Application of Different Chemical Recycling for Plastics

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Abstract. Plastics usage is always a huge part of human lives. The concern about plastics regarding their high accumulation rate is significant. Most of these plastics cannot be recycled and go to landfills instead. Traditional methods like mechanical recycling still have drawbacks in categories such as value degradation and the complexity of sorting plastic wastes. Besides mechanical recycling, chemical recycling is another option that uses chemical reactions to achieve the production of feedstock products. This research will focus on the different types of chemical recycling, including depolymerization via solvolysis, pyrosis, and purification method. Plastic polymer wastes like PET, PU, and PS can undergo these processes to be reproduced into useful monomer products that can be further polymerized back into the plastic structure.

Keywords: Depolymerization, Plastic, PET, Recycling.

1. Introduction

In today's world, plastics and their products have become essential to people's lives. The plastic serves mostly as a material for packings, such as plastic wraps or bags. Those kinds of plastic products usually share some advantageous features, which include low production cost, high resistance toward liquid, and high versatility in usage. One of the reasons why plastic materials have these properties is because of their composition of plastics. The composition of plastics is made by polymer structure, and that structure is produced by monomer compounds such as ethylene, propylene, styrene, and many other compounds. As the global economy keeps growing over the last several decades, the demand for plastics also increases as well. This leads to a large production of plastic. And the issues of plastic pollution have become more prevalent in different regions and countries. One major cause is the rapid accumulation of plastic waste. People produced only 2 million metric tons of plastic waste in 1950 worldwide. In 2018, the amount of plastic waste is 359 metric tons [1]. This massive plastic waste usually ends up in landfills or incinerated. Only a small amount of plastic has been recycled during the history of plastic production.

Even in places such as Europe, with strict plastic waste regulation, the recycling rate is still less than a third of the total plastic waste, which was 29.1 million tons in 2018 [2]. When lots of plastic ends up in landfills, the landfill is more like temporary storage instead of a long-term solution. The plastic material in landfills can be harmful in so many ways. First, it takes an extremely long time for plastic materials to decompose in landfills. As those plastics decompose over the years, microplastics can also be decomposed into the soil and harm the environment. Some of the other plastics may end up incinerated, producing air pollution such as the excess amount of CO_2 and CO, and other hazardous compounds produced by burning plastics, such as dioxins, furans, mercury, and polychlorinated biphenyls [3]. Burning plastics is one major cause of the current global warming situation. Landfills and burning are not the only two solutions that are being used nowadays. The way of recycling plastics can be arranged into four different categories.

There are four main categories of plastic recycling. They are primary recycling, secondary recycling, tertiary recycling, and quaternary recycling. First, primary recycling is a closed loop mechanical recycling process, and this means that the products can be recycled as glass bottles and aluminum cans. For plastics, only a limited number of plastic compounds can go through this closed-loop process, such as polyethylene terephthalate (PET) and high-density polyethylene (HDPE). The general steps of this closed loop system are starting from the separation and sorting of the plastic wastes, and then the plastic is washed. Later, after the plastic waste is dried, it will go through a recycling method like extrusion, which uses high amounts of heat to break up the long chain polymer of the plastics.

However, during processes like extrusion, sometimes, mechanical recycling cannot restore the value of recycled plastic after the recycling cycle. The plastic waste transforms into lower-value plastics. For example, some plastics include recycled PP, HDPE, and LLDPE. The tensile strength and elongation are significantly reduced after mechanical recycling [2]. This type of reduced-value recycling method is called secondary recycling instead. The lower value property of mechanical recycling is a major downside compared to other potential ways of recycling, because after mechanical recycling, most new materials cannot be re-used in areas like food and beverage packaging. The latest products from mechanical recycling usually become fibers and plastic resin [1]. Mechanical recycling also has limitations in selecting plastic condition, if one plastic is heavily contaminated, which is hard for the mechanical process to separate the useful portion with the unwanted material. As a result, a lot of common household plastics do not meet this requirement, the plastic material that regularly goes through this process is only clear PET bottles. Besides mechanical recycling, chemical recycling can restore the plastics' value through different depolymerization strategies. Chemical recycling is a process where the polymers in the plastic wastes are broken by some selective reaction into monomers or reformed into functional new molecules or polymers. Besides the value advantage, chemical recycling is more environmentally friendly than other methods such as incineration, landfills, and sometimes even mechanical recycling because chemical recycling usually has low CO_2 emissions [4].

Chemical recycling usually involves mechanisms like glycolysis, methanolysis, and hydrolysis. Chemical recycling can produce some plastics from 100% recycled plastics. Some plastic materials that can undergo chemical recycling are PET, HDPE, LDPE, PP, PVC, PS, and other materials. This research will focus on the use of chemical recycling toward different plastic materials that people often use daily, the limitations of chemical recycling, and those depolymerization methods. In addition, this research will view the process of plastic chemical recycling with their depolymerization strategies. The following section will discuss these materials' depolymerization strategies and reaction mechanisms in their chemical recycling.

2. Current issues for plastic recycling

People commonly use and see seven types of plastics in their daily life. These seven types are polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), and other polymer-based plastics that are relatively rare in usage. All of those plastics are needed in the production of everyday household objects. PET is often used as beverage bottles and plastic trays. HDPE and LDPE can be used for bottles, toys, and recycling bins. However, not every plastic material can be recycled under the current technology. For example, plastic products such as coatings, packaging films, adhesives, and sealants cannot be recycled due to their properties. This article focuses more on the plastic that currently can be recycled first and explore different polymerization methods regarding these plastics.

Because the demand for those plastics is always high due to the massive daily usage, the type of plastics that contribute the most must be prioritized over those that contribute least to plastic waste. Based on the proportion of total wastes that were collected in 2018, out of the total, 40.3% are PET, followed by 21.6% of HDPE and then 10.2% of PP. As shown in Figure 1, some other types of plastic only accounted for a smaller percentage, such as PS and PVC [5]. Numerous plastics wastes control methods are currently used to deal with plastic waste, whether they are recyclable or not. The first standard conventional method is landfilled. Based on the UN environment program, approximately 36% of all plastics are used for packaging, and 85% of those plastics end up in landfills [1]. Even in the short term, landfills may be an excellent way to store away to prevent environmental impact. However, from a long-term perspective, with this high production of new plastics, water and solids contamination risks are incredibly high. Furthermore, landfills take lots of space, and space is not something that each country is afforded these days. Another major backfire of using landfills to store plastic waste is energy inefficiency. From a sustainability standpoint, the energy that produces the plastics and the materials can never be recycled and reused because the plastic wastes are all sitting in landfills. Other methods like incineration became another way of dealing with plastic debris. About 8% of the total plastic production went through this process [1]. The significant benefits of incineration are that it does not need space for plastic storage and can achieve energy recovery by burning plastic materials. However, air pollution from burning plastic is significant. Therefore, recycling has become the central solution for plastic waste.

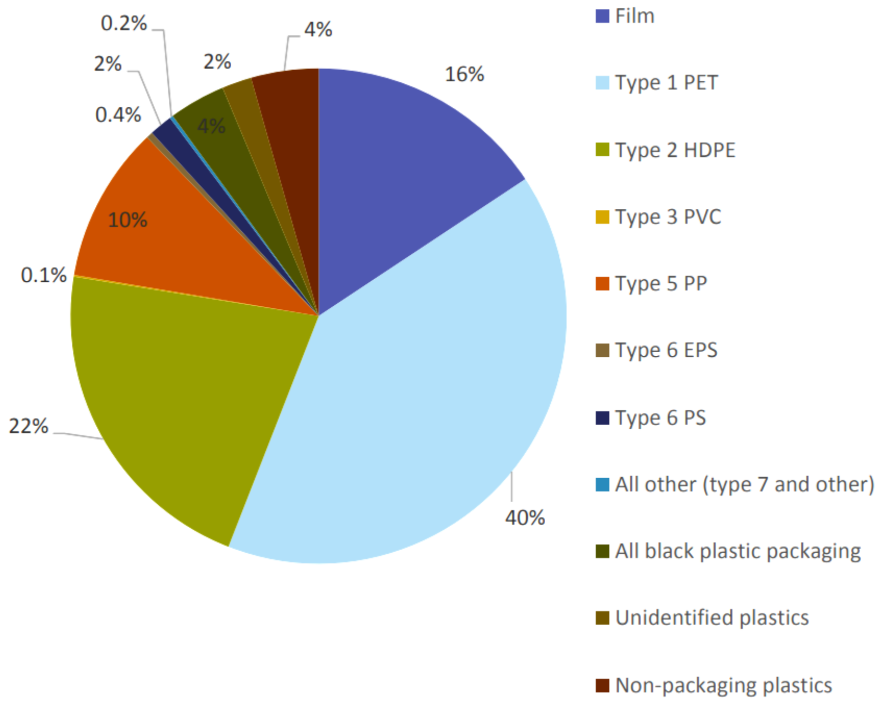

Figure 1. Composition distribution of plastics composed of polymers [5]

3. Chemical Recycling

Mechanical and chemical recycling are the two main recycling methods for plastic waste. Because of the downside of mechanical recycling mentioned in the introduction, chemical recycling is the best option because it is still relatively new compared to mechanical recycling. The following paragraphs will discuss some of the significant chemical recycling methods, including depolymerization, pyrolysis, purification, and other techniques.

3.1. Depolymerization via solvolysis

Plastic recycling mechanisms in the chemical world can be divided into two main categories. One is the polymer depolymerization method by solvolysis, and the other is pyrolysis. Those two processes have their own advantages and limitations. The following paragraphs will focus on the different polymers' depolymerization mechanisms in different conditions and some of their recent and future development. Polyethylene terephthalate (PET) is one of the most widely used polymers on the market. Chemical recycling of PET in the industrial application uses cleavage of specific functional groups by a reagent such as glycols, methanol, and even water. The effective mechanisms will be discussed.

PET glycolysis is the most common way to depolymerize PET. PET glycolysis can go through a process of glycolysis to achieve depolymerization. This process can be described as the transesterification between the ester group from PET and a diol molecule that is usually an ethylene glycol (EG) reagent. As a result of the transesterification, a product of monomer bis(2-hydroxyethyl) terephthalate (BHET) was obtained. The ester linkages are broken during this process and replaced with hydroxyl terminals [6]. The monomer product BHET can be re-condensated into PET to achieve a closed loop cycle of recycling wasted PET.

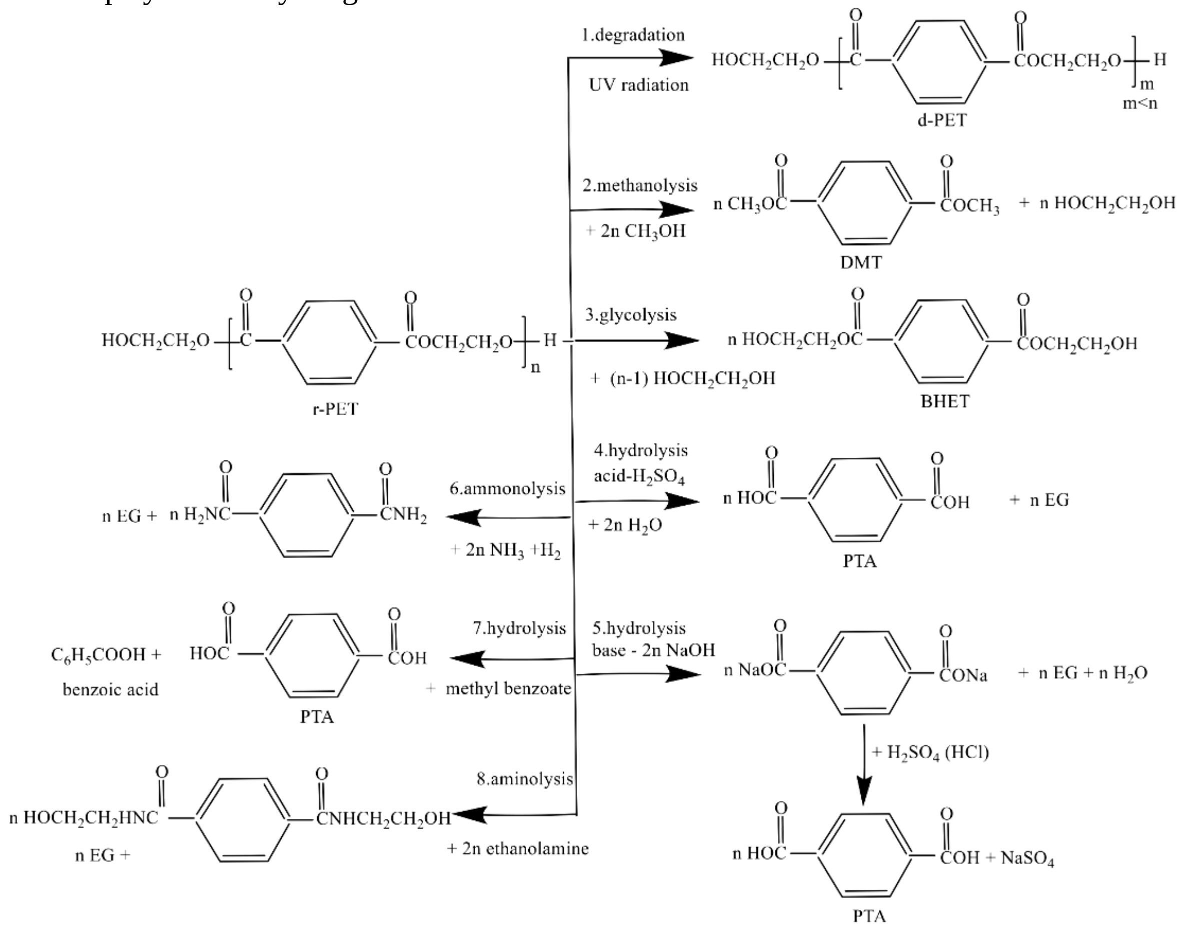

Figure 2. Possible reactions to recycle PET [7]

Additionally, the renewed material maintains the same value as the virgin stocks. Or even it can synthesize polymers such as unsaturated polyesters and polyurethane with a higher value. This process of glycolysis usually happens at around 180 to 240 ℃, and the reaction time is about 0.5 hours to 8 hours [7]. Two plastic recycling companies: PerPETual and poseidon plastics, are currently using this glycolysis as their primary mechanism in depolarizing waste PET, as shown in Figure 2. Methanolysis is another mechanism to recycle PET chemically. Methanolysis of PET is a process in which the methanol reacts with PET to produce two main products: dimethyl terephthalate (DMT) and EG [7]. This mechanism usually runs under high temperatures and high pressure. The catalysts of this reaction are usually metal complex, such as zinc acetate. The main advantage of this mechanism is that the methanolysis can be easily constructed in the polymer production factory. All of the recycled products can be used to produce other virgin polymers. The disadvantage of this reaction is the cost of this process is relatively high compared to the low cost of producing single-used PET. In addition, because of the specific catalyst, the presence of water would damage and poison the catalyst. Therefore, this method is not typical for industrial recycling of PET wastes.

For PET, there are lots of reaction mechanisms for recycling. Depolymerization of PET by hydrolysis can produce PTA monomer, methanolysis can produce DMT, and glycolysis can produce BHET. With different combinations of solvent, reagent, and catalyst, an optimate solution for depolymerization of a particular polymer, such as PET, has the potential to be bought up. Some current studies and future works focus on the supercritical liquid in the depolymerization of PET. Because of the properties of supercritical liquid, the reaction rate is faster than the same reaction under liquid states. The polymer can be depolymerized in supercritical fluids by solvolysis. However, one substantial downside of this method of using supercritical fluid is the extreme condition that the reaction may require. For example, PET hydrolysis with supercritical water has a significantly high rate. However, the temperature and pressure for this PET hydrolysis reaction are so high (400 ℃ and 30 MPa) that it is not practical to use this method for chemical recycling. But the extreme condition is not required for all mechanisms [8]. Sako et al. processed the depolymerization mechanism of PET to DMT via supercritical methanol. The reaction temperature is between 180 to 350 ℃ [9]. And the yield of monomer recovery of DMT and EG is almost 100% in a reaction time of 30 mins with no additional catalyst. This shows that the supercritical fluid may be a direction for improving depolymerization efficiency by reducing the temperature and reaction time.

All of these solvolysis are not just working with PET. Other polymers can also be recycled under the exact recycling mechanism. For example, recycling polyurethanes via solvolysis. Different mechanisms such as hydrolysis, aminolysis, phosphorolysis, and glycolysis can be used to depolymerize PU. Among all four methods, glycolysis is the most widely used mechanism. Glycolysis of PU is similar to glycolysis of PET. It has a transesterification process where the hydroxyl group interchanges the ester function from the glycol [10]. Some common catalysts for this glycolysis are diethanolamine (DEOA) with the reagent ethylene glycol. The reaction leads to the formation of a polyol, which is the aim of recycling PU [11]. The new recovery of polyols can be used to produce new PU. The glycolysis of PU usually happens at 180-220 ℃, which is not too high to damage the value of the new recycled products. From a review study on the development of solvolysis regarding depolymerization of PUs, glycolysis is the most technologically and economically mature compared to hydrolysis, aminolysis, and phosphorolysis [10]. A company called Getzner developed a mechanism of glycolysis for recycling PU wastes, as shown in Figure 3.

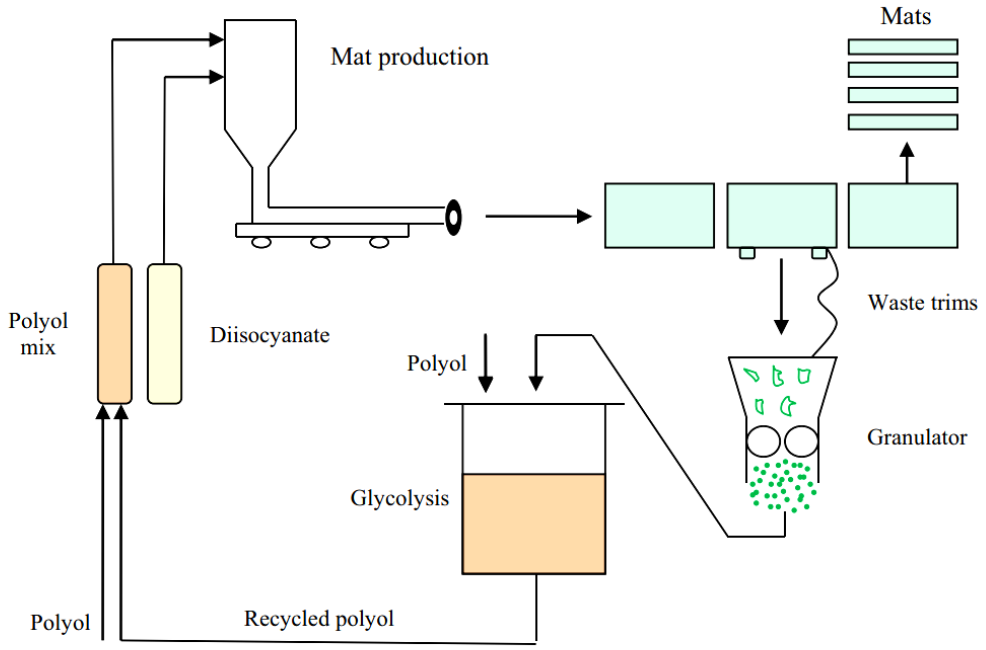

Figure 3. The designed Glycolysis process [7]

Aminolysis and phosphorolysis processes are still in the laboratory stage. Hydrolysis is mainly in the stage of pilot plant. Even though glycolysis runs a lot on an industrial scale, the products under this mechanism are usually a mixture of polyols, glycolysis agents, and other derivatives that are harder to reuse. From the example of depolymerization of PET and PU, solvolysis as a chemical mechanism is already in use for industrial plastics recycling, but future developments are still highly needed. For now, advance methods like combination method that normally use more than one solvolyses mechanism are already being developed. Method such as glycolysis-methanolysis, methanolysis-hydrolysis which occur at low temperature with no extreme condition required, the final yield product is usually quite high compared to the conventional method [12]. However, lots of those methods are still in the laboratory phase, it still needs more work to be used for the industrial field.

3.2. Pyrolysis

Another chemical recycling method that is commonly used is pyrolysis. Pyrolysis is the thermal decomposition method of plastics in an oxygen-free environment. This process can be broken down into three parts. The solid material/plastic wastes are first turned into a pyrolysis reactor. They are heated to a high temperature without oxygen. And then the vapor from the first process is condensed into a condenser. Lastly, the liquid from the vapor is stored in an accumulation tank. The liquid is the recycled products that are usually used as fuel or converted into monomer products. The heating process usually requires extreme high temperatures that are around 370-420 ℃.

Therefore, not all polymers can endure this degradation from the heat. For PET, an experiment done on the pyrolysis of PET at 450 ℃ shows that it can produce terephthalic acid (TA) and oligomers [7]. Even if this mechanism can acquire the monomer, this method will never apply into a bigger industrial scale. This is because pyrolysis of some polymers including PET also generates a lot of liquid and gas side products. The separation step for these side products may be quite complicated, so it is not efficient enough for the industrial field to recycle PET.

For PE, the major issue with using pyrolysis to recycle is the thermal degradation of PE by random scissions at C-C bond. There will be additional mixture products due to the two radical chains that are produced by breaking the C-C bonds. Additionally, the quality of the new recycled monomer products is also poor compared to the virgin product. The melt flow index of new recycled LDPE is only at 0.02 g/10 min compared to 2.25 g/10 min from virgin LDPE [13]. This change in properties shows that depolymerization via pyrolysis may not work so well. Therefore, depolymerization of PE through pyrolysis is mainly to yield oil or fuels as an energy recovery.

Some of the other polyolefin like polystyrene can actually be recycled by pyrolysis, there are several companies that are focusing on recycling PS. One of the strategies is converting PS into liquid styrene monomer using pyrolysis that is similar to the pyrolysis of PE. The lighter hydrocarbons and short oligomer are separated and softened for further application, same as the process after solvolysis. However, the temperature is around 550 degrees Celsius. Pyrowave, a chemical recycling company uses microwave as an assisted energy source to depolymerize PS, so the reaction temperature drops to around 400 ℃ [13]. There are more areas where pyrolysis is used as part of chemical recycling. Recent development of this technology is focusing on catalyst pyrolysis, assisted-mechanism like the microwave, and more efficient oil/fuel production. The high temperature requirement for many pyrolysis is the greatest barrier to overcome for this technology in the long term.

3.3. Purification

After the extraction process, the plastics/polymers undergo another process called dissolution. The dissolution of polymers is controlled by two transport processes; they are solvent diffusion and chain disentanglement. Many different factors can change the result of dissolution, such as the type of polymers, the size, and weight of the molecule, temperature, and others. For example, if a polymer has a high molecular weight, the dissolution effect is more controlled by the disentanglement of the polymers instead of solvent diffusion [14]. Therefore, selecting an excellent solvent to dissolve the targeted polymers is crucial. For polymers PMMA and PS, they dissolved faster in benzene compared with toluene. There are several selection rules regarding the solvent. First, because polar compound attracts polar, nonpolar compound attracts nonpolar, high polarity polymers are easier to dissolve in high polar solvents. Secondly, as the interaction between the polymer and solvent increases, the polymer-polymer interaction will decrease, and eventually, the polymer will dissolve into the solvent. Lastly, if the solubility parameters of the solvent and polymer are equal or similar, they can dissolve more efficiently [14], as shown in Figure 4. After the polymer is dissolved in the solvent, it can be crystallized selectively under different conditions. This method of recycling plastics is called the dissolution/reprecipitation method. This method can be used in the recycling of thermoplastic polymers. There are more recent developments in this concept of recycling plastics. From one study on the potential of finding new pure and blended organic solvents, they discovered that by having a different solvent, the dissolution temperature can decrease and still maintain a close or even higher recovery percentage for different types of polymers [15].

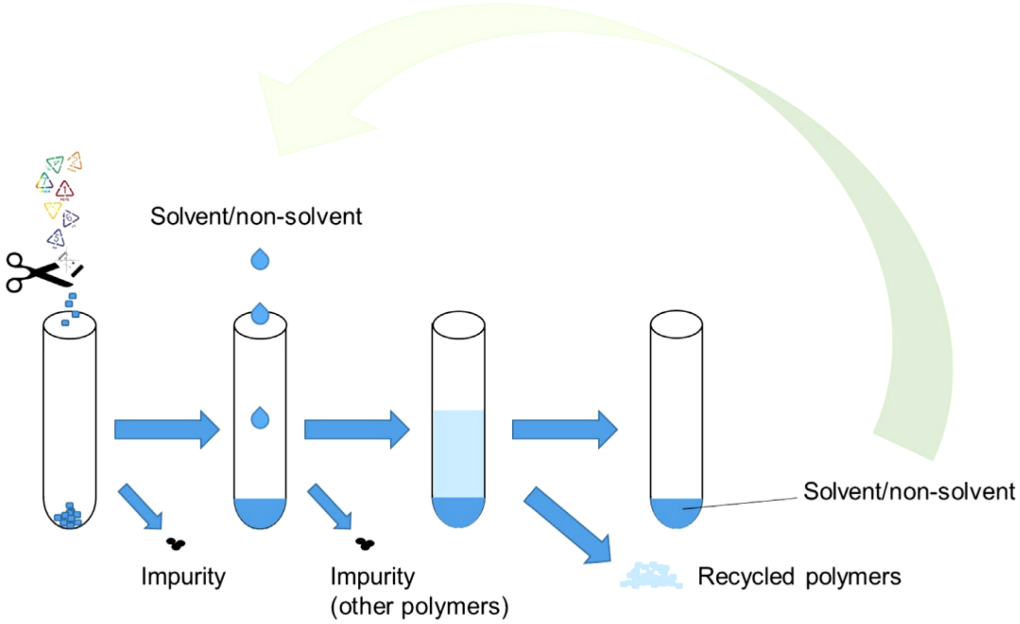

Figure 4. The principle of the dissolution methods [14]

For example, the original turpentine solvent can give a recovery percentage of 99.4 for LDPE, 92% for HDPE, and 98% for PP. When the solvent changes into a 1:3 turpentine/pete (B) mixture, the recovery percentage is poor among all three polymers. However, after examining a different amount of mixture for the solvent, similar recovery percentages were obtained from the solvent, such as 9:1 turpentine/pete (B). Those blend solvents that works significantly also decrease the dissolution temperature, which prevents the temperature from reaching the melting temperature of those polymers. This method can be applied to recycling thermoplastics on a larger scale. Some benefits of using this method include lower risk of degradation from heat, great removal of contaminants, and the properties of the recycled product is similar compared to virgin products. However, there are also some limitations in using this method currently due to the high technical skills required, and the cost of this process can be increased if it is applied to large-scale recycling of plastics.

4. Conclusions

The current primary industrial method of recycling plastic still focuses on the mechanical mechanism a lot. Still, more and more attention is transferred to chemical recycling because it is more environmentally friendly and can restore the value of the wastes in its virgin products. Methods of chemical recycling include depolymerization, pyrolysis, and purification. Each of these methods has its uniqueness in its use. Out of these three, pyrolysis is often a more direct solution by using excess amounts of heat to break the structure of the polymer and restore it as a new recycled monomer. But the downside of this method is also significant. Depolymerization strategies of chemical recycling mainly involve different solvolysis mechanisms. The catalyst and conditions for different polymers vary. Therefore, finding the best combination of solvent, polymer, catalyst, temperature, and other factors is critical for the further development of this technology. Lastly, new rising technology like purification has potential because their recycling path is more chemically planned. However, how to embed those laboratory works into massive industry usage is the next challenge for the development in this direction. In general, chemical recycling as an essential solution for plastic wastes should be further developed because it still has a lot of potential.

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