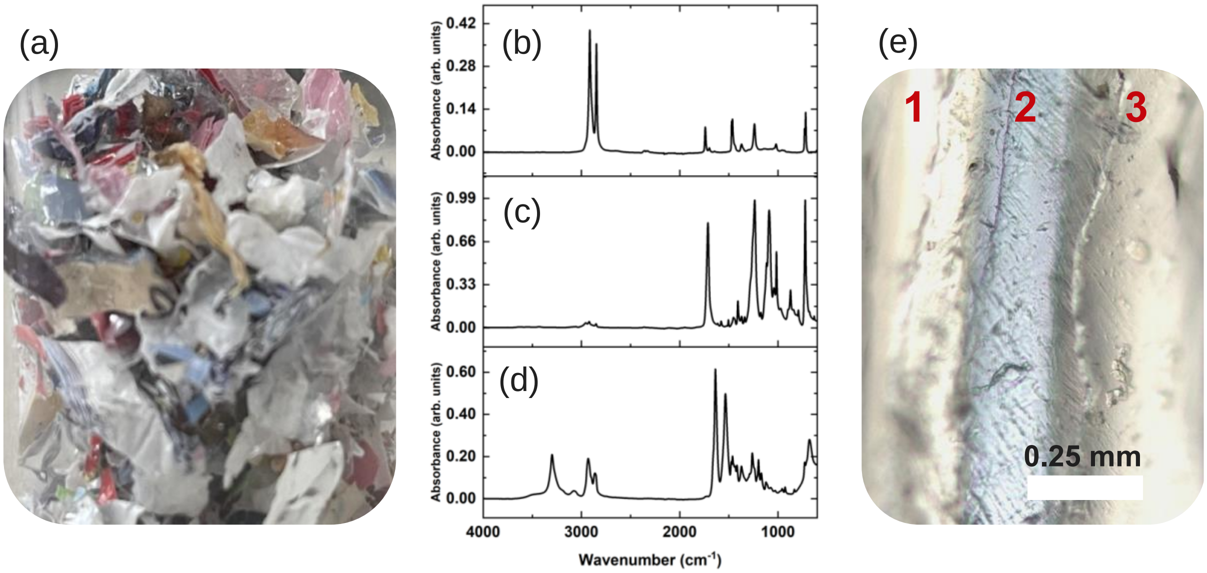


Figure 5.2 Characterization of the post-industrial mixed plastic waste (MPW). (a) MPW feed, (b) IR of one sample indicating PE, (c) IR of one sample indicating PET, (d) IR of one sample indicating PA, and (e) optical microscopy image of one sample indicating the presence of multilayer plastic components.

5.3.2 Developing the 10 STRAP steps with a polymer physical mixture

The COSMO-RS calculation results and experimental demonstrations were used to identify potential solvent candidates for selective polymer dissolutions in each step and to determine the optimal separation sequence of the 10 polymers. In general, polymers like PS and PVC can be dissolved at relatively low temperatures in different solvents [37-40]. For this reason, these two polymers were selected for the first two steps in STRAP with the 10-component physical mixture. For example, toluene, tetrahydrofuran (THF), and styrene have been previously identified as good solvents for PS [31]. Solubility calculations in these solvents show that toluene has excellent selectivity for PS at a low temperature. Therefore, toluene at 35 °C was selected as the solvent for PS, and this dissolution was placed as the first in the separation process. Since THF was predicted to only have a high solubility with PVC at its boiling temperature, this was selected as the second step (Table 5.1). It is preferred to achieve the polymer precipitation via a reduction in temperature since this has economic and environmental benefits [26, 41]. However, both PVC and PS required the addition of an antisolvent for their respective precipitation after the dissolution. Following these first steps, one difficult separation to achieve with dissolution is between polyolefins like PE and PP, due to their similar structures. In previous studies, PE and PP have been effectively separated by chromatographic methods and gravity separation and ozonation [42, 43]. Normally, when it comes to separation by dissolution, the same solvents can dissolve both and different temperatures can be used to achieve the desired separation. For example, p-cymene can dissolve both PE and PP at 95 and 120 °C, respectively. Other solvents like toluene, xylene, and tetrahydrofuran (THF) have been disclosed to be selective for PP, LDPE, and HDPE at different temperatures, ranging from 50 to 160 °C [44]. In our 10-step system, o-xylene was selected for the sequential dissolution of LDPE, HDPE, and PP at different temperatures. According to our solubility predictions, o-xylene can target LDPE, HDPE, and PP at 80, 95, and 115 °C, respectively; in steps 3, 4 and 5 in STRAP (Table 5.1).

An important parameter in polymer dissolution that needs to be considered is the molecular weight since an increase in molecular weight decreases dissolution rates [23]. Tougher polymers with higher molecular weight distributions will require elevated temperatures for their proper dissolution in STRAP and if multiple polymers have comparable molecular weights these might be more challenging for a selective dissolution. After the dissolution steps for the polyolefins, in step 6, EVOH was dissolved in a 60% DMSO-40% water (v/v) mixture, which has been used effectively for STRAP with other materials like rigid and flexible multilayer packaging films in the recovery of EVOH [26, 28].

Table 5.1 COSMO-RS predicted polymer solubilities for each STRAP step at the specified temperature.

Step	Solvent	T (°C)	Polymers and their solubilities (unit: wt%, bolded values are target polymers)									
			PS	PVC	LDPE	HDPE	PP	EVOH	PA66/6	PET	PA6	PA66
1	toluene	35	**5.72**	1.12	0.13	0.11	1.74	0.00	0.01	0.01	0.00	0.00
2	THF	67		**19.10**	2.09	1.45	2.88	1.12	1.33	0.99	0.52	0.26
3	o-xylene	80			**3.43**	2.17	1.46	0.01	0.14	0.18	0.12	0.03
4	o-xylene	95				**5.04**	3.42	0.04	0.39	0.53	0.35	0.09
5	o-xylene	115					**9.65**	0.33	1.29	1.88	1.23	0.33
6	DMSO/water	95						**7.67**	0.03	0.00	0.01	0.00
7	1,2-PDO	125							**3.35**	0.05	2.17	0.92
8	GVL	160								**12.45**	7.71	4.14
9	DMSO	145									**8.41**	3.56
10	formic acid	90										**16.90**

Another difficult separation is for the three PAs in the physical mixture: PA6, PA66, and PA66/6. Common solvents that have been used for the dissolution of PAs are DMSO and formic acid, along with diols [45, 46]. To support solubility predictions, these solvents were tested experimentally to observe potential dissolutions and determine possible steps to dissolve each polyamide separately. As seen in Table 2, PA6 was only soluble in DMSO and formic acid, at 145 °C and 60 °C, respectively. PA66 was only soluble in formic acid at 60 °C, and PA 66/6 was soluble in DMSO at 145 °C, 1,2-propanediol at 125 °C, and GVL at 160 °C. Based on these observations, the steps to achieve selective dissolution of the different PAs in the physical mixture were: PA66/6 dissolution in 1,2-propanediol at 125 °C, PA6 dissolution in DMSO at 145 °C, and PA6 dissolution in formic acid at 60 °C. The solubility predictions for these steps indicated preferential dissolution for each PA (Table 5.2). The last polymer in the 10-component physical mixture was PET and solvents like GVL, NMP, and DMSO have been used for this purpose [25, 47, 48]. To ensure optimal selectivity, the PET was dissolved before PA6 and PA66, at 160 °C in GVL.

Table 5.2 Experimental solubility of PA6, PA 66, and PA6/66 in different solvents. Green is soluble and red is not soluble, at the specified temperature.

Solvent	**Temperature (°C)**	**PA 6**	**PA66**	**PA66/6**
DMSO	145	🟩 2	🟥	🟩
60% DMSO-40% water (v/v)	95	🟥	🟥	🟥
2-propanol	80	🟥	🟥	🟥
1-butanol	100	🟥	🟥	🟥
1,2-propanediol	125	🟥	🟥	🟩 1
formic acid	60	🟩	🟩 3	🟥
GVL	160	🟥	🟥	🟩

After the solvent selection for each step, the process was demonstrated with the 10-component physical mixture. Table 5.3 shows the results for the recovery of the polymers after each step in STRAP, and this was 89% or higher for each polymer. This recovery confirms the separation of one component per step. This was further confirmed with the FTIR of each recovered fraction, which was for the most part comparable to the pure polymer before STRAP (Figure 5.3). As seen in Figure 5.3(h), the only polymer that presented possible cross contamination after STRAP was PET. Additional peaks were detected after 3000 cm^{1}, one of these pertaining to N-H stretch at around 3300 cm^{-1} which is characteristic of PA [49]. These peaks indicate contamination of the PET with a residue of PA66/6 from the previous step, since that polymer is also soluble in GVL at 160 °C. The rest of the recovered polymers showed comparable IR signatures to the corresponding pure polymers.

Table 5.3 STRAP steps for the recovery of 10 common packaging polymers from a physical mixture.

Step	Polymer	Solvent	Temperature (°C)	Dissolution time (hr)	Antisolvent	Recovery (wt%)
1	PS	Toluene	35	0.5	IPA	89.06%
2	PVC	THF	67		IPA	93.16%
3	LDPE	O-xylene	80			90.84%
4	HDPE	O-xylene	95			92.30%
5	PP	O-xylene	115			97.61%
6	EVOH	60% DMSO-40% water (v/v)	95	1		90.60%
7	PA66/6	1,2-PDO	125			99.30%
8	PET	GVL	160			106.72%**
9	PA6	DMSO	145			99.13%
10	PA66*	Formic acid	70	/		97.03%

*PA66 was recovered as residue from the physical mixture

**Solvent retention

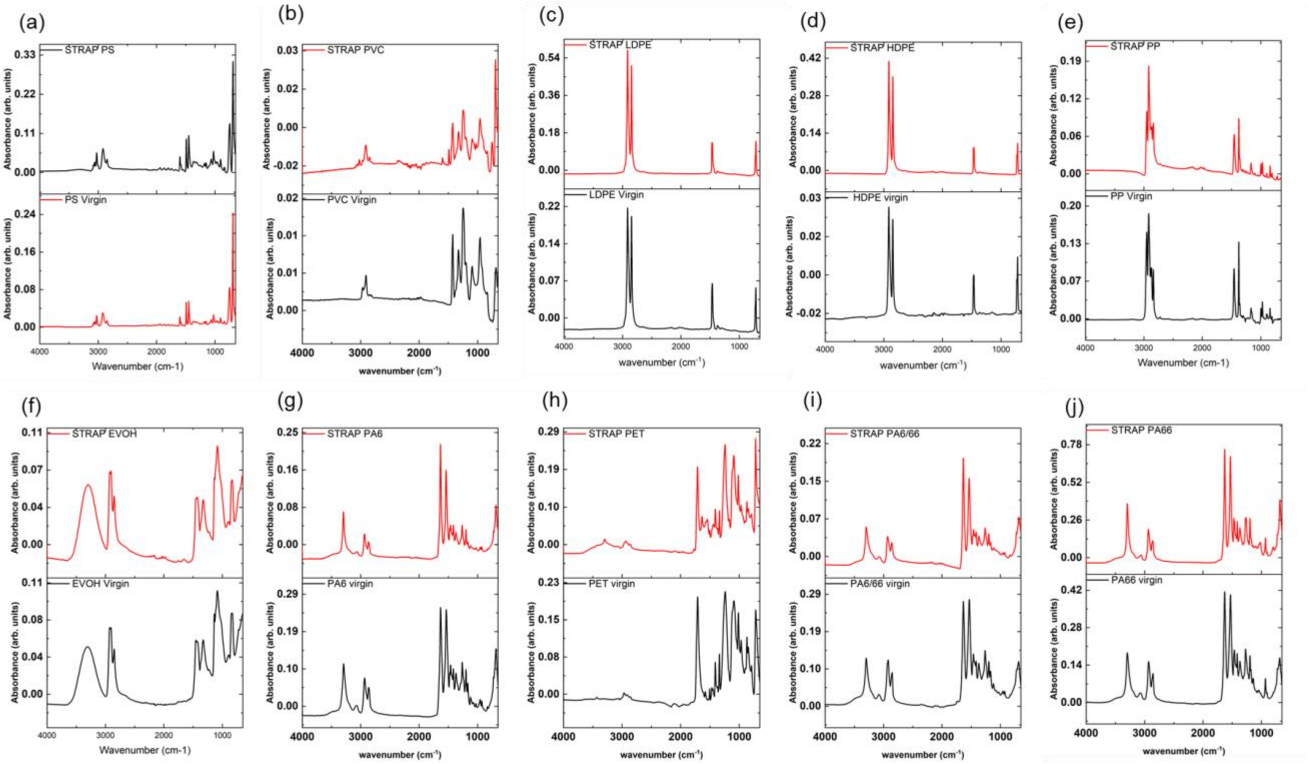


Figure 5.3 IR spectra of the recovered STRAP polymers from the physical mixture (in red) and the virgin polymers (in black): (a) PS, (b) PVC, (c) LDPE, (d) HDPE, (e) PP, (f) EVOH, (g) PA6, (h) PET, (i) PA6/66, and (j) PA66.

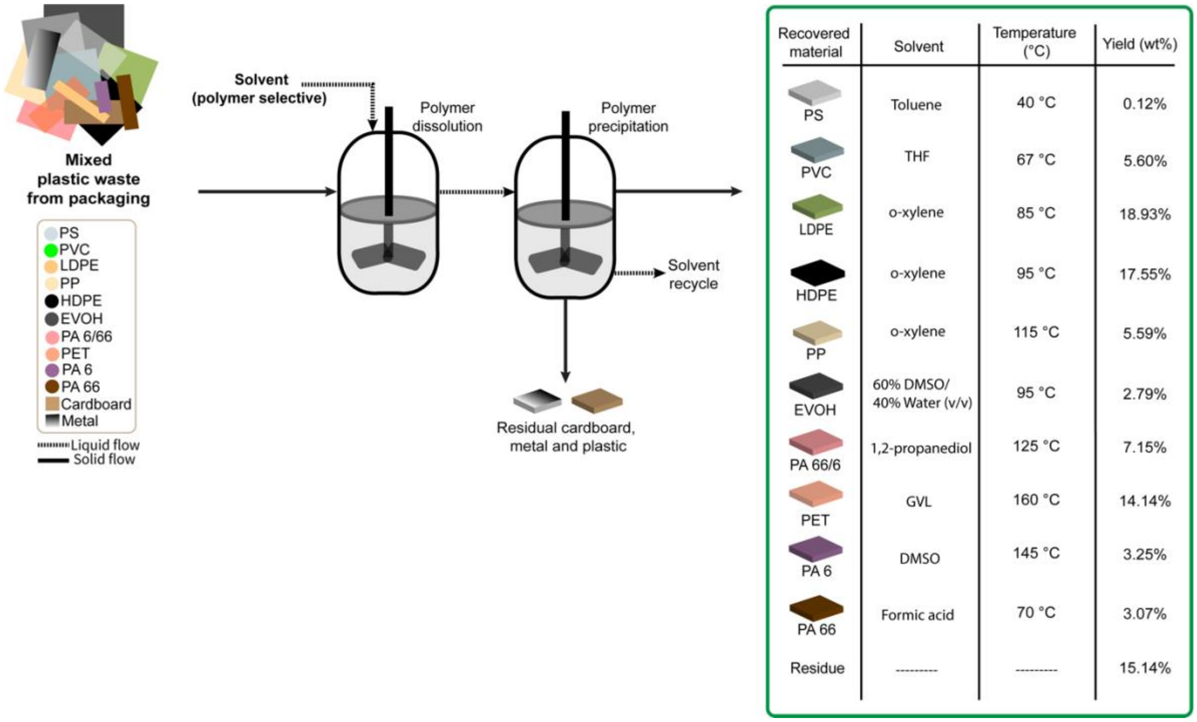
The thermal properties of each resin were analyzed with DSC to determine any changes after their recovery by STRAP. As seen in Table 5.4, the melting ($T_{m,2}$) and crystallization temperatures ($T_{c,2}$) of the polymers before and after STRAP were comparable. One noticeable difference was found in the melting temperature of the PET resin after STRAP, possibly correlating with the contamination of PA 66/6. In our previous studies, dissolution-based processes like STRAP did not significantly affect the thermal properties of the recovered polymers.

Table 5.4 Thermal properties of the polymers before and after STRAP.

Step	**Polymer**	**Before STRAP**		**After STRAP**	
		$T_{m,2}$ (°C)	**$T_{c,2}$** (°C)	**$T_{m,2}$** (°C)	**$T_{c,2}$** (°C)
1	PS	107.29	103.20	110.76	108.25
2	PVC	86.19	82.16	90.40	82.42
3	LDPE	111.24	99.73	110.89	97.58
4	HDPE	128.4	111.57	127.02	114.68
5	PP	163.51	116.94	160.71	115.23
6	EVOH	183.42	153.56	178.92	154.27
7	PA 66/6	188.72	123.21	185.15	137.87
8	PET	242.21	154.31	221.91	145.91
9	PA 6	221.76	159.49	212.24	169.78
10	PA 66	258.98	213.70	260.97	228.70

5.3.3 Demonstration of STRAP with the post-industrial mixed plastic waste (MPW)

The 10 dissolution steps that were developed with the physical mixture targeting PS, PVC, LDPE, HDPE, PP, EVOH, PA66/6, PET, PA6, and PA66, were applied to the post-industrial MPW of interest. Figure 5.4 shows the yields of each fraction recovered from the 10 STRAP steps. Majority components recovered were LDPE, HDPE, and PET.



Recovered material	Solvent	Temperature (°C)	Yield (wt%)
PS	Toluene	40 °C	0.12%
PVC	THF	67 °C	5.60%
LDPE	o-xylene	85 °C	18.93%
HDPE	o-xylene	95 °C	17.55%
PP	o-xylene	115 °C	5.59%
EVOH	60% DMSO/ 40% Water (v/v)	95 °C	2.79%
PA 66/6	1,2-propanediol	125 °C	7.15%
PET	GVL	160 °C	14.14%
PA 6	DMSO	145 °C	3.25%
PA 66	Formic acid	70 °C	3.07%
Residue	---------	---------	15.14%

Figure 5.4 Solvent-targeted recovery and precipitation (STRAP) with post-industrial mixed multilayer waster (MPW) from packaging waste.

5.4 Conclusions

Selective polymer dissolution can be an effective way to recover different components from plastic waste mixtures. This was demonstrated by STRAP with physical mixtures containing LDPE, HDPE, PS, PVC, EVOH, PET, PP, PA6, PA66, and PA 66/6, in which a sequence of steps were developed for their individual recovery. Our computational tools allowed us to predict solubility values for the targeted polymers and guide our solvent selection and experimental conditions for each step. This process was then demonstrated with a post-industrial mixed plastic waste (MPW) and LDPE, HDPE, PET, EVOH, and PA66/6 were successfully recovered. In a real scale process, this method can be used to determine approximate compositions of the plastic waste feed and reduce the number of steps to only recover the main components. Additionally, it can be used to separate polymers of interest as a pretreatment for other recycling technologies. Future work will focus on applying this methodology to post-consumer mixed plastic waste and further characterizing the fractions recovered from the MPW.

5.5 References

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Chapter 6. Accumulation of plastic additives in post-STRAP solvents

6.1 Introduction

Plastics are not just the polymer component, but a mixture of the polymer with additives that are included in the formulation for different purposes. Plastic additives provide the necessary functional properties to the final plastic product, and these include plasticizers, flame retardants, lubricants, slip agents, pigments, and thermal stabilizers [1, 2]. Plastics can also contain residual processing aids and unreacted monomers from the polymerization process [2]. One prominent additive, plasticizers, can be found in the rage of 10 to 70% (w/w) in a single plastic [1, 3]. Plasticizers aid in the processability of different polymers, lowering the viscosity, and enhancing the overall stability [4]. Common plasticizer groups are phthalates, adipates, and benzoates [1]. Following plasticizers, flame retardants (brominated compounds) can make up to 25% (w/w) and fillers (calcium carbonate, talk, zinc oxide) can make up to 50% (w/w) of the plastic [1].

All these plastic additives are beneficial for the final plastic product, however, there are concerns regarding their migration and response to different recycling methods. Plastic additives can leak during use to the environment, can release during mechanical recycling or incineration, and can leach to water supplies after landfilling. If the additives can’t maintain their stability and compatibility during the mechanical recycling process, these can degrade and further diminish the properties of the recycled plastic [5]. Mechanically recycled plastics can contain additive degradation products from slip agents, lubricants, and antioxidants [6]. During chemical recycling processes, the target is usually the conversion of the main polymer and normally little attention is paid to the other components that might be present, including additives. In a study by Jerdy et al., the effect of different additives on the pyrolysis and catalytic decomposition of polyethylene (PE) over zeolites. The additives the authors studied were an amine light stabilizer, antioxidants, and an acid scavenger. They found that these can winder the reaction rates due to various reasons, including exchange with catalytic sites and competitive adsorption over an acid catalyst [7]. Their study demonstrates the importance of considering plastic additives and impurities whenever chemically converting them since it can dictate the process design and parameters, if the additive concentration is high enough. Plastic additives can also be removed via dissolution or purification recycling processes. These approaches use solvents to selectively dissolve the polymer or the impurity and achieve the desired separation. Ügdüler et al. published a comprehensive review on the use of different solvents for the extraction of additives for plastics [8]. Antioxidants, brominated flame retardants, stabilizers, lubricants, and phthalates have been removed using various solvents. This demonstrates the promising applicability of solvents for this purpose, potentially serving as a pretreatment for other recycling technologies in which additive or impurity content is a sensitive parameter.

The Solvent-Targeted Recovery and Precipitation (STRAP) is a dissolution-based process that has been demonstrated for the recovery of various polymeric components from rigid multilayer films, flexible multilayer films, and disposable facemasks [9-11]. In this Chapter, we looked at the removal of plastic additives from a number of virgin resins by the STRAP method. The main objective was to gain an understanding on how the additives or impurities build up in the solvent, how can this potentially have an effect over the solvent recyclability and ultimately the polymer properties.

6.2 Materials and methods

6.2.1 Materials

The polymer resins (LDPE, HDPE, PET, PA6, PA66) were received from Amcor. The PS and PP resins were received from Sigma-Aldrich. The solvents toluene, gamma-valerolactone, and dimethyl sulfoxide (DMSO) were received from Sigma-Aldrich.

6.2.2 Experimental procedure

The virgin resins (LDPE, HDPE, PP, PET, PS, PA6) were dissolved in their respective solvents to simulate the STRAP process. As seen in Figure 6.1, the polymer and solvent were combined in a 250 mL round bottom flask that was connected to a reflux condenser with a cold-water supply line. The round bottom flask, which would contain the corresponding solvent and solids, was partially submerged in a 1500 mL dish containing silicone oil as a heat transfer fluid. The system was heated to the desired dissolution temperature with an electric heat plate equipped with a magnetic stir drive and the stirring rate was adjusted to have constant mixing. The following processing step were performed for solvent collection after polymer dissolution: (1) dissolving the specific polymer in the selected solvent, then separating the solubilized polymer from the rest of the polymers via mechanical filtration, (2) reducing the solvent temperature and/or adding an antisolvent to precipitate the dissolved polymer, and (3) separating the precipitated polymer from the solvent via mechanical filtration. The solvent that was recovered after the mechanical filtration as analyzed with gas chromatography mass-spectrometry (GCMS) and high-temperature gas chromatography with a flame ionization detector (GC-FID).

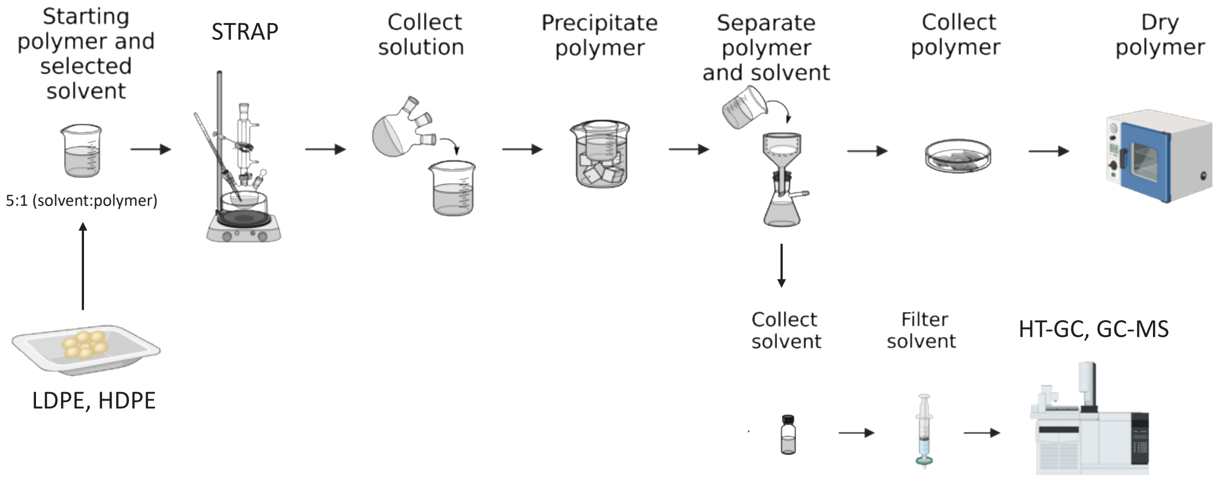

Figure 6.1 Experimental procedure for solvent collection and analysis after polymer dissolution in STRAP.

6.2.3 Adsorption experiments

Two different adsorbents, activated carbon and silica gel, were used for the removal of plastic additives from solvents used in STRAP. Various amounts of the solids (5, 10, 20, 30, 40 and 50 g) were mixed for 25 minutes with toluene containing diethylene glycol dibenzoate (DGD) plasticizer to observe its potential removal from the solvent.

6.2.4 Solvent characterization

The recovered solvents after STRAP were analyzed with gas chromatography-mass spectroscopy (GCMS) to detect species that accumulate in the solvents after STRAP. A Shimadzu GCMS-QP2010 with a DB-5 column (Agilent) at a maximum temperature of 310 °C was used, with helium as the carrier gas. The linear-chain alkanes were quantified with a Shimadzu GC-FID equipped with an MXT-1HT column at a maximum temperature of 415 °C, with hydrogen as a carrier gas.

6.3 Results

6.3.1 Solvent characterization of post-STRAP solvents used for HDPE and LDPE dissolution

Our initial analysis targeted pure polymer resins to observe any solvent buildup of impurities after polymer dissolution in STRAP. In Figure 6.2, we compare the GC chromatogram of pure toluene, toluene after LDPE dissolution, and toluene after HDPE dissolution. It was observed that after a single LDPE dissolution there was accumulation of PE oligomers (short-chain linear alkanes) in the range of C9 to C35 remained in the solvent. The presence of these alkanes could be from unreacted monomers after the polymerization process [2]. Removal of these short-chain oligomers caused an increase of the number-average molecular weight (M_N) and a decrease in the dispersity index (PD) of the LDPE after STRAP, suggesting a narrower molecular weight distribution [12]. In addition to this, a plasticizer, diethylene glycol dibenzoate (DGD) was also detected in the solvent. This plasticizer is commonly found in polymer resins as a substitute to phthalates, which is the most common class of plasticizers [13]. DGD happens to be an environmentally friendly plasticizer that has benefits in its good compatibility, low volatility, resistance to oil, water, and light [14]. Removal of the plasticizer from the LDPE would cause an effect in its properties, particularly an increase in its viscosity. This emphasizes the need for a potential reintroduction of plasticizers to polymers after STRAP, if they were removed in the polymer dissolution step. This would guarantee that STRAP polymers have comparable properties to the starting polymers. Lastly, fluorinated compounds were detected in the toluene after LDPE dissolution, most likely per- or polyfluoroalkyl substances (PFAS) that would be present in the virgin polymer to provide stability or serve as processing aids during polymer production [15]. Our GC-MS method was able to identify the presence of fluorinated compounds but could not discern between specific structures. Similarly, the toluene sample after HDPE dissolution also showed the presence of short-chain PE oligomers, with the possibility of having chains longer than

C40. The diethylene glycol dibenzoate or the fluorinated substances were not detected in the toluene after HDPE dissolution; however, an antioxidant BKF was observed in the solvent. The presence of plastic additives in the toluene will depend on the affinity of the plastic additive to stay in solution and the initial composition of the resins that are considered for the dissolution process. Additional methods will be required to characterize non-volatile components and have a complete analysis on additive accumulation in the solvents.

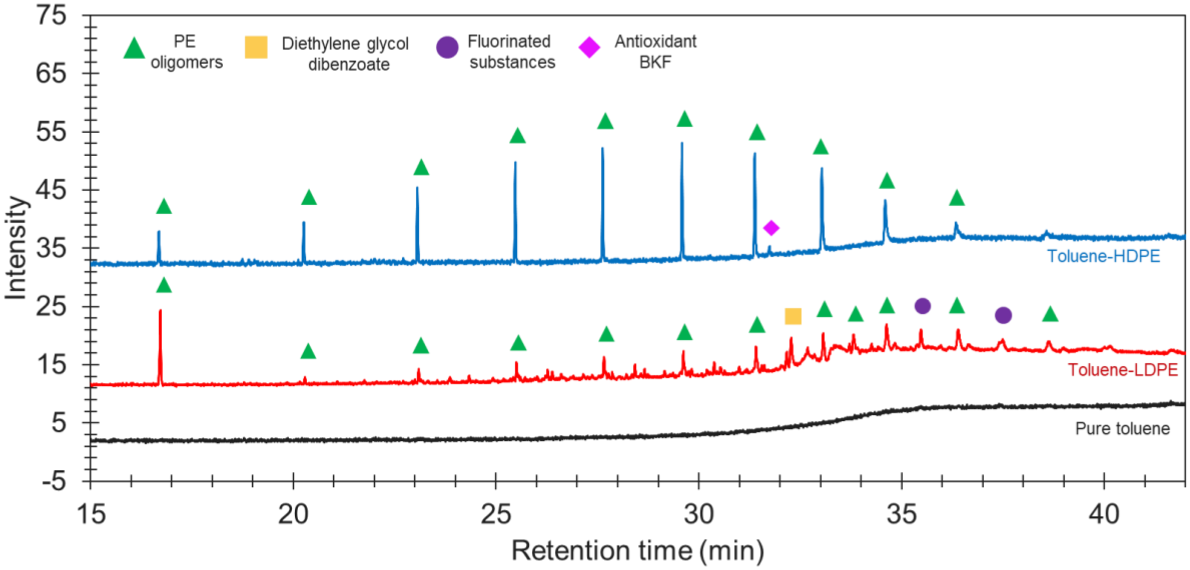

Figure 6.2 Chromatogram of pure toluene (in black), toluene after LDPE dissolution (in red), and toluene after HDPE dissolution (in blue).

6.3.2 Quantification of linear alkanes and diethylene glycol dibenzoate

The toluene samples recovered after each polymer dissolution were analyzed with GC-FID to quantify some of the components that were detected in the post-STRAP solvents. As was discussed in the previous section, three major compounds were detected in the toluene after LDPE dissolution. Short-chain PE oligomers, in the range of C9 to C35, remained in the solvent with concentrations from 5 to 32 PPM when the ratio of solvent to polymer is 1:5 in STRAP. These concentrations increase as the solvent is reused in STRAP. As seen in Table 6.1, after two solvent uses for LDPE dissolution, the PE oligomer concentration is present in the range of 6 to 52 ppm, and more carbon numbers are detected. After 3 uses, the concentrations ranged from 20 to 100 pm. At the lab scale, these concentrations do not affect the reusability of the solvent for polymer dissolution. However, in larger scale systems this needs to be taken into consideration to ensure optimal dissolution performance and avoid significant buildup of these oligomers in the solvent and the equipment. For this reason, solvent purification systems should be put in place, from a process design point of view. The DGD plasticizer concentration was also quantified in the toluene after one LDPE dissolution, and it was found to have a 16.8 ppm concentration in the solvent. The toluene after HDPE dissolution had linear chain alkanes in the range of C16 to C40, with concentrations in the solvent from 6 to 110 PPM.

Table 6.1 Concentration of linear alkanes (PE oligomers) in toluene after sequential dissolutions of LDPE in STRAP.

Linear alkane number	**Concentration in toluene-LDPE (PPM)**		
	1 Use	**2 Uses**	**3 Uses**
C15	-	13.6	19.9
C16	-	-	12.7
C20	5.6	13.8	20.5
C22	8.2	22.9	37.7
C23	-	16.7	26.7
C25	-	35.0	35.6
C26	19.2	35.0	63.9
C27	-	21.2	39.7
C28	21.0	29.4	61.0
C29	12.3	13.5	48.2
C30	10.3	19.4	46.1
C31	7.9	31.2	87.0
C32	9.5	13.2	27.7
C33	12.9	`6.7	36.1
C34	12.9	17.3	96.3
C35	31.7	25.6	52.3
C37	-	-	30.9
C38	-	51.6	106.4

6.3.3 Solvent characterization of post-STRAP solvents used for the dissolution of PP, PS, PET, PA6, and PA66/6

Following our work with LDPE and HDPE, we aimed at analyzing the solvents that were used to dissolve PP, PS, PET, PA6 and PA 66/6. Table 6.2 summarizes the solvent to polymer ratios and the major components detected in the solvent by GCMS. In most cases, residual monomers, solvent impurities, and plastic additives were found.

Table 6.2 Major components detected in different solvents after polymer dissolution and precipitation in STRAP.

Polymer	Solvent	Solvent to polymer ratio	Major components identified in solvent
HDPE	Toluene	5:1	PE oligomers, antioxidants
PP	Toluene	5:1	PP oligomers
LDPE	Toluene	5:1	PE oligomers, plasticizers, fluorinated substances
PS	Toluene	5:1	(2, 3-Diphenylcyclopropyl)methyl phenyl sulfoxide, trans-
PET	GVL	12:1	Propanoic acid Pentanoic acid, 4-oxo-, acetic acid 2(3H)-Furanone, dihydro-5-methyl-5-(2-methylpropyl)-
PA6	DMSO	10:1	Caprolactam, dimethyl sulfone, 2(3H)-Furanone, dihydro-5 methyl
PA66/6	DMSO	12:1	Caprolactam, dimethyl sulfone

6.3.4 Adsorption of diethylene glycol dibenzoate plasticizer

Diethylene glycol dibenzoate (DGD) is a plasticizer present in different plastics . It was observed that this plasticizer can remain in the toluene after the LDPE has been dissolved and precipitated. The removal of the plasticizer from the resin can have effects on the polymer properties. Readdition of the plasticizer should be considered to achieve optimal performance with the recycled plastics. A concern is that repeated solvent use can increase the DGD concentration, and this compound would need to be removed from the solvent before it affects its efficiency for polymer dissolution. These studies were done using two adsorption solids, activated carbon and silica gel, for the removal of DGD in toluene with an initial concentration of 225 ppm. As seen in Figure 6.3(a), the DGD concentration decreased with an increase of activated carbon during mixing. For silica gel, this decrease was much more abrupt with an increase in the amount of solids, as seen in Figure 6.3(b). This provided evidence that adsorption would be a viable way of removing plasticizers that accumulate in the solvents after STRAP. Further optimization would be needed to understand adsorption isotherms and limitations to which components the solids can adsorb and remove form the solvents.

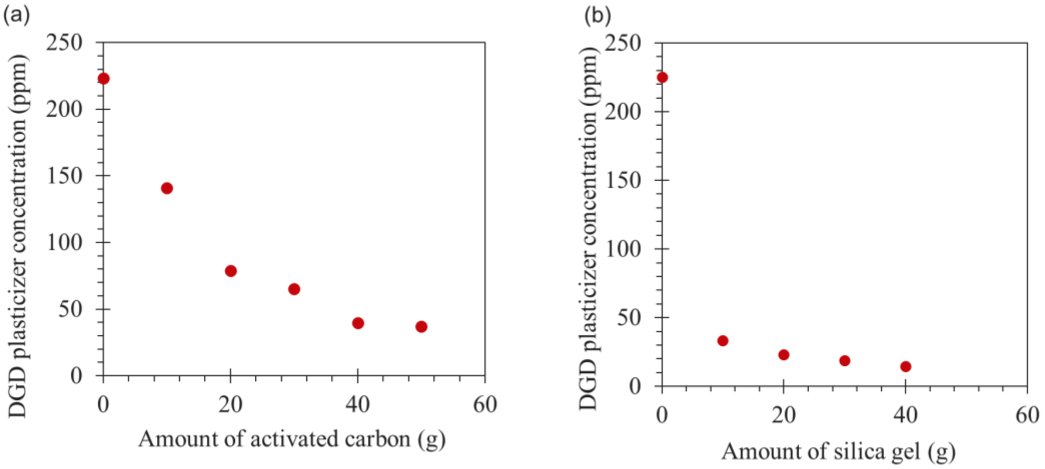

Figure 6.3 Removal of diethylene glycol dibenzoate from toluene using different amounts of solids for adsorption: (a) activated carbon and (b) silica gel.

6.4 Conclusions

Dissolution-based recycling approaches are of intertest for several reasons, one of them being a potential pathway for the removal of plastic additives or impurities during the recycling process. In this Chapter, an initial study was conducted to detect species that buildup in solvents after the STRAP process. It was observed that after the dissolution of polyolefins like LDPE and HDPE, some of the major substances that remain in the solvents were short-chain oligomers, plasticizers, antioxidants, and fluorinated compounds. Specifically for LDPE, a diethylene glycol dibenzoate (DGD) plasticizer was found in the solvent after STRAP. If the removal of plasticizers affects the plastic properties after recycling by dissolution-based methods, these should be readded to ensure optimal performance. It was determined that with sequential solvent use, the concentration of the short-chain oligomers increased. This would have implications regarding solvent efficiency and recyclability and needs to be considered with larger-scale STRAP processes for plastic recycling. Employing solids for adsorption is a viable option for solvent purification and our initial analysis demonstrated this with the removal of DGD plasticizer from toluene. Future work will focus on solvent characterization with plastic waste, removal of per- and polyfluoroalkyl substances (PFAS) with STRAP, and optimization of adsorption steps for impurity and color removal from solvents and polymers. Furthermore, other solvent characterization techniques like liquid chromatography mass-spectrometry (LC-MS), nuclear magnetic resonance (NMR), and combustion ion chromatography (C-IC) will be considered for a thorough solvent characterization after STRAP.

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Chapter 7. Conclusions and future directions

7.1 Conclusions

The Solvent-Targeted Recovery And Precipitation (STRAP) strategy can deconstruct multilayer films into their constituent resins with a series of solvent washes that are guided by thermodynamic calculations of polymer solubility. This process has been experimentally shown with rigid multilayer films, printed multilayer films, disposable facemasks, and mixed plastic waste. The thermodynamic computational tools have provided accurate solubility predictions for the polymers of interest, helping shape the STRAP process for all the above-mentioned plastic waste streams. The first demonstration of STRAP with clear rigid multilayer films proved its feasibility with post-industrial waste and potential economic benefits. However, as discussed in Chapter 2, the main cost drivers of the STRAP process were the distillation units needed for the separation of solvents and antisolvents for reuse in the process. We showed that the use of antisolvents in STRAP can be reduced by replacing them with solvents or solvent mixtures that enable a temperature-controlled polymer dissolution and precipitation. This was observed with our STRAP-B process which produced comparable yields of PE, EVOH, and PET, and was more efficient in the polymer separation than STRAP-A, while using less amounts of antisolvents. One challenge with any type of recycling technology is the heterogeneity of the plastic waste feed. This was considered in the STRAP process with a rigid multilayer film composed of PE, EVOH, PET, PETG, and EVA, as well as a printed multilayer film composed of PE, EVOH, PET, PU inks, and a PU binder. The latter was efficiently processed by STRAP in Chapter 3, in which efficient color removal from the PET was observed with GVL, after recovering the other polymer components, PE and EVOH. This was achieved after the computational modeling tools suggested polymer-selective solvents in the presence of the inks and for solvents to develop an ink removal step. The properties of the recovered polymers were comparable to the corresponding pure resins and the separation of these with STRAP could be economically feasible at a large scale and reduce environmental impacts when compared to the production of films from virgin polymers.

In a circular economy, recycled materials should find the same or similar applications as the original waste. This can ensure that the material maintains its value and it is not downgraded to other applications. This aspect was explored with STRAP in Chapter 4, where a PE recovered from packaging waste was produced back into a plastic film. Three methods were considered for the recovery of PE from a post-industrial printed multilayer film: a filter bag system, a Soxhlet extraction setup, and a jacketed dissolution vessel. These methods were considered to increase the production of PE for cast film production and allowed us to understand how various processing parameters can influence the properties of the films. The jacketed dissolution vessel provided improvements in color and removal of impurities from the PE. The solvent to plastic ratio proved to be an important parameter, where higher ratios reduced the buildup of impurities in the solvent. This study demonstrated that STRAP polymers can be recycled back into plastic films, enabling the potential circularity of these packaging materials.

To further expand the applicability of STRAP to more complex plastic waste feedstocks, in Chapter 5, a 10-step sequence was developed to separate common packaging polymers with our computational tools. The polymers included in this sequence were LDPE, HDPE, PP, PS, PVC, EVOH, PET, PA6, PA66, and PA66/6 and recoveries of 89% or higher were achieved in STRAP for each polymer in a model physical mixture. The sequence was later applied to a post-industrial mixed packaging waste and the main components recovered by selective dissolution were LDPE, HDPE, and PET. In a real scale process, this method can be used to determine approximate compositions of the plastic waste feed and reduce the number of steps to only recover the main components. Additionally, it can be used to separate polymers of interest as a pretreatment for other recycling technologies.

The post-STRAP solvents were characterized to determine the buildup of impurities after polymer dissolution and precipitation. In Chapter 6, it was found that after the dissolution of polyolefins like LDPE and HDPE, some of the major substances that remain in the solvents were short-chain PE oligomers, plasticizers, antioxidants, and fluorinated compounds. Since plasticizers and other processing aids are removed from the plastics after dissolution, the readdition of these should be considered if a deterioration in properties is observed. After sequential solvent use for LDPE dissolution, the concentration of the short-chain oligomers increased. Since solvent recyclability is an important parameter, both economically and environmentally, the buildup of these components needs attention specially with larger-scale STRAP processes to maintain solvent efficiency. Adsorption steps can be a viable option for the removal of impurities from post-STRAP solvents.

Overall, significant progress has been made with these findings in understanding the fundamentals and relevant process parameters in STRAP. Furthermore, our work has led to the development of accurate polymer solubility predictions with various computational tools, assessments of potential environmental and economic benefits, an understanding of solvent impurity buildup and removal, and a demonstration of recycling STRAP polymers back into films. Our team will continue working towards our objectives in conveying scientific principles with selective polymer dissolution and gaining an understanding of process design parameters to recycle current complex plastic waste feedstocks with STRAP.

7.2 Future directions

7.2.1 Removal of fluorinated substances from plastic waste

Per- or polyfluoroalkyl substances (PFAS) are additives widely present in different industries, including building and construction, electronics, automotive, coatings and paints, lubricants, and plastics [1]. Specifically for plastics, PFAS provide stability and serve as processing aids [2]. Since these molecules are very chemically stable, they can persist in ecosystems [3]. Additionally, PFAS have been found in humans and have been related to health issues [4]. For these reasons, there have been many efforts in developing novel ways for their removal from different environments. For example, PFAS have been removed from water via adsorption with activated carbon, ion exchange resins, proteins, or amine-containing sorbents [5-8]. Alternatively, PFAS can be chemically converted to other products. Trang, et al. demonstrated the mineralization of perfluoroalkyl carboxylic acids (PFCAs) at mild conditions to produce fluoride ions and carbon-containing by-products [9]. PFCAs can also be thermally decomposed [10]. In a different study, Jenness, et al. degraded PFAS with silylium catalysts. Additionally, PFAS can also be deconstructed via photo-chemical/catalytic oxidation/reduction or chemical reduction [11, 12]. Overall, PFAS degradation mechanisms can involve defluorination, head group cleavage, or unimolecular reactions [13].

In Chapter 6, post-STRAP solvents contained fluorinated substances after LDPE dissolution and precipitation. This polymer/PFAS separation could be a viable option for STRAP to be applied as a purification method in harmful additive removal. Future work will focus on using our computational framework to determine preferential polymer or additive dissolution., as well as experiments to demonstrate this separation. At the lab scale, STRAP can be conducted with known short-chain PFAS molecules and common polymers. Other additives of interest can be included in this study, like phthalates, to quantitively demonstrate that a dissolution process can efficiently separate these compounds from plastic waste. In our current PFAS characterization methodology, we are limited by the volatility of the molecules and detection limits with GCMS. Other characterization methods to consider are liquid chromatography-mass spectroscopy (LC-MS), high-resolution mass spectrometry (HRMS), combustion ion chromatography (CIC), inductively coupled plasma tandem mass spectroscopy (ICP-MS/MS), among others [14].

7.2.2 Adsorption of impurities in post-STRAP solvents

The solvents after STRAP can contain short-chain polymers, plasticizers, antioxidants, fluorinated substances, slip agents, and color components. Proper solvent reuse is important to ensure a dissolution-based recycling technology is economical and environmentally friendly. Further studies are needed in the sequential use of solvents in STRAP and the effect of impurity buildup on the solvent efficiency and process equipment. In Chapter 6, it was demonstrated that oligomers can accumulate in the solvent after sequential dissolutions and for this reason, quantitative studies need to be included with other impurities like plasticizers, PFAS, and color components. This will give us an insight into process performance and product properties with solvent reuse. So far, in Chapter 4, n-dodecane was used around 11 times for the recovery of PE from a printed multilayer film and no significant reduction in the PE recovery was observed. However, impurities were visibly present in the reused solvent.

The accumulation of impurities in the solvent raises concerns about the need for solvent purification. One option for this processing step is by distillation, however, this tends to be a very energy intensive separation. An alternative is by employing adsorption solids that can selectively separate the dispersed impurities in the solvent. Our initial study in Chapter 6, showed that this is a feasible step within STRAP, as was observed with the adsorption of diethylene glycol dibenzoate from toluene using activated carbon or silica gel. Adsorption is also of interested in the removal of color components from the solvents and plastics, since ideally, a colorless recycled plastic is preferred. In a recent publication, Van Melkebeke, et al. looked at the adsorption of an amino ketone-based red dye from PS solutions with activated charcoal [15]. In our work in Chapter 3 and 4, even after choosing a polymer-selective solvent in the presence of inks, there could still be color components present in the final polymer. Future work in STRAP will involve the addition of an adsorption step to purify our solvents and further remove color components that could hinder the final polymer aesthetics and properties. Adsorption of other common additives like flame retardants, titanium dioxide, and fillers like calcium carbonate can be included in the future goals [16]. This can be supported by incorporating our characterization techniques with GCMS, GC-FID, ICP, and including UV-Vis spectroscopy for color quantification.

7.2.3 Production of other plastic films with STRAP polymers and pilot-scale system support

Our recent efforts have focused on exploring the potential applications of polymers that were recovered by the STRAP process. In Chapter 4, we demonstrated that a PE from a printed multilayer film can be turned back into a plastic film and potentially be incorporated as a packaging material. In that study, a jacketed dissolution vessel provided improvements in filtration and optimized heating during the dissolution step. Further work will focus on designing a larger jacketed dissolution vessel that could process more plastic to increase the recovery of the target polymers in kg quantities. Different types of mixing, filter sizes, viscosity measurements, pressurization, and adsorption containers can be considered for a comprehensive analysis of the influence of these parameters on the final polymer properties. In this system, variables like impurity buildup after continuous solvent use, adsorption of impurities during dissolution, and proper filtration conditions can be studied. The procedure and handling in this system can be made more convenient by including a closed container for sample collection after dissolution and filtration. The materials recovered from this system can be grinded, extruded into pellets, and converted to different plastic products like films to understand their properties and potential applications. The learnings from this system will support the design and operation of the STRAP pilot system at Michigan Technological University.

7.3 References

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