Removing Carbon Black Pigment from ABS Material

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Abstract

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As we continue using plastics, the quantity of plastic waste also continues to pollute our land and oceans. To mitigate the plastic waste crisis, various firms are trying to recycle polymers. However, plastics often contain many additives and colorants, that pose additional challenges to recycling. Removing these contaminants is necessary to increase the polymer's recyclability and ensure that the recovered polymer still has economic value by restoring thermal and mechanical properties. Solvent extraction has shown promising results by removing some insoluble contaminants without altering the material's chemical and mechanical properties. This study will investigate the recyclability of ABS (acrylonitrile butadiene styrene) polymer and its contaminants' removal, especially Carbon Black (CB) pigments. A three step method has been developed and optimized using solvent, collector solvent, and anti-solvent. Ethyl acetate was chosen to solubilize ABS (step 1) and methanol and hexane to precipitate ABS (step 3). Deionized water was selected to successfully attract CB (step 2) thanks to hydrogen bonding. The results of the recovered ABS (46-75%), showed that both mechanical and chemical properties were similar to the initial ABS, through TGA, DSC, FTIR, and GPC analysis. Remarkably, color measurements assessed the removal of CB pigment with L values up to 62.7 (compared with 28.5 for the initial ABS). The separation process used in this work helped purify the recycled polymer by eliminating CB pigment. As a result, the recycled material is suitable for a wider range of applications.

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Chapter 1

Introduction

As plastic production continues worldwide, the plastic waste stream has continued to increase, causing environmental and health concerns for everyone. Single-use plastics have become a necessity in our everyday lives in the medical, pharmaceutical, food packaging, and electronics industries. Similarly, rapid prototyping and additive manufacturing also contribute to a large amount of waste, as numerous industries use plastics to test designs in a cost-effective and timely way. The global plastic production in 2019 was 460 million tonnes according to Our World in Data [1, 2], but only about 9% of plastic waste is recycled [2]. The remaining waste will go to incineration, landfill, or be shipped to underdeveloped countries. This global issue shows that the traditional waste management system is failing [1, 3]. Recycling is essential in conserving natural resources and protecting the environment by reducing the number of fossil fuels used to produce plastics [4], but various challenges are decreasing the economic value of recycled plastic [5]. For instance, even after sorting and separating the plastic wastes by their types, they have various colors. One common practice is to add extra pigments to meet the aesthetic needs of the customers [6]. However, this often ends up with recycled material being exclusively black in color; thus, most recycling industries can only guarantee their customer's black materials. Although there is already profit in recycling, a true circular economy can only be realized when the recycled plastics are free of pigments so that the recycling industries can profit from manufacturing all colors.

A popular plastic used is acrylonitrile butadiene styrene (ABS) [7] due to its high strength and durability. It is often categorized as recycling number 7 – other plastics, which will end up in landfills because of a lack of proper recovery methods. Inorganic carbon black (CB) pigment is often used in ABS plastic products, as new black goods, or in recycling to cover impurities of mixed colors in recycled materials. CB is commonly used for its high distribution rate in the polymer matrix. CB can also affect the performance and applicability in the next use of the recycled plastic [8, 9], thus being considered as a contaminant. Unfortunately, traditional recycling methods often degrade the polymer and do not concentrate on removing pigments from the polymer matrix [5]. The removal of contaminants will yield higher quality recovered plastics, and increase the recyclability, functionality, and profitability of the recycled plastic. A possible method to remove contaminants that limits degradation is the solvent-based extraction process, which involves dissolving the polymer in a solvent to make a solution and then recovering the polymer through precipitation [10, 11]. Techniques, such as filtration, membrane separation, or centrifugation, can then be performed after dissolution to remove the contaminants. This extraction process has been studied on high-density polyethylene (HDPE) [12], ABS [5, 13, 14], polystyrene (PS) [15] and several blends [16]. Unfortunately, there are no universal solvents that can dissolve or precipitate all the possible plastic types and the contaminant removal process usually requires multiple steps, which depends on the particle size and solubility of the contaminant. Our preliminary study found that although these methods work, the efficiency is low for CB removal.

The manufacturing of CB particles includes an oxidation treatment that allows the presence of functional groups (i.e. hydroxyl or carboxyl groups) [17]. These functional groups have polar hydrogen-oxygen bonds, permitting hydrogen bonding with other molecules [18]. This results in the following two phenomenons. First, CB particles have a complex structure, with a particle size that can be as small as 20 nanometers, the functional groups of the particles make them form chains that can form a structure ranging in size from 100 nanometers to a few micrometers. Filtrating contaminants with such a large size range is challenging. As well, the CB is physically and chemically bound to the ABS matrix [19]. Second, CB particles disperse very well in the solution after ABS completely dissolves in the solvent, and even centrifugation takes a long time since the density of CB is small [15, 20]. The functional groups make the CB particles insoluble and suspended in the dissolved solution. Based on this observation, we find that mechanical separation is not enough, and we propose adding a collector solvent before the precipitation process to carry the CB away from the dissolved ABS solution. The hypothesis is that the collector solvent will attract the CB particles through hydrogen bonding from the ABS solution.

To test this hypothesis, the best solvents and anti-solvents to dissolve and precipitate ABS were chosen by testing various solvents previously used in the literature [21, 22]. Secondly, the collector solvent was introduced into the solution before precipitation. Its role is to attract the functional groups in the CB particles and separate them from the dissolved ABS solution through differences in density. By considering various factors, including the polarity, miscibility, density, and presence of hydroxyl groups, we have selected and tested two collector solvents to remove CB pigment. From there, different process parameters were tested to increase the efficiency of removing CB from the ABS polymer. Finally, the chemical characteristics of the recovered ABS polymer were verified by Fourier-Transform Infrared (FTIR) spectroscopy and Gel Permeation Chromatographic (GPC); the thermal decomposition of the recovered ABS polymer by Thermal Gravimetric Analysis (TGA); the glass transition temperature (Tg) was measured by Differential Scanning Calorimetry (DSC); and the color measurements of the recovered sample were measured by UV-Visible Spectrophotometer.

The contribution of this paper is summarized as follows.

- A novel method is proposed to efficiently remove CB from the dissolved ABS solution using a collector solvent.
- A user-friendly separation is achieved between the collector solvent and the solution, eliminating the need for a filtration process.
- Distilled water is found suitable as a collector solvent and CB extractor.

The organization for the rest of this paper is as follows. Chapter 2 is the literature review. Chapter 3 presents the material and methodology, including the solvent selection for the solubilization and precipitation of ABS. Chapter 4 presents the results and discusses them. Chapter 5 presents the environmental analysis of the solvent-based recycling processes. Finally, Chapter 6 concludes the report. Additional figures and calculations can be found in Appendix A and B.

Chapter 2

Literature Review

2.1 Synthesis, structure, and properties of ABS polymer

Thermoplastics are known for their unique ability to undergo multiple cycles of melting and reshaping without undergoing significant chemical change [23]. ABS polymer is a commonly used thermoplastic that is often considered an engineering plastic with superior mechanical and thermal properties compared to other plastics, making it suitable for demanding applications in the automotive, electronic, and aerospace industries [23, 24]. ABS consists of three monomers: acrylonitrile, butadiene, and styrene (see the structures shown in Fig. 2.1). Each of the three monomers present in ABS contributes to distinct characteristics to the overall performance of the polymer. Acrylonitrile, for instance, enhances strength, chemical resistance, fatigue resistance, hardness, and rigidity. Butadiene imparts low-temperature ductility, impact resistance, and melt strength. Lastly, styrene increases heat resistance, processability, hardness, and rigidity [25, 26].

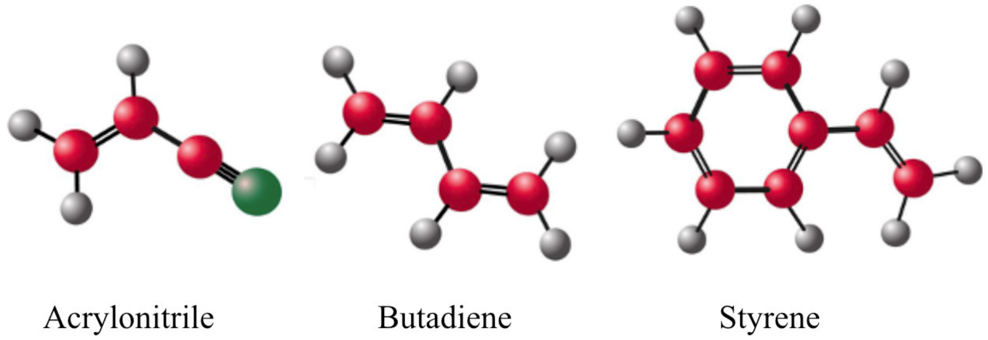


FIGURE 2.1: The molecular structure of Acrylonitrile-Butadiene-Styrene (ABS) polymer, where hydrogens, carbons, and nitrogens are represented in grey, red, and green, respectively [27].

ABS is polymerized through emulsion polymerization in water using surfactants. This process allows monomers to be linked in a specific manner that contributes to the ABS structure [25,26]. Butadiene is polymerized first, creating rubber particles in the water. Styrene and acrylonitrile are then both polymerized around and grafted to the rubber particles, leading to rubber particles being dispersed in a styrene-acrylonitrile (SAN) phase, as shown in Fig. 2.2 (a and b). The presence of the rubber particles grafted enables the formation of crazes but not their propagation, and according to Moore et al. [26], these crazes play a crucial role in the material's ability to resist impact. The arrangement between the polymer phases imparts rigidity and strength to the material while the presence of the rubber phase enhances its impact resistance and flexibility. These properties of ABS can be controlled by various factors, including the composition and molecular weight of SAN, the size and distribution of polybutadiene rubber particles, and the grafted ratio of SAN chains on the polybutadiene particles [25]. Typically, resin producers formulate ABS with an average composition of approximately 21−27% acrylonitrile, 12−25% butadiene, and 54−63% styrene [25].

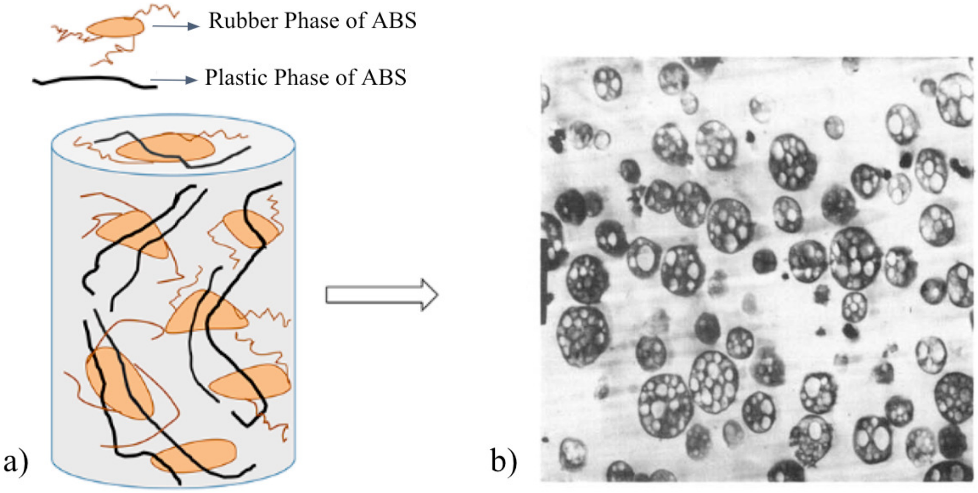


Figure 2.2: (a) Illustration of the ABS polymer structure, and (b) under a microscope with rubber particles being dispersed in a styrene-acrylonitrile (SAN) phase [26].

2.2 Recycling of post-consumer plastic

2.2.1 Mechanical recycling

Recycling post-consumer plastics is challenging due to the presence of different types of polymers, blends, multilayered structures, and additives [24,28]. A common recycling method is mechanical recycling which consists of collecting, sorting, washing, and grinding, followed by an extrusion process that is then quenched and pelletized, and these pellets are injection molded into final products [7,28,29], as shown in Fig. 2.3.

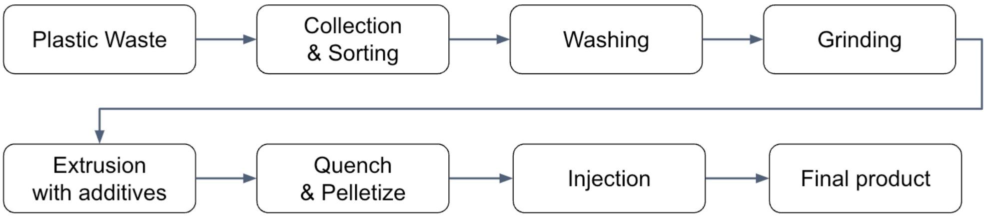


Figure 2.3: The mechanical recycling process from collection to final product.

The implementation of sorting techniques to effectively segregate post-consumer plastics is crucial during the preprocessing steps of recycling, as they significantly streamline the process for recyclers by minimizing the time and effort needed to separate the various types of plastics. This segregation is essential as the mixing of polymers leads to lower mechanical properties as they are not compatible together. Examples of sorting techniques include electrostatic, density, and optical separation [4,30]. Among them, density separation is often used since each type of plastic has its own density [31,32]. For example, ABS polymer has a density of 1.18 (g/m^3), polyethylene terephthalate (PET) has a density of 1.56 (g/m^3) and polypropylene (PP) has a density of 0.90 (g/m^3) [23]. However, sorting techniques are not sufficient to remove contaminants at a molecular scale that are mixed in the resins, such as pigments.

Furthermore, in the melting/extrusion process, the plastic is exposed to elevated temperatures which leads to the degradation of the polymer's thermal and mechanical properties [16]. The degradation of these properties can have several negative consequences for recycled plastic. For instance, the mechanical strength and toughness of the recycled plastic may be compromised, impacting its suitability for certain applications that require specific performance characteristics. This affects the end-of-life of the recycled plastic, and recyclers need to restore certain properties to enhance stability and performance [8, 16, 30]. Additives or stabilizers can be incorporated into the recycled plastic during the melting process to enhance performance and ensure it meets the desired specifications for various end-use applications. However, these additives can impact future recycling cycles since there is no way to identify which additives and what quantity were used in the initial recycling process. This lack of identification can lead to adverse consequences for subsequent recycling attempts, potentially hindering the recycling process.

2.2.2 Chemical recycling

The aforementioned of challenges can be mitigated through chemical recycling. Two methods that can be used are depolymerization and solvent extraction. The advantage of these methods is that mixed and/or soiled waste materials can be recycled efficiently with limited pretreatment required [24, 33]. This is especially effective with certain plastic items that either are made up of different plastics (i.e. children's toys), contain toxic additives such as thermal stabilizers or flame retardants (i.e. electronic devices), or contains food waste (i.e. food packaging) [24, 34]. Current research also demonstrates that these techniques enable recycling plastics without causing degradation [5, 14, 35].

Firstly, depolymerization enables the conversion of complex materials. This process typically occurs through the cleavage of covalent bonds within the polymer structure and can be achieved using heat or by introducing a catalyst [36]. During depolymerization, the polymer chains undergo scission, resulting in the production of monomer units. This breakdown allows for the recovery and reuse of valuable monomers, which can be used as raw materials for the synthesis of new polymers or other chemical compounds. Fig. 2.4 shows the depolymerization of PET. Depolymerization of some polymers, such as ABS, is more difficult due to their covalent bonds being stronger than in PET and thus more difficult to break during the process [36–38]. According to Barnard et al. [37] this process has been successful with polyesters (PES), polyamides (PA), PET, and polymethylmethacrylate (PMMA). Patents for PET depolymerization [39] are used commercially by firms like Loop Industries (Terrebonne, QC).

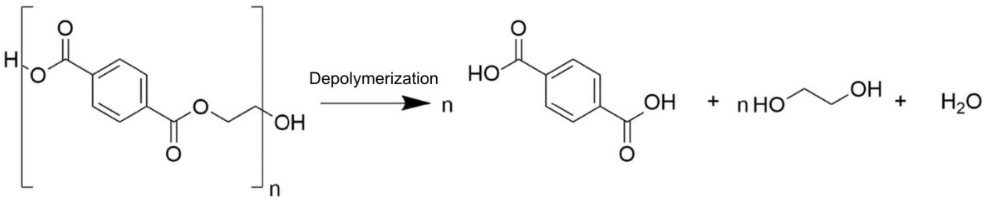


FIGURE 2.4: The breakdown of the polyethylene terephthalate (PET) polymer through depolymerization.

The other method is solvent extraction (dissolution-precipitation) and it consists of solubilizing the polymer in a solvent to untangle the polymer chains and precipitate back into a polymer. It is often used to remove contaminants such as toxic additives since the contaminants will remain in the liquid phase during the precipitation step. Filtration is then sufficient to separate contaminants from the precipitated polymer. The general schematic of the process is shown in Fig. 2.5. It has been successful in restoring the polymer's mechanical and thermal properties [5, 12, 16, 21, 22]. It's important to note that this process does not break any of the polymer's covalent bonds.

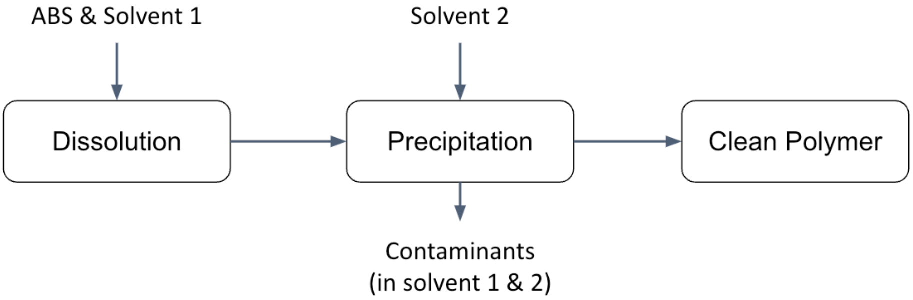


FIGURE 2.5: The solvent-based recycling process for ABS polymer is dissolved in solvent 1, contaminants are removed, and precipitated back with solvent 2.

The Hansen Solubility Parameters (HSP) can be used to choose the proper solvents to solubilize the polymer. HSP analyzes the energy of the dispersion forces, intermolecular forces, and hydrogen bonds between molecules to calculate the relative energy difference (RED) which is then compared with the polymer [21, 40–42]. If the internal forces are similar, the solvent will solubilize the polymer. Achilias et al. [43] have applied these parameters to find solvents for recycling electronic waste containing polymer blends of ABS, polycarbonates (PC), and PS. These different polymers are able to be separated and recovered through dissolution-precipitation processes, where they found an increase in polymer recovery percentage with high dissolution temperature and lower polymer concentrations. Arostegui et al. [35] have tested the degradation of ABS when 4 cycles of solvent-extraction were conducted. The continuous cycles did not affect the chemical structure of the material but had a small effect on the thermal and mechanical degradation of the polymer properties. Similarly, Ferreira et al. [12] showed a 40% efficiency rate to recover materials such as HPDE from food packaging waste. The solvents used were recovered and reused for additional cycles of dissolution-precipitation and also showed a similar efficiency rate. They have concluded that solvent extraction is more efficient in the removal of contaminants and recovery of the polymer. Anderson et al. [5] went beyond and also removed flame retardants from PC/ABS electronic waste blends, with a 70% recovery rate of the material. The removal of contaminants was not the focus of the above works. Most recently, Lu et al. [14] tested the dissolution-precipitation process on ABS toy waste using acetone and water, respectively. The work was successful without degrading the polymer, however, the focus of the work was not to remove any pigments. Moreover, Polystyvert (Anjou, QC) is currently using solvent extraction methods to recycle PS material at an industrial scale. The removal of contaminants was not the focus of the above works.

2.3 Carbon Black (CB) pigment

The widely used CB pigment has a global production exceeding 15 million metric tons annually [19] and extensive applications across various industries. Notably, approximately 73% of it is utilized in the manufacturing of automobile tires, 20% for non-tire rubber products, and 7% in the production of paints, inks, coatings, and plastics compounding [19, 44]. For post-consumer plastic materials, the presence of CB pigment serves a crucial purpose by concealing impurities and satisfying the customer's aesthetic preferences. As a result, recycled plastic is typically only available in one color, black. In order to cater to diverse market demands and expand the usability of post-consumer plastics in various applications, there is a need to explore methods for removing pigments from the resin. Therefore, our focus lies in developing effective techniques to remove CB pigment from plastic resins applied specifically on ABS. By achieving successful pigment removal, we can unlock the potential for creating ABS plastic in a broader spectrum of colors, catering to a wider range of industries and consumer preferences. Thus, enhancing the versatility of post-consumer plastic and promoting sustainability by reducing the need for virgin plastics.

CB is a fine black powder produced by the incomplete combustion of hydrocarbons. CB particles possess complex structures with varying degrees of aggregation and branching. It is characterized by nanoscopic spherical primary particles which are randomly branched chain-like structures, as shown in Fig. 2.6 (a) [19,44,45]. These structures fuse into aggregates during the manufacturing process. The particle size of CB can vary in size as small as 20 nanometers to form a structure size ranging from 100 nanometers to a few micrometers.

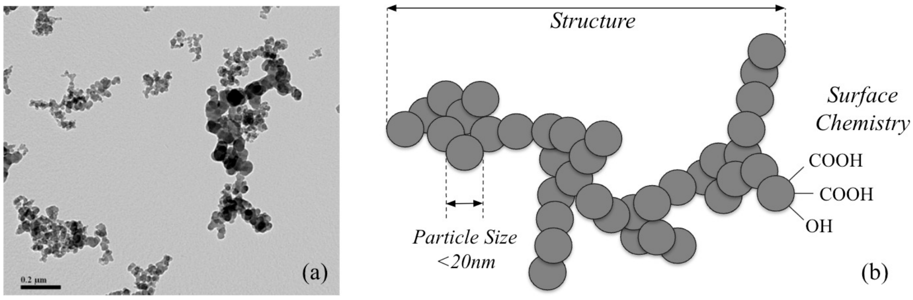


Figure 2.6: (a) Microscope image of carbon black (CB) aggregates [46]. (b) Representation of CB aggregates structure.

The particle size distribution of CB particles is crucial as it affects the color intensity, dispersion, and other performance attributes [44]. Whereas the surface area and porosity influence the CB particle's adsorption capacity, dispersibility, and reinforcing properties. Moreover, surface chemistry plays a critical role in the reactivity, properties, and behavior of the CB particle, affecting the interaction with other materials [17,22]. Figure 2.6 (b) illustrates the surface chemistry of CB particles. Functional groups, such as hydroxyl (-OH), carboxyl (-COOH) groups, etc., are present on the CB particles, imparting a high level of polarity and reactivity to their surfaces. These functional groups are responsible for making the CB particles highly attractive and interactive with other molecules. Moreover, the interaction between CB and polymer chains is important to understand how to remove it, and they are both physical and chemical, as shown in Fig. 2.7 [19,44,47]. The physical interaction can be easily overcome due to its low energy interaction (e.g. Van der Walls). However, the chemical interaction between CB and a polymer is more problematic as a direct covalent bond is observed between CB particles and polymer chains. In the case of styrene-butadiene rubbers (SBR), Wilke et al. [19] determined that a polymer that is chemically bonded to CB represents 0.86% of the total resin. It is thus important to note that, when trying to remove CB from ABS, chemically bounded CB may remain in the final recycled resin [19].

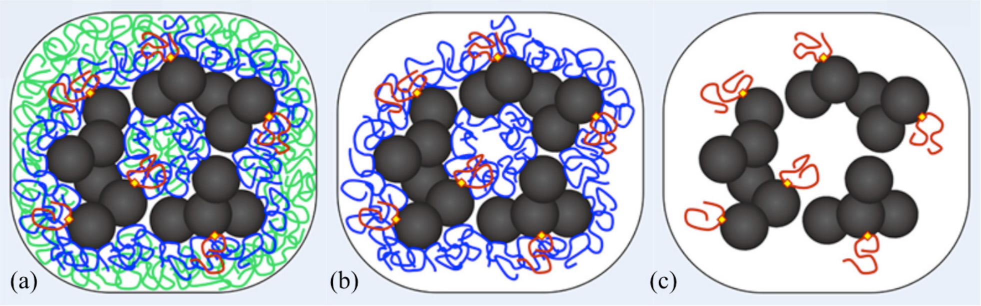


FIGURE 2.7: Schematic representation of the interaction between CB and polymer with (a) CB-filled rubber compound (uncured), (b) CB with total bound rubber (physically and chemically bound), and (c) CB with chemically bound rubber [19].

The observation of the surface chemistry allows us to utilize a separation technique known as liquid-liquid extraction to remove CB particles from the ABS solution with the help of immiscible polar solvents. Arend et al. [13] have been successful in the removal of inorganic pigments such as titanium dioxide (TiO_2), chromium(III) oxide (Cr_2O_3), and iron(III) oxide (Fe_2O_3) from ABS through surface filtration. The process consisted of passing the dissolved ABS through filter paper with a pore size of 4-12 microns. They achieved a pigment reduction rate of 80% for both titanium and iron and 90% for chromium in the recovered ABS [13]. Kol et al. [15] using filtration and centrifugation parameters to remove inorganic pigments such as TiO_2 and Cr/Sb/Ti oxide from PS. They were successful in removing 80% of the inorganic pigments using filtration and 100% using centrifuge from a PS solution using xylene and limonene. They also attempted these methods on CB pigment, however, they were not successful. Filtration experienced complete blockage, and since the particles have a low density (1800 kg/m^3), the sedimentation time was very slow with centrifugation [15,20]. Similarly, patents also exist that remove the color from polymeric material by using a non-aqueous extraction solvent comprising of a nitrogen-containing organic base (i.e. an ammonium salt, and an alkanol) [20]. However, none have been able to remove CB efficiently from ABS since CB particles vary greatly depending and application.

Chapter 3

Material and Methods

3.1 Material

The ABS samples were pelletized from a spool of filament obtained from Stratasys (Rehovot, Israel). Moreover, for testing purposes virgin ABS pellets from Ineos (London, UK), and CB pigment of 100 nanometers particle size from Birla Carbon (Mumbai, India) were obtained for validation of this proof of concept. Solvents used in this work were obtained from Fisher Scientific (Hampton, New Hampshire, USA) and VWR (Anachemia) namely: toluene, ethyl acetate, methyl acetate, dichloromethane (DCM), methanol, hexane, ethylene glycol, and distilled water. Table 3.1 gives a summary of the chemical compounds used in this study.

Table 3.1: List of solvents used in this work, including their density and function. Solvents are used to dissolve ABS polymer, anti-solvents are used to precipitate ABS polymer, and collector solvents are used for CB extraction.

Solvents	Function	Density (kg/m^3)
Toluene	Solvent	866
Ethyl Acetate	Solvent	902
Methyl Acetate	Solvent	934
Dichloromethane (DCM)	Solvent	1325
Methanol	Anti-solv.	791
Hexane	Anti-solv.	659
Ethylene Glycol	Collector	1113
Distilled Water	Collector	1000

3.2 Verification methods and epuipment

3.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

Changes to the chemical compositions were analyzed using FTIR (NICOLET MAGNA from Thermo Fisher Scientific). The samples are analyzed for the composition of ABS (acrylonitrile, butadiene, and styrene) as well as CB pigment. The FTIR takes 3 measurements and outlines an average into wavelength range. The spectra were compared with the general chemical library spectra.

3.2.2 Thermogravimetric Analysis (TGA)

The thermal degradation of the recovered samples was measured using TGA (TGA 550 from TA Instrument).The analysis detected whether any solvent remained in the matrix of the recovered ABS samples, as they would be evaporated at the boiling temperature before the degradation temperature of ABS. The samples approximately 10mg in size, were tested starting from a room temperature of 23°C and heated to 800°C, at a heating rate of 10°C/min under nitrogen. The samples were continuously weighed to measure the weight lost as the temperature increased.

3.2.3 Differential Scanning Calorimetry (DSC)

The thermal properties were measured using DSC (Q20 from TA Instrument). A sample of approximately 10mg in size, was tested starting from a room temperature of 23°C and heated to 300°C and then back to 40°C, with a heating rate of 10°C/min. The test was conducted under nitrogen at a flow rate of 20cm^3/min. The glass transition temperature (Tg) was obtained by analyzing the DSC curve, which represents the temperature at which the polymer transitions from a glassy, rigid state to a rubbery, amorphous state.

3.2.4 Gel permeation chromatography (GPC)

The molecular weight distribution (MDW) was measured using GPC (Agilent 1260) at the University de Montreal. A Waters Styragel HR column (WAT044228) was used for MWD of up to 600 kDa. Samples were dissolved in tetrahydrofuran (THF) at a concentration of 10$wt\%$ and stirred at room temperature. Next, all the samples were diluted with THF to a final concentration of $0.1wt\%$ and filtered through a 0.1-micron nylon PTFE syringe filter prior to injection. PS standards varying from 500 Da to 400 kDa were used to create the calibration curve (refer to Fig A.8).

3.2.5 Color measurement

The color measurements were found using a UV-visible spectrophotometer (Ci7800 from X-Rite). The color of the samples before and after the recycling process was measured to determine if CB was successfully removed. These results were also compared to virgin ABS with no pigment. First, the recovered samples are flattened separately into a disc using a bench top manual hot press (Carver) at around 200°C. Once the sample was flattened and cooled back down to room temperature, the color was measured using CIELABS method. The measurement is conducted by converting wavelength vs. intensity curves into L values according to the CIELABS standards [48]. These values translate to the visible spectrum based on the reflection of the spectrometer.

3.3 Solvent selection for solubilization and precipitation

In this section, the selection of solvents for both solubilization and precipitation steps will be discussed. During the dissolution step, the polymer is added to a solvent to create a polymer solution. In the precipitation step, the polymer is recovered, which can be done by evaporating or using an anti-solvent. Among them, using an anti-solvent is a common method to precipitate polymers from polymeric solution. The best-performing solvents were selected based on previous studies and tested on ABS filament material. To select the best solvent for the solubilization step was prepared by dissolving 0.5g of ABS filament in 40mL of each selected solvent. Each test was subject to both constant stirring of 160 rpm and heated on a hot plate (YAECCC 79-1 or Corning PC-620D). The solubilization was conducted at different temperatures depending on the solvents, to speed up the dissolution process. Thus, the boiling point of each solvent was taken as a reference for the temperature to dissolve with; toluene at 100°C, ethyl acetate at 70°C, methyl acetate at 50°C, and DCM at 35°C. Table 3.2 summarizes the different solvents tested and their performance based on the

Table 3.2: Performance of solvents tested to dissolve 0.5g of ABS with 40mL of the solvent.

Solvents	Boiling Temp (°C)	Dissolving Temp (°C)	Time (min)
Toluene	110	100	90
Ethyl Acetate	77	70	50
Methyl Acetate	57	50	71
DCM	40	35	62

Table 3.3: Performance of anti-solvents tested to precipitate on 0.5g of ABS dissolved in 40mL of ethyl acetate and the anti-solvent.

Anti-Solvents	Mass of recovered ABS (g)	Yield (%)
Methanol	0.47	94
Hexane	0.44	88

total time to dissolve the ABS material. It was found that using ethyl acetate was significantly time-efficient, with a dissolution time of 50 minutes, and thus continued to be used for further testing in this work.

Similarly, the best possible anti-solvent to precipitate the polymer was determined. Each test was conducted with the previous ABS solution (0.5g of ABS dissolved in 40mL of ethyl acetate) and 40ml of each anti-solvent was added at room temperature to precipitate without the addition of heat and manually stirring with a lab spatula. Here, both methanol and hexane were tested as anti-solvents. The duration of the precipitation step was less than 1 minute, and therefore the time required for the precipitation was not considered a critical factor. Table 3.3 summarizes the performance of methanol and hexane as anti-solvents in terms of the mass of ABS recovered. Both were successful in recovering ABS, with a yield of 94% for methanol and 88% for hexane. Thus, both were continued to be used and analyzed.

3.4 Method

The solvent extraction method in this work includes the following steps: dissolution, liquid-liquid extraction (separation), and precipitation. The final process that was selected is demonstrated in Fig. 3.1. To start, 0.5g of ABS filament pellets were dissolved in 40mL of ethyl acetate to form an ABS solution. To speed up the process, the mixture was heated to 70°C, just below the boiling point of ethyl acetate, and the beaker was covered with a lid during the process to minimize solvent evaporation.

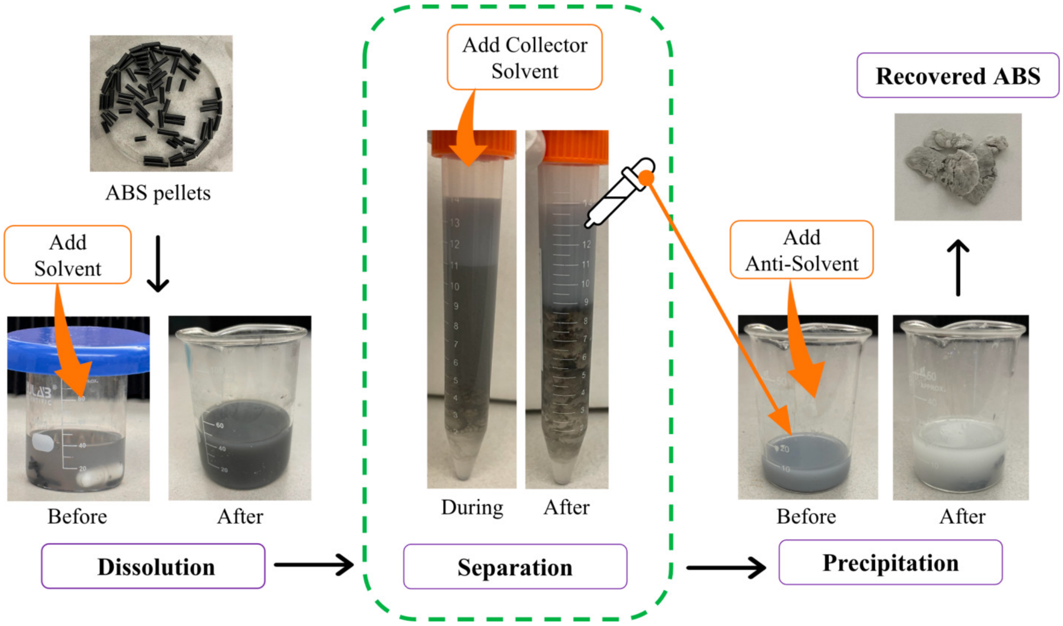


FIGURE 3.1: Overview of the solvent-extraction process using liquid-liquid extraction process to remove CB. ABS polymer is dissolved using a solvent, CB pigment is separated using a collector solvent, and ABS polymer is precipitated back using an anti-solvent. The ABS polymer is recovered and dried before analysis.

Continuous stirring at 160rpm and monitoring of the temperature with a probe sensor was also performed throughout the process.

Next, the ABS solution was left to cool back to room temperature and then was divided between 5-6 plastic test tubes (7mL) for testing purposes and to allow for efficient mixing. An equal amount of collector solvent was then added to each test tube. After that, each closed test tube was sealed and shaken vigorously by hand for a few seconds to mix them together. The solvents then separated themselves based on their differing densities, and the collector solvent pulled the CB particles away from the ABS solution and was removed. When the separation was complete, we were left with an ABS solution in the upper portion of the test tube and CB with the collector solvent at the bottom portion of the test tube. Next, the ABS solution in the upper portion was extracted using a pipette into a new beaker, and equal parts of anti-solvent were added to precipitate ABS and mixed with a lab spatula. The precipitated ABS was removed from the solvent and dried at 90°C for 3-4 hours before any testing analysis was performed.

Chapter 4

Results and Discussion

4.1 Removal of CB pigment from ABS

In this section, the preliminary filtration test, parameters affecting the collector solvent efficiency, and the separation process will be discussed. Firstly, filtration methods were attempted to remove CB after the solubilization of ABS. As previously described, CB aggregates form insoluble particles, thus filtration methods, in theory, should be able to capture the CB particles. The same ABS solution was prepared and passed through a series of filter papers (Labasics) consecutively by decreasing pore sizes from 20 to 1.5 microns to accommodate the CB particle size variation.

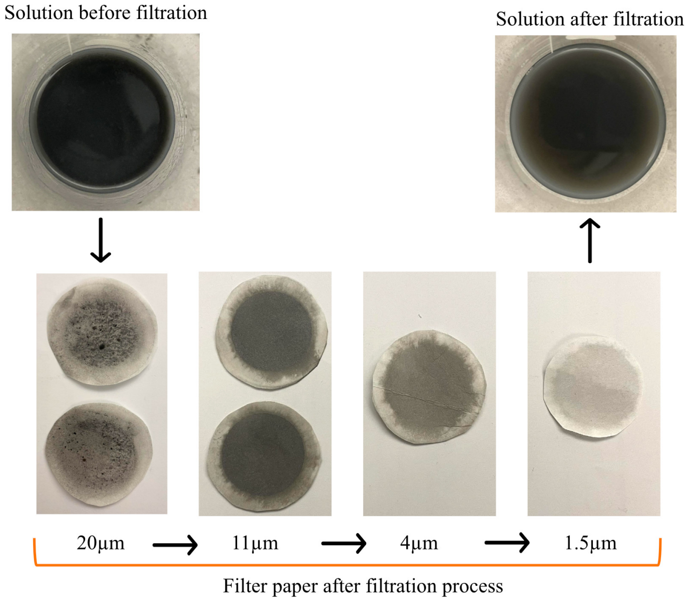


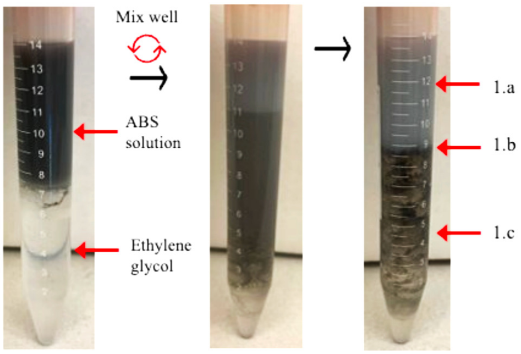
FIGURE 4.1: Results from filtration process, where filter papers decreased in pose size to extract CB.

Fig. 4.1 shows the filtration results on the dissolved ABS solution in order of filter paper pore size used. The filter paper's pores decreased in size to prevent clogging and facilitate the solution would pass through with ease. The results show that some quantity of the CB was collected on each filter paper from the ABS solution, with sizes 20 and 11 microns getting blocked and requiring additional filter papers to pass all the ABS solution. After the filtration cycles, the solution remained black in color which indicates the presence of CB particle contaminants. Thus, the filtration method is not efficient for removing CB pigment from post-consumer plastics.

To mitigate this challenge, a collector solvent is used in this work for liquid-liquid extraction to remove CB from the ABS solution during the separation step. The main role of the collector solvent is to extract the suspended CB particles from the ABS solution through surface chemical affinity and be immiscible with ethyl acetate. The collector solvents tested in this work are ethylene glycol and distilled water since they are both polar solvents, are immiscible, and have greater densities than ethyl acetate. Fig. 4.2 illustrates the interaction between the ABS solution and collector solvents. First, 1g of ABS filament was dissolved in 60mL of ethyl acetate and heated to 70°C. Next, equal parts (7mL) of ABS solution and collector solvent were added to a plastic test tube at room temperature. When first added together, the collector solvents and ethyl acetate do not mix together. Thus, they are mixed together by vigorously shaking the test tube for a few seconds. Afterward, the solvents start to separate from each other, and the CB particles are attracted to the polar hydroxyl groups of the collector solvents. As a result, the color of the ABS solution changed, and we observed fewer CB particles in the upper portion of the test tube. After the separation step was complete, three different phases were observed for both collector solvents: (a) ABS and ethyl acetate, (b) CB, ethyl acetate, and collector solvent, and (c) CB and collector solvent. A difference in density between the collector solvent and ABS solution allows the collector solvent to travel downwards with gravity through the solution, carrying the CB particles with it and remaining at the bottom portion of the test tube, as shown in Fig. 4.2 (1.c and 2.c). The polarity and density of the collector solvents contribute to the efficiency of removing the CB particles. Table 4.1 shows the performance of the collector solvent which was measured based on the time it took to separate.

The collector solvents and the performance were tested when all solutions were at room temperature. It was observed that ethylene glycol could separate the CB from

1. Ethylene Glycol



2. Distilled Water

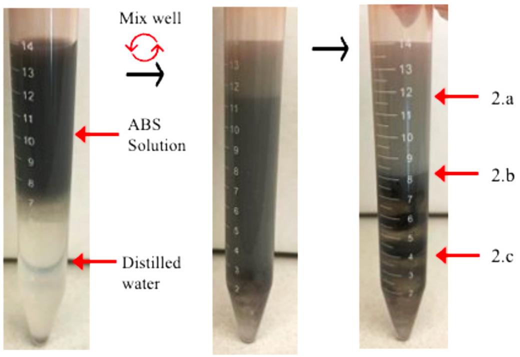


Figure 4.2: Observation of the separation process for each collector solvent tested are (1) ethylene glycol and (2) distilled water. The solvents before mixed (left) and after separation are complete (right) with (1.a and 2.a)upper portion of ABS dissolved in ethyl acetate, (1.b and 2.b) middle phase of ABS, ethyl acetate, and collector solvent, (1.c and 2.c) bottom portion of collector solvent and CB pigment. All tests were conducted at 23°C.

the ABS solution in 5 minutes while separation with distilled water took 20 minutes. The separation time is also influenced by the difference in the solvent's density. While ethyl acetate has a density of 902 kg/m^3, ethylene glycol has a greater density than distilled water, and will separate and travel downwards away from the ABS solution in less time. However, distilled water was able to attract more CB from the ABS solution since we observed a lighter color in the solution after separation was complete. This is due to the polarity of the collector solvent, where a larger polarity can attract CB away from the ABS solution more efficiently. A strong polar solvent has significantly more attractive interactions with other molecules through hydrogen bonding. In this case, distilled water with a relative polarity of 1 and has stronger interaction forces and thus attracts more CB compared to ethylene glycol [49].

Finally, to observe how much CB was removed from the ABS solution, the dissolved

Table 4.1: Performance in time and color of solution of CB extraction for each collector solvent tested in this work. All tests were precipitated with methanol.

Collector solvent	Density (kg/m^3)	Polarity	Time (min)	Solution Color
Ethylene glycol	1113	0.79	5	Grey
Distilled water	1000	1.00	20	Light grey

ABS solution (7mL) shown in Fig. 4.2 (1.a and 2.a) from each test tube was transferred into a new beaker using a pipette to conduct the final precipitation step. The ABS solution (20mL) was precipitated with the same quantity of methanol (20mL). The precipitated ABS is then removed from the solution and the samples were placed in an oven at 90°C for 3-4 hours. Table 4.2 summarizes the yield that was obtained for the recovered ABS samples depending on collector solvents (ethylene glycol or distilled water) and anti-solvents (methanol or hexane). The masses of ABS recovered after precipitation using the two collector solvents, ethylene glycol, and distilled water are significantly lower than the initial dissolved amount. The miscibility between ethyl acetate and the collector solvents could explain the loss of ABS. The middle phase, as shown in Fig. 4.2 (b), containing ethyl acetate, the collector solvent, and ABS with CB particles suspended in the solution, cannot be recovered for precipitation because it still contains CB pigment. This middle phase cannot be recovered for precipitation as it still contains CB. Thus, about 1mL of ABS solution from each test tube is lost for both collector solvents, decreasing the final yield. Another reason for this loss could be the precipitation process. It is possible that small ABS chains remained soluble in the solution after precipitation and cannot be recovered. After CB extraction, hexane was able to recover more ABS compared to methanol for both collector solvents. Whereas the association of ethylene glycol and hexane is able to recover the most of ABS.

Table 4.2: Performance of collector solvent and anti-solvent for the yield of recovered ABS.

Collector solvent	Anti-solvent	Yield (%)
Ethylene glycol	Methanol	23
Ethylene glycol	Hexane	82
Distilled water	Methanol	46
Distilled water	Hexane	75

The recovered precipitated samples are compared visually to evaluate the performance of the collector solvents at removing CB. Fig. 4.3 shows each precipitated

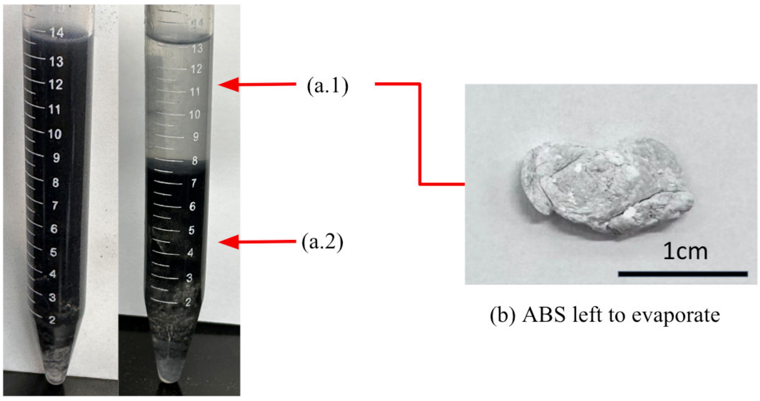
FIGURE 4.3: The recovered samples precipitated using methanol including (A) ABS filament, (B) recovered ABS using filtration methods (no collector solvent used), (C) recovered ABS using collector ethylene glycol, and (D) recovered ABS using collector distilled water.

sample compared to virgin ABS with no pigment (A). The sample using filtration methods (B) is also included in this figure for comparison and shows the sample remained black in color. The samples recovered with ethylene glycol (C) and distilled water (D) are both grey in color, indicating that there are some remaining traces of CB in the polymer matrix, however, a significant amount was removed. Distilled water was more efficient in removing CB during the separation process, since we observed less CB in the polymer matrix, leaving the recovery polymer a light grey, whereas the sample using ethylene glycol remains dark in color. From these findings, distilled water was used in this work as the collector solvent as it was able to remove more CB.

4.2 Validation with virgin materials

To verify the effectiveness of the CB extraction technique employed in this study, virgin ABS (without pigment or additives) and CB pigment were used. It's worth noting that only dissolution was conducted without polymerization with the virgin materials. The aim was to establish whether CB particles, suspended within an ABS solution, would be attracted to the distilled water. Additionally, this test provided better control over the size of CB particles. For this test, CB pigment with 100 nanometers particle size was chosen as it is easily accessible in the market. Depending on the application and requirements, resin manufacturers will load around 0.25-3% of CB pigment into the polymer [50].

To start 3g of virgin ABS and 1mg (0.3% polymer/pigment) of CB pigment were dissolved in 80ml of ethyl acetate. To facilitate the process, the mixture was heated to 70°C, covered with a lid, and continuously stirred at 160 rpm. Once the dissolution was complete, the solution was cooled down back to room temperature. Then, equal volumes (7mL) of the solution and distilled water were combined in a test tube. The test tubes were sealed and shaken vigorously to ensure thorough mixing. Fig. 4.4 (a) shows the separation process after mixing (left) and the final results after the separation was complete (right) where the ABS solution without CB (a.1), and the distilled water with CB (a.2) were observed. The upper portion of the test tube (a.1) showed that there were no traces of the CB within the ABS solution. Finally, this upper portion is pipetted into a new beaker and precipitated with methanol. It was observed that the recovered ABS was white in color, proving that distilled water can attract the CB pigment away from the ABS solution. No further analysis was completed on this section as it was simply a validation of the proof of concept between the interaction of the surface chemistry of CB and distilled water as a collector solvent.



(a) Separation Process

(b) ABS left to evaporate

FIGURE 4.4: (a) Validation of the separation process with the (a.1) ABS solution, (a.2) CB pigment and distilled water. (b) The recovered ABS precipitated using methanol.

4.3 Influence of different parameters on collector solvent

In order to improve the performance of the separation process, different parameters were tested to give the best possible results for CB removal. For the following experiments, the ABS solution was prepared in the following manner. For each parameter test (temperature, size, and apparatus), the ABS solution was made whereby 1g of ABS filament pellets was dissolved in 60mL of ethyl acetate at 70°C. Distilled water was subject to different temperatures and ratios to test its performance. As well, different size apparatuses were used for the separation steps to test the effect of the surface area has on the interaction between the ABS solution and distilled water.

Firstly, to assess the impact of temperature on the CB extraction, the temperature of distilled water was modified while keeping the ABS solution at room temperature. We wanted to determine whether the temperature of distilled water would enhance CB extraction. The distilled water was cooled by adding it to a plastic test tube and placing it in a freezer or heated using a hot plate and beaker until the desired temperatures were reached.

Fig. 4.5 and Table 4.3 provides an overview and results of the final separated ABS solution and the testing conditions, with the same quantity (5mL) of ABS solution and distilled water.

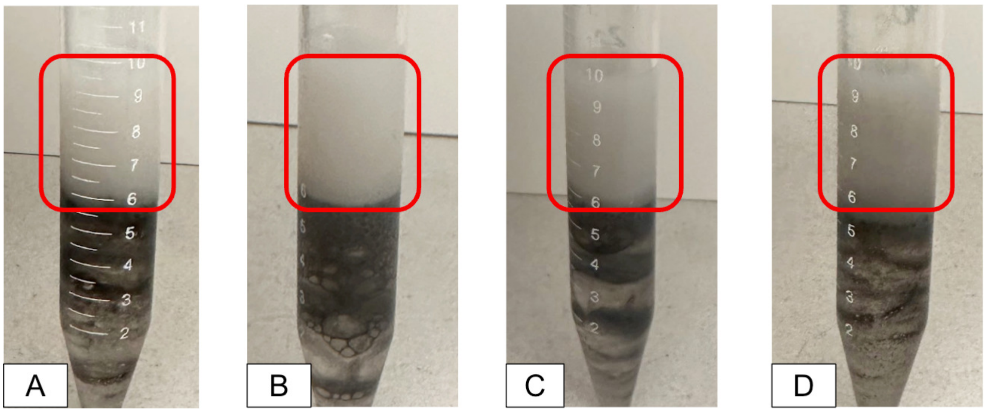


FIGURE 4.5: Influence of temperature variation on CB extraction by analyzing the upper portion of the test tubes after separation is complete. All tests were conducted with ABS solution at 23°C, while distilled water was tested at temperatures (A) -1°C, (B) 5°C, (C) 23°C, and (D) 45°C.

TABLE 4.3: Temperature of distilled water for each test and the color of the upper portion of the test tube after separation was complete. All tests were conducted with ABS solution at 23°C.

Sample	Temp (°C)	Color of ABS solution
A	-1	Very light grey
B	5	Light grey
C	23	Grey
D	45	Grey

The results show that when distilled water is at a colder temperature the ABS solution after separation is whiter in color, thus meaning more CB was removed. At elevated temperatures (C) molecules are excited and move quickly. This results in the distilled water not having enough time to attract the CB particles as it moves downwards with gravity more quickly. The opposite can be said with cold temperatures (A) where molecules move slowly and the distilled water was able to attract more CB particles. In colder temperatures, there is a reduction in energy, leading to an increased presence of hydrogen bonds. This enables water at cold temperatures to effectively attract more CB particles. Conversely, higher temperatures bring about more energy, causing the disruption of hydrogen bonds. Due to application, the process was kept at room temperature.

Next, the impact of different ratios between ABS solution and distilled water was analyzed by adding different quantities of distilled water to the same quantity of ABS solution (10mL). The aim was to determine whether the quantity of distilled water enhances the extraction of CB. Fig. 4.6 and Table 4.4 provide an overview and results of the different ratios of distilled water and ABS solution.

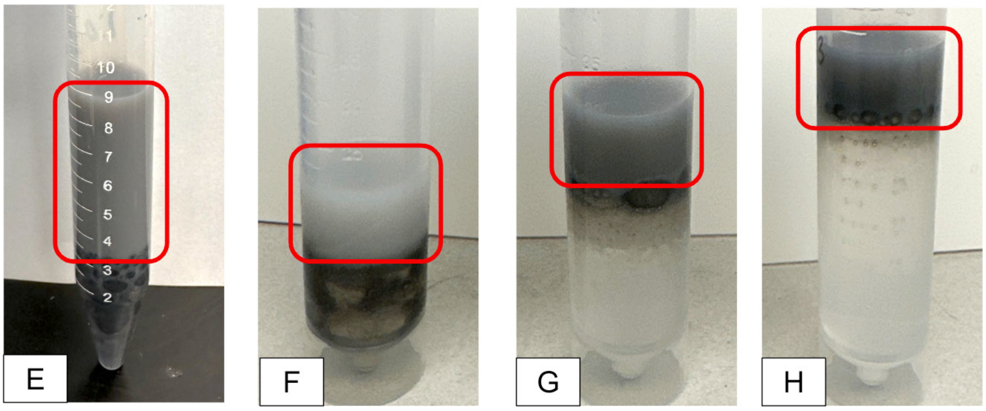


Figure 4.6: Influence of ratios variation on CB extraction by analyzing the upper portion of the test tubes after separation is completed. All tests were conducted at 23°C with 10mL of ABS solution, while changing the volume of distilled water for ratios of (E) 1:0.8 (F) 1:1, (G) 1:2, and (H) 1:3.

Table 4.4: Volume of distilled water for each test and performance to CB extraction. All tests were conducted at 23°C and 5mL (Sample E) or 10mL (Sample F to H) of ABS solution.

Sample	Volume (mL)	Ratio	Results (Yes/No)
E	4	1:0.8	N
F	10	1:1	Y
G	20	1:2	N
H	30	1:3	N

The results using 1:1 ratio, as shown in Fig. 4.6 (F), demonstrate that CB was removed more efficiently from the ABS solution since it was observed to be white in color. More CB particles were observed in the bottom portion of the test tube compared to the other tested ratios. Fig. 4.6 (E), (G), and (H) show that the ABS solutions remained dark in color after separation. In particular, there was no CB extracted at the bottom portion of the test tube with increased volumes of water. Thus, these ratios were not successful. These results revealed interesting patterns, indicating that the proportions of ABS solution and distilled water play a significant role in the distribution of CB particles within the ABS solution. However, further analysis is needed to understand the specific mechanisms behind this phenomenon. One possible explanation is related to the highly polar nature of water molecules. Due to their strong attraction to each other, water molecules tend to stay together to remain in a stable environment. When the test tube is shaken, the water molecules become unstable. Thus, they move downwards with gravity to reach stability again. When there are more water molecules compared to ABS solution molecules (G and H), they can easily accomplish this rearrangement quickly. As a result, the molecules return back to stability but do not attract CB particles with them. Furthermore, with fewer water molecules (E), only a few CB particles are extracted. When the quantities are even between water and ABS solution (F), the water molecules are more likely to interact with the CB particles while moving downwards to reach stability.

Finally, we investigated the influence of the surface area size between the ABS solution and distilled water. The aim was to determine whether the surface area of the apparatus played a role in enhancing the separation rate of CB particles, where with greater surface area there will be more extraction of CB. To address this, a variety of containers with different sizes and diameters were utilized such as graduated cylinders and beakers. A consistent 1:1 ratio of distilled water to ABS solution for each apparatus was maintained. Fig. 4.7 and Table 4.5 summarize the specific apparatus that was used and the results that were observed.

The results of the experiment revealed that the apparatus with the largest surface area, the beaker (L), exhibited the highest extraction of CB particles where the ABS solution is light grey in color. The larger surface area of the beaker provided more points of contact and interaction between the ABS solution and distilled water as they separated from each other. This increased contact area allowed for enhanced

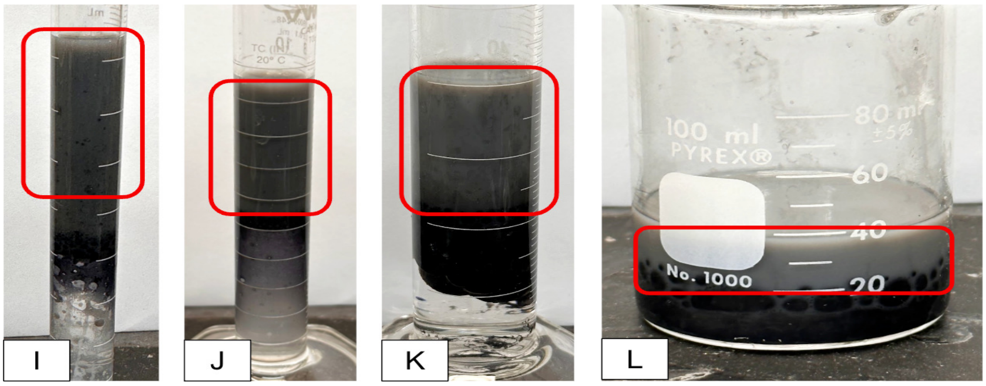


FIGURE 4.7: Influence of surface interface on CB extraction by analyzing the upper portion of the test tubes after separation is completed. All tests were conducted at 23°C and the diameter of the apparatus (I) 10.7mm, (J) 13.0mm, (K) 25.6mm, and (L) 56.6 mm.

TABLE 4.5: Size of the diameter of each apparatus tested and the performance. All tests were conducted with a 1:1 ratio of ABS solution and distilled water at 23°C

Sample	Size (mm)	Color of ABS solution
I	10.7	Dark grey
J	13.0	Dark grey
K	25.6	Dark grey
L	56.6	Grey

diffusion and mixing with the CB particles, facilitating a more effective extraction. Additionally, with a larger apparatus, the water has a shorter distance to travel downward through the ABS solution, compared to other size apparatus which allows more attraction of CB particles. These findings suggest that optimizing the surface area in the extraction process can lead to more efficient CB removal techniques.

4.4 Impact of CB removal process on ABS polymer

From the general method described in Section 3.4, five samples were prepared with Table 4.6 summarizing the solvents and materials used for each of the samples. The samples include virgin ABS (SO), the ABS filament (S1), samples using only dissolution-precipitation methods (S2, S3), and samples including CB removal (S4, S5, S6). All results will be discussed in this section and all figures can be found in Appendix A.

Table 4.6: Summary of all samples prepared for this work. Samples were prepared using ABS filament dissolved in ethyl acetate, ethylene glycol or distilled water as the collector solvent, and methanol or hexane as the anti-solvent.

Sample	Material	Anti-Solvent	Collector Solvent
S0	Virgin ABS	-	-
S1	ABS filament	-	-
S2	ABS filament	Methanol	-
S3	ABS filament	Hexane	-
S4	ABS filament	Methanol	Distilled Water
S5	ABS filament	Hexane	Distilled Water
S6	ABS filament	Methanol	Ethylene Glycol

4.4.1 Color measurement of the recovered ABS

The color measurement was carried out using a UV-visible spectrophotometer to assess the L-value of each ABS sample. The purpose of this analysis was to compare the L-value of the recovered sample with that of both virgin ABS (S0) and the ABS filament (S1). The comparisons of L-values are used to quantify the color of a material, with an L-value of 100 corresponding to absolute white and an L-value of 0 corresponding to absolute black. Table 4.7 and Fig. 4.8 show the L-value for all the analyzed samples and Fig. A.1 from Appendix A shows the samples that were tested.

Table 4.7: Estimated L-value from the color measurement using a commercial colorimeter and our approach.

Sample	Anti-solvent	Collector solvent	L-value
S0	-	-	94.7
S1	-	-	28.5
S4	Methanol	Distilled water	44.7
S5	Hexane	Distilled water	62.7

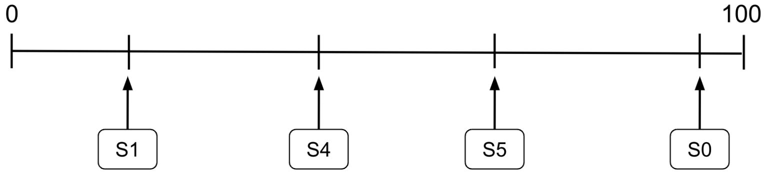


Figure 4.8: Representation of the estimated L-values from the color measurements for each sample. S0 corresponds to virgin ABS with no pigment, S1 corresponds to the ABS filament, and S4 and S5 are with CB extraction.

For reference, the L-value of virgin ABS (S0) with no pigment was found to be 94.7, suggesting a color closest to white, while the L-value of the black ABS filament (S1) was measured to be 28.5. In comparison, in the samples where CB was extracted using distilled water and precipitated with methanol (S4) or hexane (S5), the L-values provided an indication of the whiteness, thereby quantifying the amount of CB removed during the solvent-based recycling process. Interestingly, S5 exhibited a whiter color, with an L-value of 62.7, closer to the reference L-value of 100. On the other hand, S4 has an L-value of 44.7, indicating a relatively less white appearance. An increase of L-value by 16.2 (S4) and 34.5 (S5) compared with S1 demonstrates the efficiency of the proposed recycling method for CB removal.

This finding indicates that hexane causes the precipitation to be a whiter sample, suggesting more CB particles being removed compared to the sample treated with methanol. It is important to note that, the formation of a flat disc using a hot compression machine, can have an impact on the sample color. Moreover, the CB extraction process developed in this work is not perfectly standardized, meaning that the differences observed between hexane and methanol can be affected through varying parameters, such as concentration, solvents, etc. The most important conclusion is that the proof of concept was obtained for CB removal from ABS resin.

4.4.2 Thermal stability on recovered ABS polymer

To begin, it is essential to study how the thermal stability of the recovered samples of ABS changes when subjected to elevated temperatures. Moreover, it is important to evaluate the polymer's purity and thermal properties. This is done through TGA and DSC analysis which is discussed in this section.

Firstly, a comprehensive analysis of the thermal degradation of the recovered ABS samples was conducted through TGA analysis. This is to ensure that the degradation temperature of the recovered samples is not affected by the solvent-based recycling method. This knowledge holds paramount significance, as it could lead to undesired consequences during the manufacturing stage such as reduced mechanical strength. The degradation curves are depicted in Fig. A.2 to Fig. A.4 in Appendix A.

The results indicated that all samples underwent degradation within the temperature range of 300 to 500°C, corresponding to the degradation temperature of ABS polymer. Notably, all samples exhibited a substantial loss of over 90% of their original mass during the test. The primary degradation for all samples occurred within the temperature range of 340 to 450°C, evident from the weight loss curves. Moreover,

Fig. A.2, reveals no thermal degradation to the recovered ABS material for samples when methanol was used to precipitate (S2 and S4). Fig. A.3 reveals similar results were found when hexane was used to precipitate (S3 and S5). This outcome suggests that the process of solvent-based recycling did not impact the thermal stability of the plastics even with CB extraction.

The TGA analysis also demonstrates an initial weight loss between 0 to 200°C. This attributes to the evaporation of solvents that remained in the polymer matrix. Comparing the boiling point of the solvents we know that methanol (65°C) will evaporate first followed by hexane (69°C), ethyl acetate (77°C), and finally water (100°C). The results show that samples S2 and S3 both have weight change before 100°C, therefore anti-solvents remained in the polymer matrix.

Fig. A.4, shows the results obtained when different collector solvents are used, namely distilled water (S4) or ethylene glycol (S6). Once again, an initial degradation of 5% was observed in the sample using ethylene glycol, occurring around 200°C, close to the boiling temperature of ethylene glycol (197°C). Conversely, such weight loss was not observed when using distilled water. This finding supports the decision not to employ ethylene glycol as a collector solvent as it would be challenging to remove it from the polymer matrix. Anderson et al. [5] also reported 20% ethylene glycol remained trapped in the recovered polymer.

This implies that the extraction process does not influence the polymer's thermal degradation. However, the choice of solvents and drying method is important to ensure that it does not remain in the polymer matrix. Other works [5, 14, 35, 51] show similar thermal degradation temperatures for ABS material after solvent-based recycling methods, even with different solvents used for dissolution. It's important to note that Arostegui et al. [35] reported changes to the thermal degradation temperatures as a consequence of low molecular weight compounds dissolution such as additives. Cress et al. [51] had similar results for ABS filament and indicated an increase in thermal stability due to the lack of chain scission that is normally found with polymer degradation.

Next, the DSC analysis was used to determine the thermal stability of the recovered samples. The Tg is obtained which represents the temperature at which the amorphous material undergoes a transition from a glassy, rigid state to a rubbery, more flexible state. ABS usually has two Tg temperatures; one is linked to the polybutadiene phase and the other is linked to the SAN phase and the Tg generally ranges from -78°C to -90°C and from 105°C to 115°C, respectively. Fig. A.5 for samples S1 and S2, shows only the upper temperature range because the DSC equipment used cannot go below room temperature. Table 4.8 summarizes the Tg for all the recovered samples.

TABLE 4.8: Summary of DSC analysis for the glass transition temperature (Tg) for Samples 1 to 5.

Sample	Anti-solvent	Collector Solvent	Tg (°C)
S1	-	-	108.9
S2	Methanol	-	110.7
S3	Hexane	-	111.6
S4	Methanol	Distilled water	109.3
S5	Hexane	Distilled water	113.3

The results show that there was a minimal increase in Tg between samples. As can be seen, the Tg of the SAN phase is approximately 110.7°C for S2 and 109.3°C for S4 for samples using methanol, which is similar to the original material with Tg of 108°C for S1. This increase in Tg was more pronounced for samples using hexane with 111.6°C (S3) and 113.3°C (S5). For comparison, Cress et al. [51] showed the results of multiple cycles of mechanically recycled ABS filament, where the affected Tg decreased after one cycle of recycling by 1-2°C and remained steady for other consecutive recycling cycles. Other research has shown a similar trend for ABS material using solvent-based recycling methods, where the first cycle decreases by 10°C but then remains steady for consecutive cycles of recycling [35]. The method developed in this work is promising since the goal is for the plastic material to be recycled multiple times in its lifetime without drastic modifications. The increase in Tg observed in this work means that the material becomes more rigid and less flexible at higher temperatures. The solvent-based recycling process can effectively remove low molecular weight components, such as additives or impurities. These components can act as plasticizers, reducing the Tg. Thus, when they are removed in solvent-based recycling methods, it contributes to an increase in Tg [14]. Similarly to the finding in this work, Lu et al. [14] results also showed an increase of 3°C for the Tg from the original ABS toy waste due to the loss of the plasticizers during the recycling process making the polymer more rigid with a higher Tg.

4.4.3 Chemical influence on recovered ABS polymer

The recovered samples were analyzed to evaluate if any chemical changes occur with the solvent-based recycling method. This was done through FTIR and GPC analysis, which will be discussed in this section.

The FTIR tests were conducted on the recovered samples and the virgin ABS to identify possible composition changes. Fig. A.6 shows the results of the solvent-based recycling method on the recovered samples using different anti-solvents (S2 and S3) compared with the ABS filament (S1). We observed a significant overlap between all the peaks, indicating that ABS remained stable during recycling. The results show the characteristics bands of ABS consistent with acrylonitrile at 2238cm^{-1} with C≡N group; butadiene at 967 and 910cm^{-1} with C=C group; and styrene at 3027, 2863, 1602, and 1493cm^{-1} with the aromatic CH group (Ar-CH). A large stretching band was observed from 3500 to 3100cm^{-1} a characteristic of the OH stretching, which is often attributed to humidity. Therefore, the chemical structure of the recovered ABS samples, when compared to virgin ABS, was not altered by the overall recycling process used in this work.

Interestingly, a signal in the 1720 to 1760cm^{-1} range is observed in all ABS samples. This signal can is generally attributed to C=O stretching groups (ketones, carboxylic acids, etc.). The latter are present in contaminants such as CB particles and additives. Fig. A.7 shows the FTIR spectra for the virgin ABS with no CB (SO), ABS filament (S1) compared to the recovered sample with CB extraction and precipitated methanol (S4) and hexane (S5). Comparing the area under the peak around 1720cm^{-1} for these samples can quantitatively indicate how much CB remains in the sample. Table 4.9 summarizes the area under the C=O stretch signal. Samples using

Table 4.9: Summary of the FTIR analysis for the area under the peak at wavenumber 1720cm^{-1} for the C=O stretch signal for Samples 1 to 5.

Sample	Anti-solvent	Collector Solvent	Peak Area
S1	-	-	218.1
S2	Methanol	-	44.1
S3	Hexane	-	49.8
S4	Methanol	Distilled water	41.3
S5	Hexane	Distilled water	39.3

only dissolution-precipitation (S2 and S3) show a decrease in the C=O attributed to soluble additives removal from the original ABS filament. A more important decrease in the signal intensity is observed for samples S4 and S5 which include CB extraction and precipitation steps. Sample S5, which was recovered with hexane, has a smaller signal intensity at 1720cm^{-1} compared with S4 (precipitation with methanol). This observation supports the color measurement results, where S5 has an L-value closest to 100, attributed to a whiter sample with less CB. Thus, the FTIR shows no observable changes to chemical composition, and the CB removal is analyzed by the signal intensity.

Next, the GPC analyzed any changes in MWD, more specifically to Mw and Mn, and indicated whether any mechanical properties were affected by the solvent-based recycling method when compared to ABS filament. The Mw provides information about the size and mass of a molecule, and the Mn takes into account the relative abundance of different chain lengths and provides insight into the overall size of the polymer sample. With the ratio of Mw and Mn, we obtain D and it gives an indication of the MWD. Table 4.10 summarized the samples and GPC results with additional distribution curves and the calibration curve for GPC is shown in Appendix A.

TABLE 4.10: Summary of the GPC analysis for the molecular weight (Mw), the number average molecular weight (Mn), and the polydispersity index (D) are given for Samples 1 to 5.

Sample	Anti-solvent	Collector Solvent	Mw (kg/mol)	Mn (kg/mol)	D
S1	-	-	188	109	1.72
S2	Methanol	-	167	109	1.53
S3	Hexane	-	191	119	1.60
S4	Methanol	Distilled water	174	107	1.62
S5	Hexane	Distilled water	172	105	1.64

The distribution between all samples shows a small variation in Mw and Mn. More specifically, the ABS filament (S1) compared to the solvent extraction method using methanol (S2) shows a decrease in Mw but no change to the Mn. This was not the same observation with hexane (S3), in which a small increase in both Mw and Mn was observed. From these results, changing the anti-solvent used for precipitation does affect the MWD. Similarly, a change in Mw and Mn was observed when CB was extracted, where S4 and S5 all show a decrease in Mw and Mn when compared with S1. This decrease could be explained by the degradation of the polymer. Usually, chemical reactions are slow in a solid-state medium which explains why polymer degradation is generally measured in years. However, when the reactions are in a liquid-state medium, (i.e. together in a solvent) it is more likely for them to interact and react together, causing degradation such as chain scission at a much faster rate. This explains why, when polymers are solubilized in a solvent, degradation can occur and thus affects Mw. On the contrary, S3 shows an increase in Mw. In this case, the small chains could be soluble in ethyl acetate and hexane which can explain the overall increase of Mw in the ABS. Thus, no significantly large differences were observed but showed that the solvents do affect the MWD. Overall, a decrease of Mw, Mn, and D after the process is attributed to lower chains and degradation of ABS in the solution during the solvent-based recycling methods used in this work. Other works [5,14,35], all showed similar results for MWD with ABS polymer. Solvent-based recycling can reserve the bulk Mw of the recovered material, particularly for the relatively high Mw fraction [5].

Chapter 5

Environmental Impact Analysis

Plastic pollution has become a significant environmental challenge, causing severe harm to ecosystems, wildlife, and human health. Recycling is often seen as a viable solution to tackle this issue, with solvent-based processing being one of the methods and has shown potential for reducing the environmental impact. The main advantage of solvent-based recycling is its ability to transform complex plastic waste, including mixed or contaminated plastics, into reusable materials. This process also reduces the demand for new virgin plastic materials derived from fossil fuels. This can lead to lower greenhouse gas emissions and conserve valuable, non-renewable resources. While solvent-based processing offers several benefits, it also comes with a set of environmental impacts that need to be considered. The solvents used in the recycling process can be hazardous to the environment and if not handled properly may pose risks to ecosystems and human health.

A comparison between the production of virgin ABS (ie. primary material) and solvent-based recycling methods are discussed in this section. For this, we estimate the embodied energy and CO_2 equivalent emissions. The embodied energy is the sum of energy required for each step in the process to convert the material into a new manufactured product. The CO_2 equivalent represents the amount of greenhouse gas whose atmospheric impact has been standardized to that of one unit mass of CO_2. While solvent-based recycling generally requires less energy than producing new plastic, the process still demands significant energy input. Depending on the energy source, this could lead to indirect environmental impacts such as increased reliance on fossil fuels. Anderson et al. [5] conducted an analysis of the energy consumption and CO_2 emissions associated with producing and recycling ABS material using DCM and methanol as solvent and anti-solvent respectively. The study determined that solvent extraction is the most energy-efficient and environmentally friendly option, requiring only 39 MJ/kg of energy and emitting 1.9 kg/kg of CO_2. Lu et al. [14] also studied the environmental impacts and estimated similar embodied energy and CO_2 emission for the solvent-based recycling method on ABS toy waste where acetone and water were used as solvent and anti-solvent respectively. In addition, it is possible to recover the solvents for reuse during the dissolution-precipitations process or to use solvents with low toxicity and impact on the environment [52, 53]. Overall, implementing solvent-based recycling technologies could contribute to reducing the release of harmful substances into the environment and improving the sustainability of plastic recycling while removing hazardous additives and restoring polymer properties.

The environmental analysis used in this work is the same method as Anderson et al. [5] and Lu et al. [14]. Fig. 5.1 shows the summary of the production of primary material and solvent-based recycling based on the calculations estimated by the REMADE calculator. Additional details of the calculations can be found in Appendix B. The calculations considered the full process including collection, preparation processes (sorting, screening for metal, density, air separation, washing, drying, and optical sorting), solvent-based recycling processes, and extrusion. The calculations also include the new CB extraction steps used in this work. The process considered includes dissolution, separation, and precipitation of the ABS using ethyl acetate, distilled water, and methanol, respectively. The estimated values for this work for embodied energy is 34.8 MJ/kg and for CO_2 emission is 1.7 kg/kg. This is less than the estimate from previous works with both Anderson et al. [5] and Lu et al. [14] using different solvents, and as a result, a larger environmental impact was estimated for their process. The solvents used have a significant impact on the embodied energy because they have different boiling temperatures, specific heat capacities, and different quantities are needed to dissolve or precipitate the polymers. This in turn makes them have different embodied energy. For example, acetone has an estimated embodied energy of 46.8 MJ/Kg, whereas ethyl acetate has an estimated embodied energy 35 MJ/Kg. Since the CB extraction involved using distilled water at room temperature, the estimated embodied energy calculated for the separation process was 0.418 MJ/kg. Thus we can estimate that the CB extraction method has no significant impact on the embodied energy of this process.

In summary, the environmental analysis showed that using solvent-based recycling methods is successful in recovering high-quality ABS while reducing the environmental impacts of energy consumption, and CO_2 emissions compared to the primary material. Moreover, the CB extraction did not add a significant energy requirement for the separation step nor did it increase the overall embodied energy or CO_2 emission.

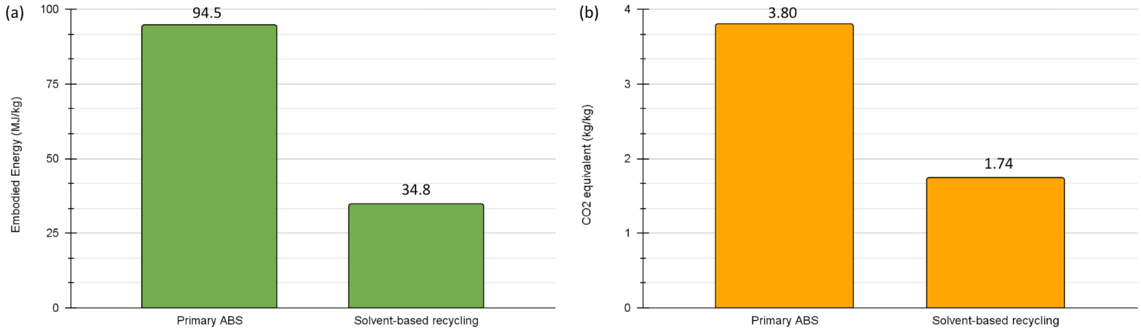


FIGURE 5.1: (a) The embodied energy and (b) CO_2 emissions of primary ABS and solvent-based recycling. All calculations were completed with the REMADE calculator.

Chapter 6

Conclusion

Recycling polymers is a highly growing field, aimed to reduce plastic waste. Many processes have been developed recently separated into three main categories: mechanical, chemical, and solvent-based recycling. While all have advantages, the main concern is the presence of contaminants such as pigments in the old resins. Most importantly, the presence of CB cannot be removed through the current recycling processes and this prohibits access to colourful recycled resins. The global target of this work was to develop a process that was able to remove CB from ABS polymer. After literature research, the solvent extraction process was selected. However, an extra separation process was needed to allow CB extraction and this separation step was studied in this work.

To begin the experimental study, the solvents for solubilization and precipitation of ABS were carefully chosen. Ethyl acetate was chosen for solubilization while methanol and hexane were both investigated as anti-solvent for precipitation. Dissolution and precipitation are the main steps of the solvent-based recycling process but does not allow CB removal. Liquid-liquid extraction technique was utilized to extract CB before precipitation using a collector solvent. Distilled water was determined to be the most efficient collector solvent. Further studies were conducted showing a very important pattern: a 1:1 ratio between ABS solution and collector solvent is essential. Other ratios do not allow any CB extraction. Other tests conducted showed the importance of different parameters such as surface interface or temperature. The results showed that a larger surface interface and colder temperatures yield more CB extraction.

Analyses were carried out on recovered ABS at room temperature and precipitation with methanol or hexane with overall yields ranging from 46 to 75%, respectively.

The most important analysis was the color measurement, which showed a huge improvement in the whiteness of the sample with L-values going from 44.7 to 62.7 for methanol and hexane respectively, compared with 28.5 for ABS filament starting material. Moreover, FTIR analyses assessed the removal of carbon black and the absence of chemical degradation of ABS. GPC analyses showed a small decrease in molecular weight due to chain scissions occurring during solubilization. In addition, TGA and DSC proved no alteration of the final recovered ABS after the three step process. TGA showed some solvents remained in the matrix, noticing the importance of polymer drying and solvent selection

To support the benefit of this new process, an environmental analysis calculation was conducted to determine the impact of the solvent-based recycling method, including the CB removal process. The calculations showed that the CB extraction does not require significant energy consumption or CO_2 emissions, and thus, does not increase the environmental impact, compared to traditional recycling methods.

Finally, future works should focus on the optimization of the process and mainly on the scaling-up of the CB extraction step. Indeed, polymer dissolution-precipitation is well known in the industry whereas liquid-liquid extraction from polymer solutions is not described yet. More efforts are needed on this step. At a lab scale, other solvents will be studied for the CB extraction. One way to increase CB extraction would be to decrease ABS solution solubility in water. Ensuring adequate mixing between ABS solution and collector solvent also needs work with changing parameters. Using a method, such as a counter-current column or solvent elution process, can allow the collector solvent to pass through the ABS solution and remove CB at a continuous rate while reducing the loss of the solution. These methods would also allow the use of different collector solvents for different contaminants to be easily added to the system without additional equipment.

Appendix A

Additional Figures From Analysis

Firstly, the samples that were used for the color measurement are shown in Fig. A.1. Next, The TGA test was conducted to analyze the thermal decomposition of ABS. The results are shown in Fig. A.2 to Fig. A.4. As well, the DSC curve for S1 and S2 are also shown in A.5 for determining the Tg. Then, the FTIR test results are shown in Fig. A.6 to Fig. A.7. Finally, the MWD comparison of the GPC elution profiles are shown in Fig. A.10 to Fig. A.11. For GPC, it's worth noting that the sample size was between 0.9mg and 1.5mg depending on the sample. Thus, the polymer concentration was different for each sample and this can also affect the Mw and Mn measured.

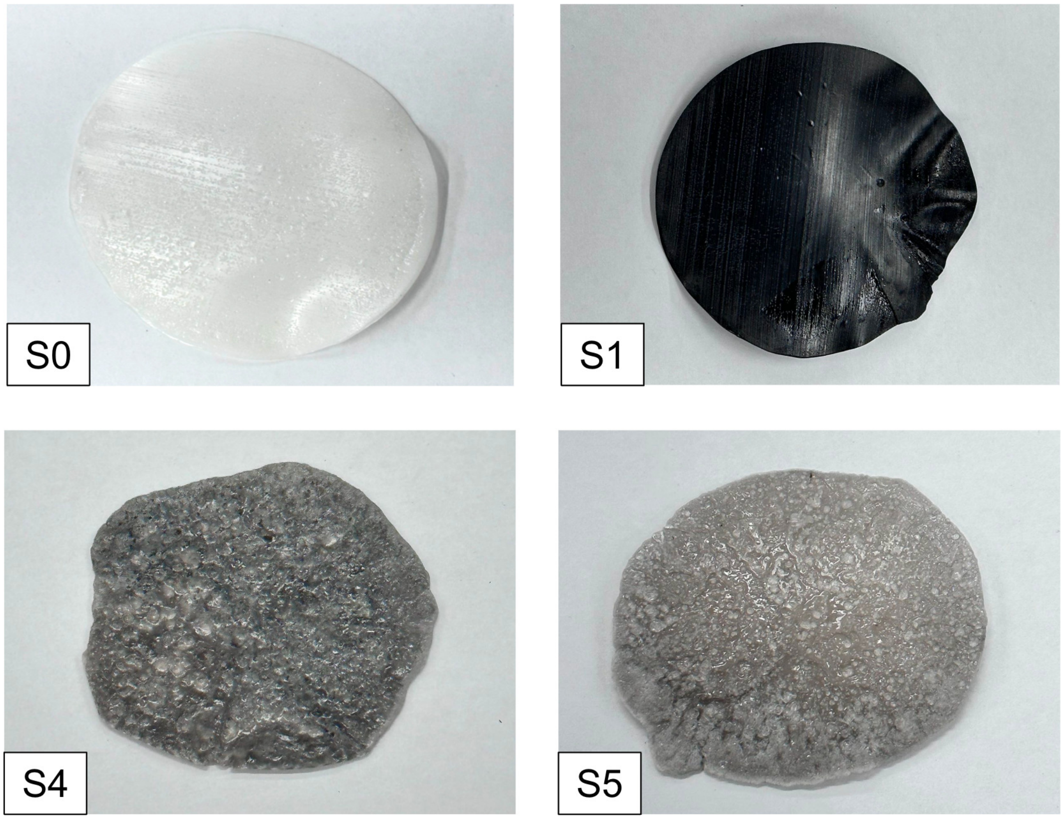


Figure A.1: Samples that were used for color measurement including virgin ABS (SO), ABS filament (S1), sample recovered using methanol to precipitate and distilled water to extract CB (S3), and sample recovered using hexane to precipitate and distilled water to extract CB (S5).

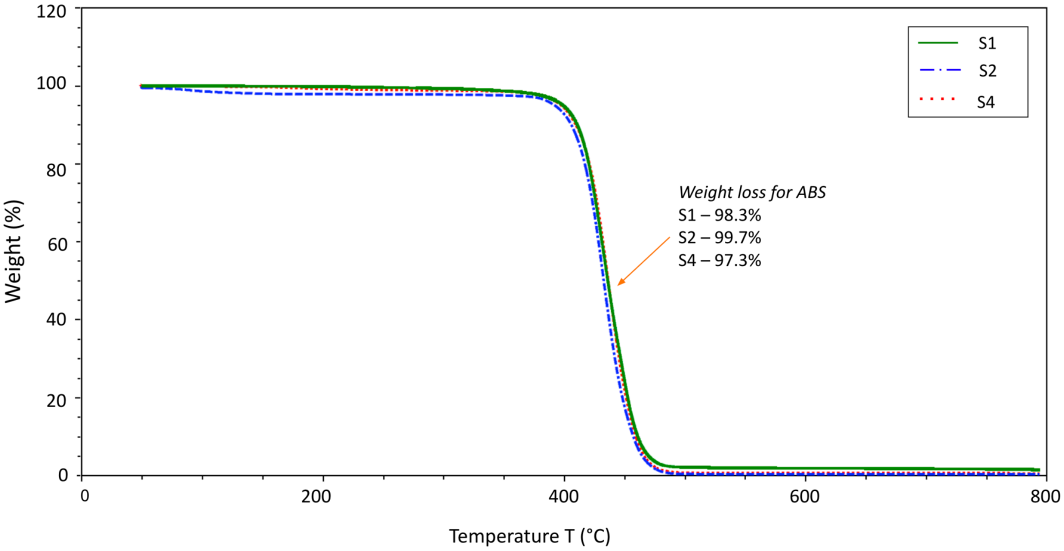


Figure A.2: TGA spectra differential thermogravimetry curves of ABS filament (S1), sample recovered methanol to precipitate (S2), and sample recovered using methanol to precipitate and distilled water to remove CB (S4).

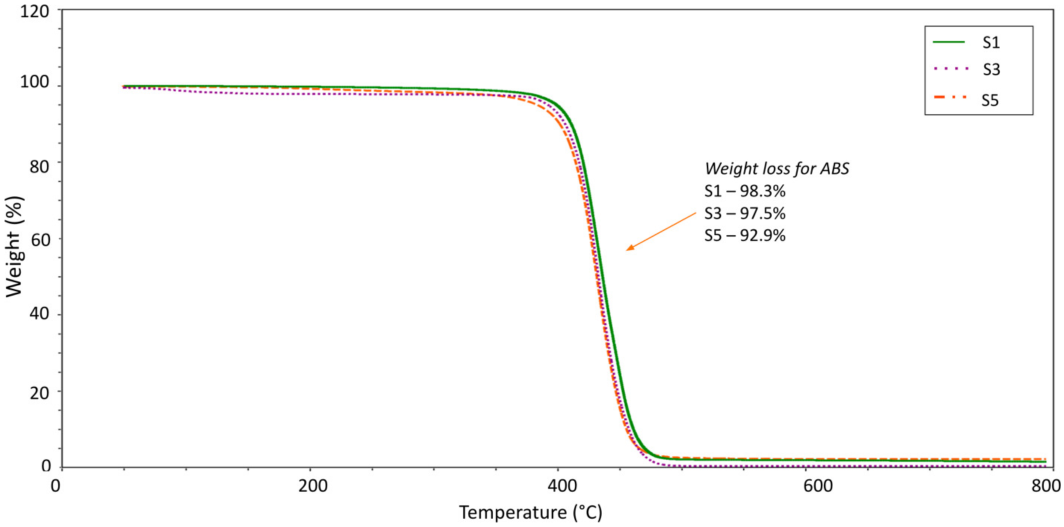


FIGURE A.3: TGA spectra differential thermogravimetry curves of ABs filament (S1), sample recovered using hexane to precipitate (S3), and samples recovered using hexane to precipitate and distilled water to extract CB (S5).

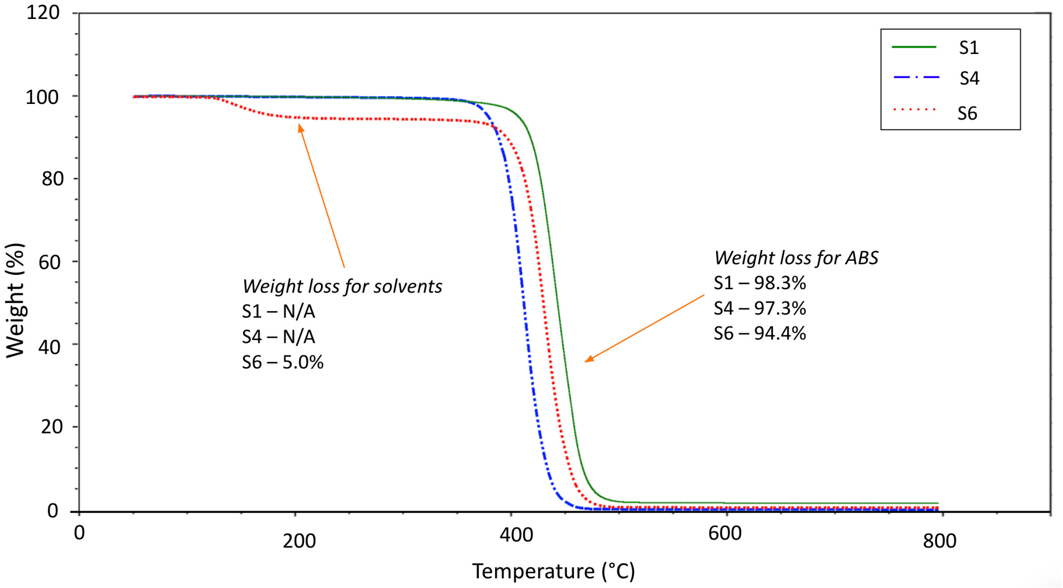


FIGURE A.4: TGA spectra differential thermogravimetry curves of ABS filament (S1), samples recovered using collector solvent distilled water (S4), and sample solvent recovered using collector ethylene glycol (S6). Precipitation was done with methanol.

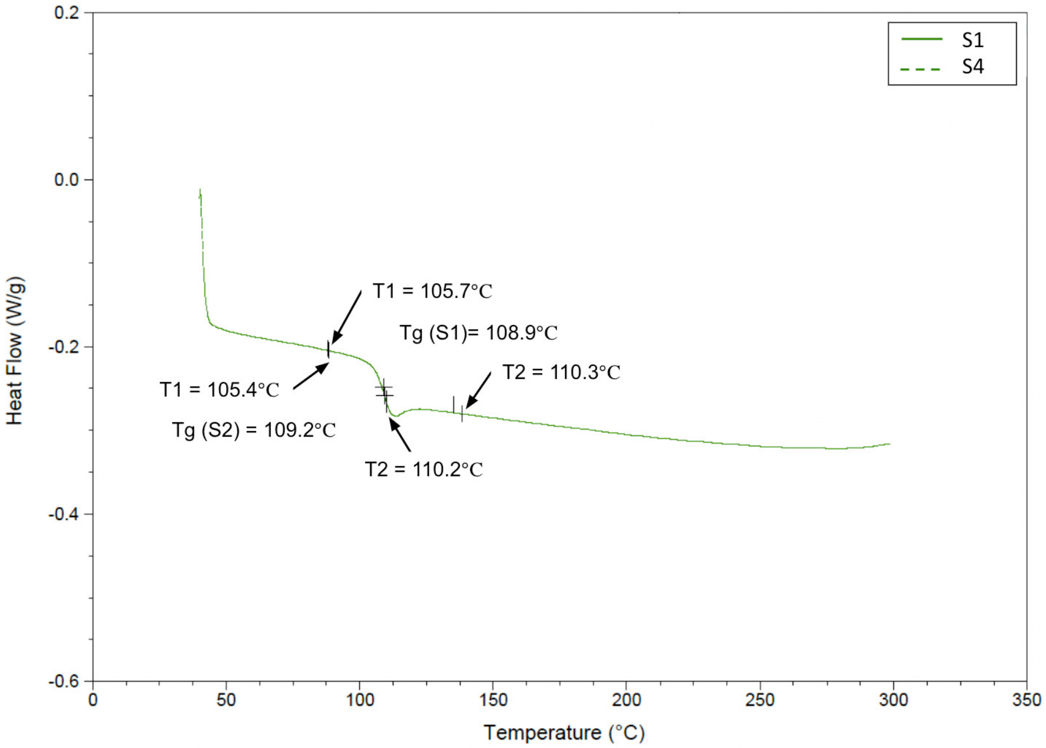


Figure A.5: DSC temperature profile of ABS filament (S1) and samples recovered using collector solvent distilled water (S4). Precipitation was done with methanol.

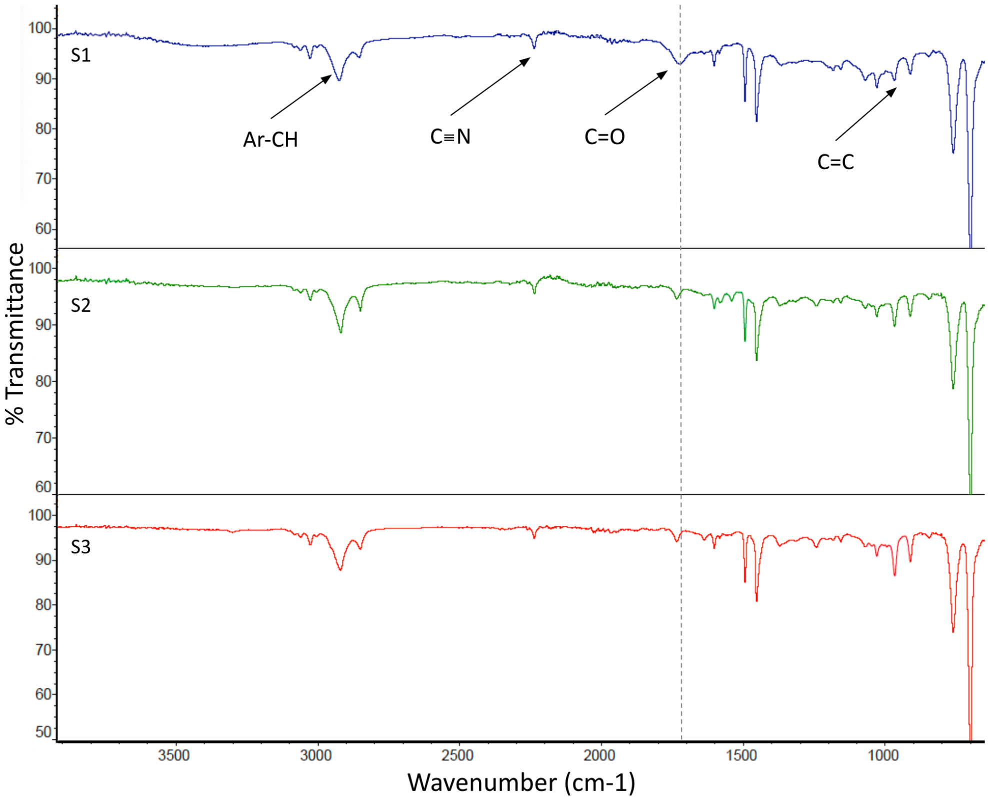


Figure A.6: FTIR spectra overlay for samples ABS filament (S1), sample recovered using methanol (S2), and sample recovered using hexane (S3).

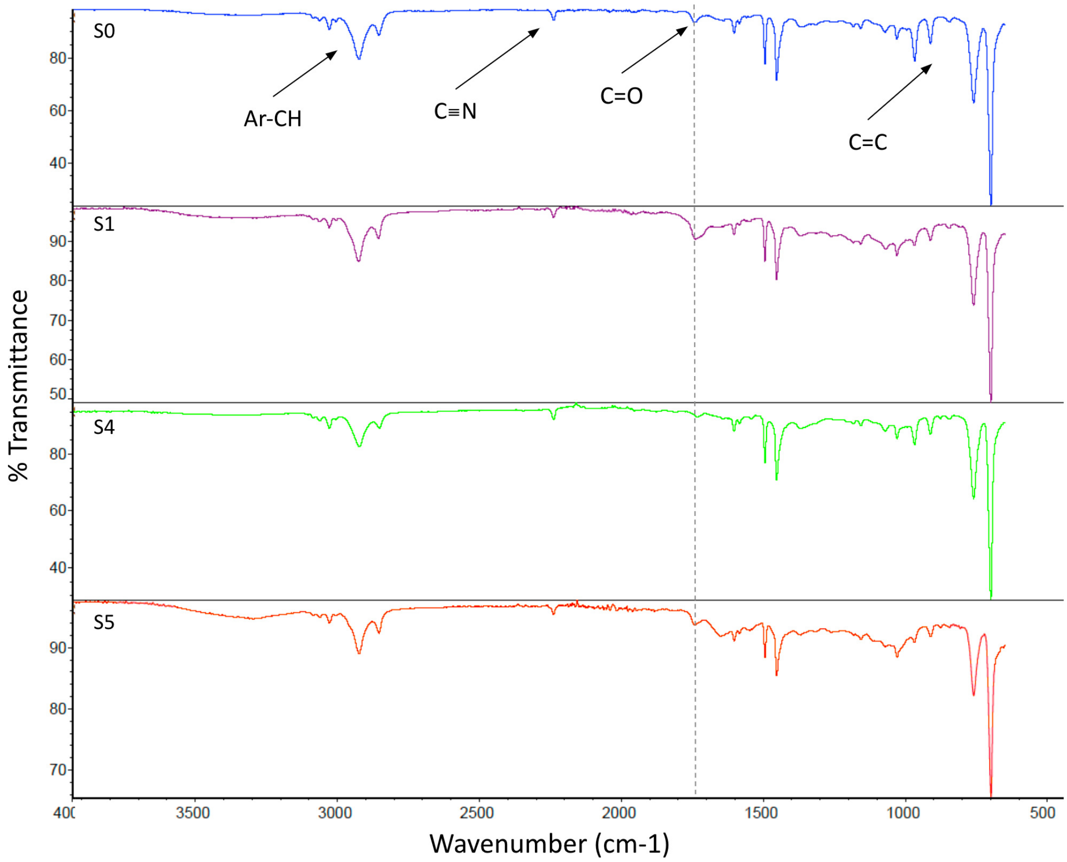
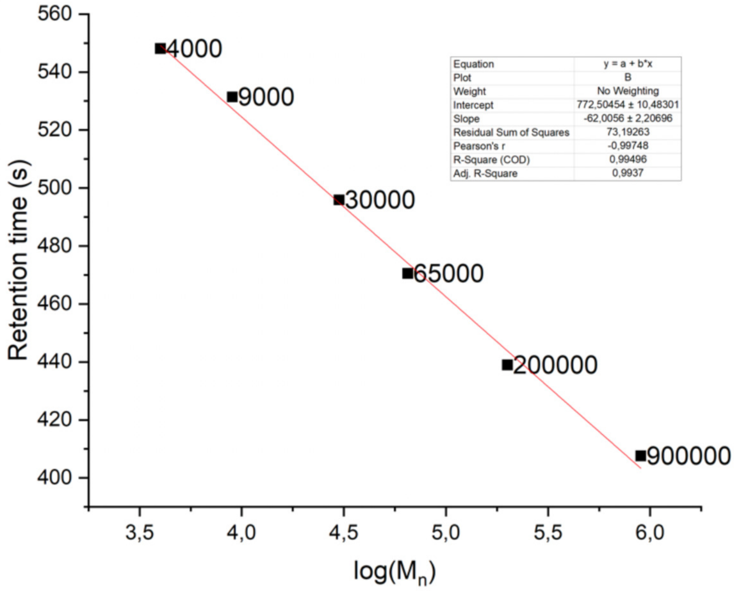


FIGURE A.7: FTIR spectra overlay for samples virgin ABS (SO), ABS filament (S1), sample recovered using methanol to precipitate and distilled water to extract CB (S4), and sample recovered using hexane to precipitate and distilled water to extract CB (S5).



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	772,50454 ± 10,48301
Slope	-62,0056 ± 2,20696
Residual Sum of Squares	73,19263
Pearson's r	-0,99748
R-Square (COD)	0,99496
Adj. R-Square	0,9937

FIGURE A.8: GPC calibration curve for the MWD with PS standards in THF.

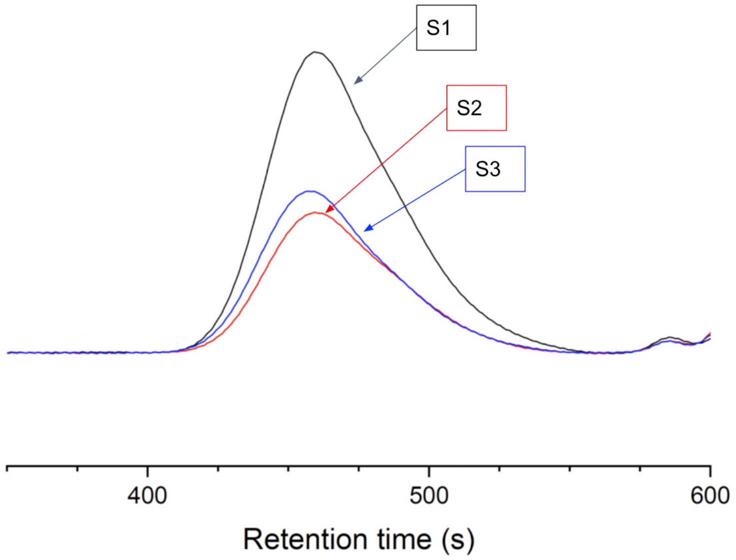


FIGURE A.9: GPC curve for MWD of ABS filament (S1), sample recovered using methanol to precipitate (S2), and sample recovered using hexane to precipitate (S3).

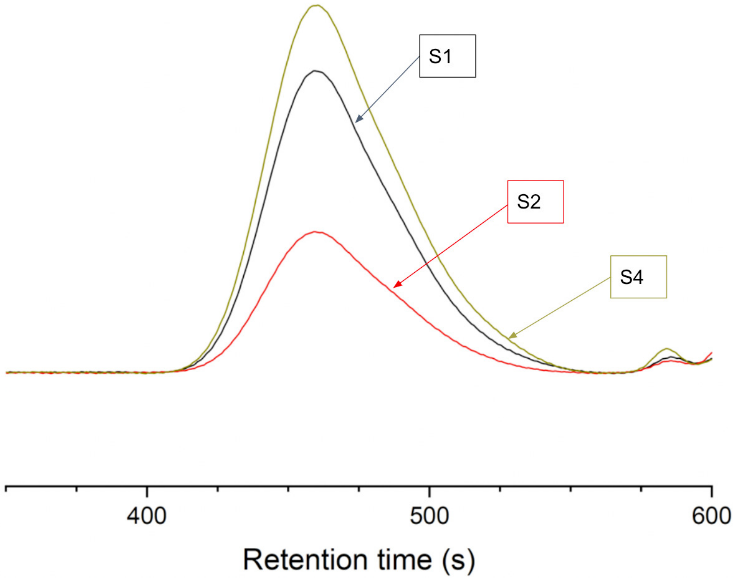


FIGURE A.10: GPC curve for ABS filament (S1), sample recovered using methanol to precipitate (S2), and sample recovered using methanol to precipitate and distilled water to extract CB (S4).

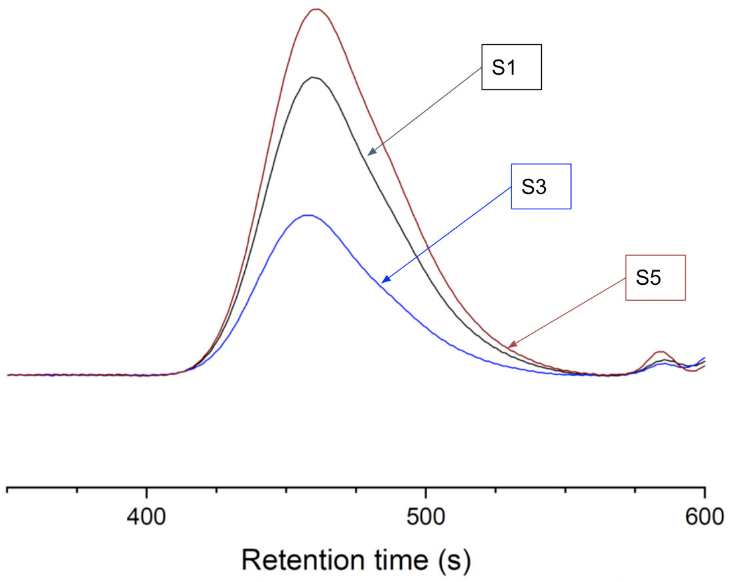


Figure A.11: GPC curve for ABS filament (S1), sample recovered using hexane to precipitate (S3), and sample recovered using hexane to precipitate and distilled water to extract CB (S5.)

Appendix B

Environmental Impact Analysis

The following section is the overview of the environmental impact calculations for embodied energy and CO_2 emissions for the solvent-based recycling method. The estimated values for the solvents and the processing steps were found using the REMADE calculator which is available online (https://remadeinstitute.org/project-impact-calculator).

B.1 Estimate for the solvent-based recycling

B.1.1 Preparation steps

Each step of the preparation steps of the recycling process needs to be included in the calculation. Since each step has its own embodied energy, and CO_2 emissions, Table B.1, summarizes the values for each individual process.

Table B.1: Estimated embodied energy, and CO_2 emissions used for each process from the REMADE calculations.

Process type	Em. Energy (MJ/kg)	CO_2 emissions
Collection step	0.5	0.03
Size reduction step	0.6	0.03
Each conveying to step	0.2	0.01
Screening or magnet step	0.2	0.01
Air separation cleaning	0.2	0.01
Wet density separation or cleaning/drying	0.3	0.02
Optical sorting step	0.2	0.01
Extrusion	6.0	0.30

To calculate the embodied energy required for the preparation steps, we must make the following assumptions: the process includes mechanical conveying steps needed to prepare the material for recycling; size reduction to turn the plastic into flakes; air separation or dry cleaning step; wet density separation step; optical step for sorting. Table B.2 shows the summary of the embodied energy calculations for all preparation steps, where x_i is the number of occurrences for that preparation step. Another assumption is that the quantity of waste collected to recover 1kg of ABS is assumed to be 1.2 kg. In summary, the total embodied energy required for collection, sorting, and material preparation is 4.32 MJ/kg.

Table B.2: Estimated embodied energy used for each preparation of the solvent-based recycling step.

Process description	x_i	EE (MJ/kg)
Collection	1	0.6
Conveying step	7	1.68
Size reduction step	2	1.32
Screening or magnet step	2	0.48
Air separation cleaning	1	0.24
Wet density separation or cleaning + drying	1	0.36
Optical sorting step	1	0.24
	Total	4.32

B.1.2 Dissolution-precipitation and extrusion steps

Table B.3 and Table B.4 give the values used for the calculations of the embodied energy and CO_2 emissions for each solvent used during the solvent-based recycling methods (i.e. ethyl acetate, distilled water, and methanol) provided by the REMADE calculator. The solvent-based recycling method needs to consider the solvent-to-polymer ratio during dissolution, the temperature at which the dissolution step takes place, the specific heat capacity of the solvent, and whether the process uses electricity to heat the solution. We assumed that there would be a 90% yield from the process since there would always be a percentage of contaminants that cannot be removed, and the electricity required for heating during the process is equal to 0.3 MJ/kg.

Table B.3: Estimated embodied energy, and CO_2 emissions for the solvents used from the REMADE calculations.

Solvent	Em. Energy (MJ/kg)	CO_2 emissions (kg/kg)
Ethyl Acetate	35.0	1.000
Methanol	36.5	0.900
Water	0.02	0.001

Table B.4: Thermal data of the solvents used in this work from the REMADE calculations.

Solvent	ΔH_V (kJ/kg)	C_p (kJ/kg-K)	Boiling Temp (°C)
Ethyl Acetate	365.7	1.90	77.1
Methanol	1100	2.53	64.7
Distilled water	2260	4.18	100

The method in this work required no filtration. Instead, the extraction of CB is calculated by using distilled water. The calculation takes into consideration that the process is conducted at room temperature without requiring additional energy. We also assumed that there would be a 90% yield from the process since the middle phase is lost where the ABS solution is mixed with the CB particle after the separation, as previously discussed.

Next, the anti-solvent used during the process also needs to be considered during precipitation. Once again the calculation takes into consideration that the process is conducted at room temperature and we assume that there would be a 90% yield from the precipitation.

Extrusion is the final step of the recycling process, where the extrusion process is estimated by REMADE to be 6.0 MJ/kg with the additional energy required for two conveying steps of the material throughout the factory. This in total has an estimated embodied energy of 6.4 MJ/kg for the extrusion step. In summary, the total embodied energy required for the solvent-based recycling of the ABS including preparation, dissolution-precipitation, and extrusion is 23.5 MJ/kg.

B.2 Final results

Table B.5 shows the summary of the required energy at each step of the solvent-base recycling process including CB extraction, where the total estimated embodied energy is 34.8 MJ/kg. The CO_2 emissions can be found to be the embodied energy divided by 20 giving a total to be 1.7 kg/kg. The final embodied energy and CO_2 emissions for primary and secondary material as well as the solvent-based recycling method using extrusion are summarized in Table B.6. We can see that the solvent-based recycling process has less embodied energy and CO_2 emissions. For comparison purposes to other works, the recovery of the solvents was not considered. This step would be more environmentally friendly so as to not throw away toxic chemicals. However, the recovery of solvent would also require some energy consumption.

Table B.5: Summary of the embodied energy for all steps in the solvent-based recycling process used in this work

Process	Em. Energy (MJ/kg)
Preparation/Collection	4.32
Solvent-based recycling	23.5
Extrusion	6.4
Total	34.8

Table B.6: Summary of the embodied energy for the production process of ABS from the REMADE calculator.

Process	Em. Energy (MJ/kg)	CO_2 emissions (kg/kg)
Primary (Virgin)	94.5	3.8
Solvent-based recycling	34.8	1.7

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