

Doctoral Dissertation (Shinshu University)

**Study on increasing mechanical properties of
recycled multi-composition thermoplastic
materials by improving interphase performance**

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Abstract

With the rise of people's awareness of eco-friendly and environmental protection, people have begun to know the importance of the sustainable development of ecological circumstances. It is known that plastic materials are applied in diverse fields due to numerous advantages such as rapid production, lightweight, low cost, and high applicability. However, most plastic materials themselves cannot be naturally degraded, which results in a huge amount of plastic wastes left in the circumstance, and causes a negative impact on the global environment. Most of the plastic waste is buried in the land and flows into the ocean, causing indelible damage to the natural ecosystem.

It is indicated that recycling is an important concept from the ecological and economical points of view, and the mechanical and thermal behaviors of materials themselves are also critical for recycling processes. To be honest, the repeated thermal treatments (melting and cooling) and mechanical ruptures during the recycling process may result in contamination (water or gas) and poor property performance. Various aspects of plastic's performance would be influenced by multiple thermal treatments if the processing temperature is not under well control, in which the intrinsic molecular chain would be cracked and damaged, and then affected the original performance. Another important issue is that the multi-composition plastic materials are too difficult to be separated and the interphase problem between different plastic components also disturbing the influencing the recycling efficiency during the process. Interphase problems resulted in different intrinsic characteristics may lead to poor results in the following recycling process and future applications. Hence, it is important to solve the interphase problem of multi-composition plastics. The compatibilizer stands for important functions including improving the phase adhesion and reducing the interfacial tension resulted from the polarity difference of different plastics. Therefore, recycling seems to be a nice solution for plastic wastes and plastic pollution, we still need to consider the specific characteristics of plastic materials and thus to obtain the most suitable for the existed plastic wastes or extend the long-term utilization of plastic materials.

In this dissertation, the main purpose is to investigate a simple and convenient method for multi-composition thermoplastic materials to solve the problems that plastic materials with various compositions cannot be recycled at the same time and to improve the recyclability and sustainable utilization of existed plastic materials and plastic wastes. Furthermore, thermoplastic material has been chosen as the primary materials due to its specific characteristic – can be reshaped and reformed after proper thermal treatment. As one of the most commonly used plastic material employed in various domains, polypropylene (PP) is selected as one of the raw materials, while another

experiment material is thermoplastic polyurethane (TTPU). Both of them are thermoplastic materials, namely can be recycled and reused after single-use based on proper conditions. Several types of processing techniques including melt-blending extrusion method, hot-pressing method, and injection method are employed based on different conditions in this study. The study is mainly divided into two parts and 4 chapters, Chapter 1 introduces the general introduction of current issues and background. Part I (Chapters 2 and 3) is “ Performance Improvement of Recycled Multi-composition Thermoplastic Materials”, and Part II (Chapter 4) is “Effects of Performance Improvement of Recycled Multi-composition Thermoplastic Materials after Cycling Utilization.”

In Part I (Chapters 2 and 3), the recycled multi-composition plastic material is composed of PP as matrix and TTPU as reinforced material. The mechanical properties, morphology observation, and thermal behaviors of multi-composition materials after recycle processes are all investigated. PP/TTPU groups with various composition ratios are melt-blended for two repeated cycles, which a small amount of compatibilizer (i.e. polypropylene grafted maleic anhydride, MA) as bridging role is added during the process. SEM images show that groups without MA, TTPU particles demonstrate a dispersive phase in the PP matrix, while the groups with MA improves the interphase problem between two materials. The impact test results have proven that the incorporation of 20 wt% TTPU and 5 wt% MA helps to improve the interphase problem, thereby yielding the impact strength of 63.01 J/ g. The tensile strength test results show that the presence of PP compensates for the insufficient rigidity and high production cost of TTPU. The flexural strength test results show that PP with high stiffness synergizes to the softness and flexural performance of TTPU. On the other hand, both of them can be properly heated to reform and reuse due to the inherent characteristics of thermoplastic materials. However, the using efficacy may be compromised as the waste may be overheating and thus damaged during the reheating process. The thermal degradation behavior, melting and crystallization behaviors of multi-composition thermoplastic materials are evaluated under appropriate considerations. In light of the thermal degradation, the presence of thermally stable PP improves the thermal stability of TTPU accordingly. From TGA results, the addition of MA is also helpful, and therefore the third thermal degradation temperature (T_{3max}) is increased by 50°C averagely when compare to neat PP. T_{1max} and T_{3max} of PP/MA/TTPU are postponed about 2 and 4 °C when TTPU content varied from 10 to 30 wt%.

In Part II (Chapter 4) is to explore the effect of multiple thermal cycles and mechanical fractures on the recycled multi-composition thermoplastic wastes, and the tensile properties, thermal behaviors and morphology observation are comprehensively discussed. It is known that with appropriate conditions, thermoplastic materials possess

a good reversible ability. They are prone to exceed the reversibility range when being repeatedly processed as they cannot bear high temperatures. The feasibility of multiple utilizations and differentiation effects are examined afterward. In this study, recycled or mechanically damaged TTPU/PP and TTPU/PP/MA wastes are used as the raw materials for the hot-pressing cycle, while MA is regarded as a bridging compatible role, thereby simulating various situations of the plastic wastes. Next, the TTPU/PP/MA groups that undergo post-2nd and post-3rd recycling are evaluated for comprehensive change. The test results indicate that without MA, TTPU/PP groups exhibit significant differentiation effects due to an increase in the polypropylene content and multiple melting–recycling cycles. By contrast, the presence of MA mitigates the overall differentiation effect of TTPU/PP groups. The ultimate purpose of this dissertation is to treat waste compounds via a simple hot-pressing approach to produce useful materials that can be used again.

As a result, this study attenuates the negative influences of plastic waste on the environment while achieving sustainable development. It is indicated that the addition of compatibilizer significantly helps solve the typical issues – interphase problems resulted from incompatibility and immiscibility between the different plastic materials and thus have a positive contribution to the sustainable development of existed plastic materials and multi-composition plastic wastes. Not only for the existed plastic materials but also for plastic wastes, the results have indicated the reusing efficiency and possibility in the subsequent recycling process and future applications.

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Chapter 1 – General Introduction

1.1. Introduction of Plastics

So far, plastic has been a commercial product comprised of polymer-based materials that are widely and possibly employed everywhere in our surrounding circumstances. A polymer is a large molecule with many repeating units bonded with each other, and generally originates from nature or man-made sources. The natural polymers include silk, cellulose, and even DNA, while the very first man-made polymers, Parkesine, is developed in the 1850s and 1860s [1]. In the 1920s, the first commercial plastic is polyvinyl chloride (PVC) that blends with extra substances to improve its plasticity [2]. Since then, Figure 1-1 shows a large amount of various plastic polymers have been developed based on different requirements such as packaging, textiles, building, and construction, etc [2, 3].

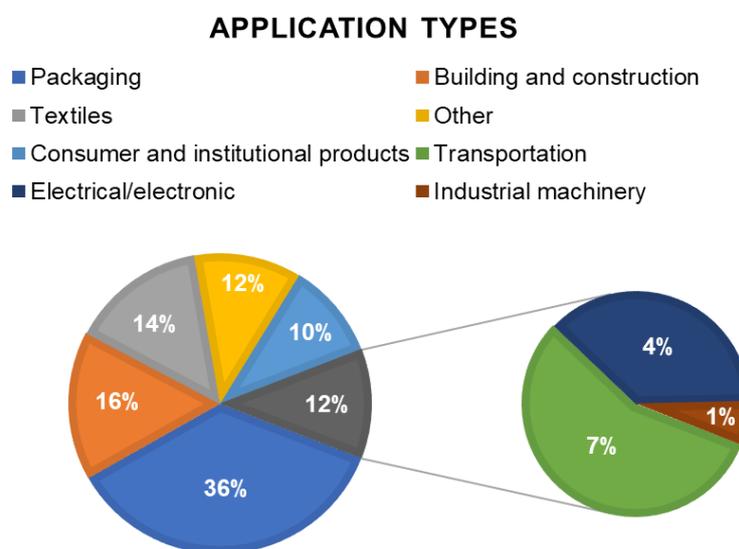


Figure 1-1. The various application types of plastic products [3].

1.1.1. Development of Plastic Materials

Since the middle of the 20th century, the evolution of plastic materials has been rapidly developed, and the ensuing speedy growth in plastic is extraordinary, surpassing most other man-made materials. From 1950 to 2015, the global consumption of plastic productions from 2 million tons to 440 million tons, and plastic is one of the most used man-made materials other than steel and cement [4]. Till now, the global plastic production is almost reached to 360 million tons in 2018 as shown in Figure 1-2 [5]. Over the past five or six decades, the global production of plastics has enormously raised and gained lots of attention in various fields due to its high versatility of materials, a wide variety of applications, lightweight, reasonable cost, and good mechanical performance.

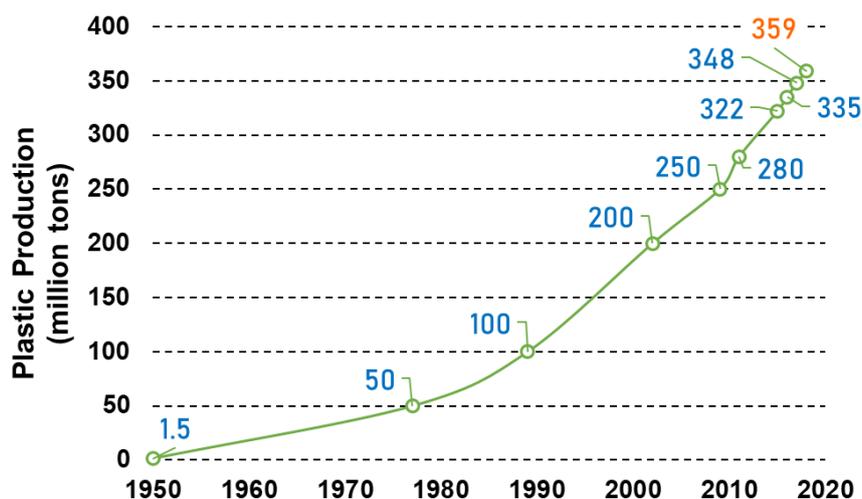


Figure 1-2. The global plastic production curve until 2018 [5].

1.1.2. Thermoplastics and Thermosets

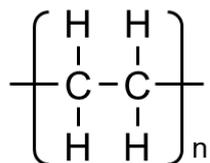
The series of plastics are composed of a wide variety of raw materials designed to meet the distinct requirements of thousands of end products in a wide range of practical fields. Plastic is one kind of polymer material composed of monomers derived from fossil hydrocarbons such as ethylene and propylene, in which the monomer is a long molecular chain that often made up of repeating chemical units. Among the various types of plastic materials, it can be mainly divided into two categories – thermoplastics and thermosets. The most significant difference between thermoplastics and thermosets is that the former one can be reformed after heating and melting, while the latter one cannot [6]. Thermoplastics are reversible after being heated, melted, hardened, that is, they can be reheated and reformed to the requirement under appropriate conditions [7]. Under the high temperature, the molecular chains of plastic polymers are loosened and start to slide against each other, and thus the solid polymer materials become viscous melt having flowability that can be reconstructed and shaped into molds. Compared with thermoplastic material, thermoset materials that process with heat treatment and construct a three-dimensional crosslinked network through the sharing of electrons, which cannot be reversed by remelted and reshaped processes.

Thermoplastic materials can be widely used for practical applications from civil goods to medical equipment based on the inherent characteristics of the materials. The common thermoplastic materials including polyethylene (PE), polypropylene (PP), polyvinylchloride (PVC), polyethylene terephthalate (PET), and thermoplastic polyurethane (TPU) are widely used as the raw materials applying in civil and industrial domains. On the other hand, unsaturated polyester, epoxy resin, silicone, phenolic resin and acrylic resins are belonged to thermosets family.

1.1.3. Most Common Plastics

Plastic is one of the substitute candidates of the past 20th century for the wide adoption of many daily applications that previously relied on metal, glass, or other conventional materials, which the plastic can reduce the heavyweight, shorten the manufacturing process, and choose the most suitable one from a variety of plastic materials according to the end needs.

Polyethylene (PE) is a popular plastic material around the world and has been employed as carrier bags and single-use containers. It is a thermoplastic polymer with carbon and hydrogen atoms (as shown in Figure 1-3) that constructed both amorphous and crystalline domains, which belongs to the polyolefin family and classifies with density and chain branching that including branched groups and linear groups. Generally speaking, low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) are parts of branched groups, and high-density polyethylene (HDPE) and ultra-high-molecular-weight polyethylene (UHMWPE) are for linear groups. High-density polyethylene (HDPE) is a commercial thermoplastic material with a high-aligned linear backbone and fewer side chains and thus provides a high crystallinity. Moreover, HDPE not only has high tensile strength but also has good chemical resistance, which is generally manufactured for packaging applications, civil textiles, and consumer goods. In addition to HDPE, LDPE is also a common material for civil products such as plastic bags, wrappers, films, or tubes. The lower tensile strength but a higher impact strength resulted from the high degree of short branching structure of itself. Unlike the long-branched LDPE, the linear low-density polyethylene (LLDPE) has a linear backbone with short and uniform branches that prone to easily slide without extra entanglement between polymer chains, and thus led to good flexibility and high impact strength as compared to LDPE. Also, LLDPE is suitable for film applications such as garment packaging, plastic film, and stretchable film by its good extension ability.



Polyethylene, PE

Figure 1-3. The chemical structure of polyethylene, PE.

Polypropylene (PP) is one of the plastic material that achieved industrial grade and is frequently applied in everyday objects like food packaging, snack wrappers, microwave containers, automotive parts, plastic toys, etc. In 2019, the report from

Plastics Europe Market Research indicated that demand for polypropylene is 19.2%, which is much higher than that of LDPE/LLDPE (17.5%) and HDPE/MDPE(12.2%) [5]. Polypropylene is a semi-crystalline thermoplastic polymer with a linear hydrocarbon structure composed of repeated propylene units as shown in figure 1-4, which is derived from the polyolefin family. The molecular structure is similar to that of polyethylene except for an extra methyl side chain that can improve the mechanical property and heat resistance. Based on the different side-chain compositions, the atactic, isotactic, and syndiotactic groups are three types of polypropylene family. The atactic polypropylene (aPP) arranges with irregular methyl (CH₃) groups and the methyl groups only display on the single side of propylene is called isotactic polypropylene (iPP). Besides them, syndiotactic polypropylene (sPP) has alternative methyl groups on each side of the linear backbone [8]. There are two major commercial product types of polypropylene – homopolymers and copolymers. The homopolymer group only contains propylene monomer and it has been practically applied as rigid pipes, machine covers, plastic toys, automotive products, electronic products, civil and industrial textiles. The copolymer group is widely employed in the domains that requiring high strength condition, and features with random or block ethene groups. The copolymer type has relatively good flexibility and good impact resistance that is suitable for automotive and electrical equipment. Additionally, polypropylene has been considered as a potential material for food-safe products due to its strong, flexible, easy molding property, and high-temperature resistance characteristic [9].

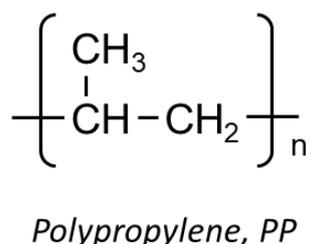
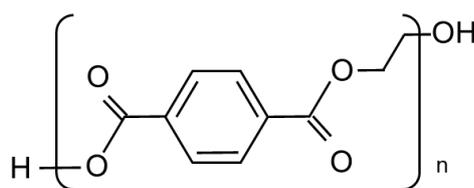


Figure 1-4. The chemical structure of polypropylene, PP.

In addition to polypropylene, polyethylene terephthalate (commonly called PET) is also a generally produced plastic that commonly applied in beverage containers, water bottles, or fibers used for civil and industrial textiles [10]. The molecular structure of polyester consists of repeated ethylene terephthalate units (as shown in Figure 1-5), and itself possessed good mechanical, thermal and chemical resistance that commercially employs as sheets for packaging and containers for food or drink. Also, PET has a good electrical insulating ability that is appropriate for the automotive and electronics industries as an alternative for the metals and thermosets. In our daily life, the everyday consumption product is the various kind of water bottles or drinks containers that

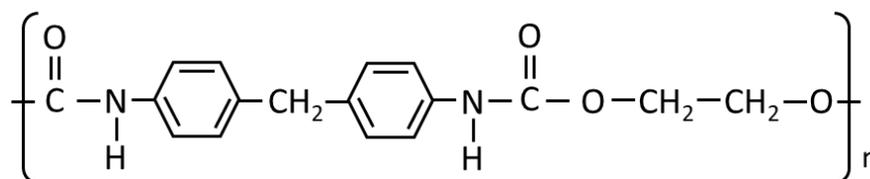
are composed of a PET bottle and a PP cap.



Polyethylene Terephthalate, PET

Figure 1-5. The chemical structure of polyethylene terephthalate, PET.

One of the typical thermoplastic materials that have good elasticity, durability, and processability is thermoplastic polyurethane (TPPU), which is usually selected as the materials for demand applications such as automotive, wires, or films. Thermoplastic polyurethane (TPU) belongs to the thermoplastic elastomer (TPE) family, and it is a linear segmented block copolymer [11]. A thermoplastic elastomer is a kind of polymer material that exhibits rubber elasticity at normal temperature but has plasticity when heated. TPE is a potential candidate as being suitable for easy processes, diverse manufactures, and the recycling purpose to decrease the production cost. TPU has a multiblock structure that alternatively comprised of hard segments (HS) and soft segments (SS), which the former segments responsible for mechanical performance and the later ones provide the rubberlike elasticity [12]. The hard segment in polyurethane structure is composed of diisocyanate group and diols, while the soft segment is constructed with polyols containing flexible ester or ether groups as shown in figure 1-6. The incompatibility between the hard segments and soft segments leads to the phase separation phenomenon. That is to say, the hard segments are dispersed in the soft segments because of the physical-crosslinking aggregations caused by the intramolecular hydrogen bonding of hard segments [13]. Thermoplastic polyurethane has been widely used in civil products such as textile coatings, sports and garments and industrial applications including automotive interiors, instrument panels, transfer belts, etc [14].



Thermoplastic polyurethane, TPPU

Figure 1-6. The chemical structure of thermoplastic polyurethane, TPPU.

As shown in Figure 1-7, it is indicated that the global plastic production has been

enormously climbed up to a very high amount since 1950, which clearly proved that the polyolefin family are the main members including polyethylene (including LDPE, LLDPE (16%), and HDPE (13%)) and polypropylene (PP (17%)) [15]. Moreover, PS, PVC, PET, and PU are also important members of plastic products. The above-mentioned plastic materials greatly contribute to a high percentage of 96% of the total amount of plastic productions [2, 15].

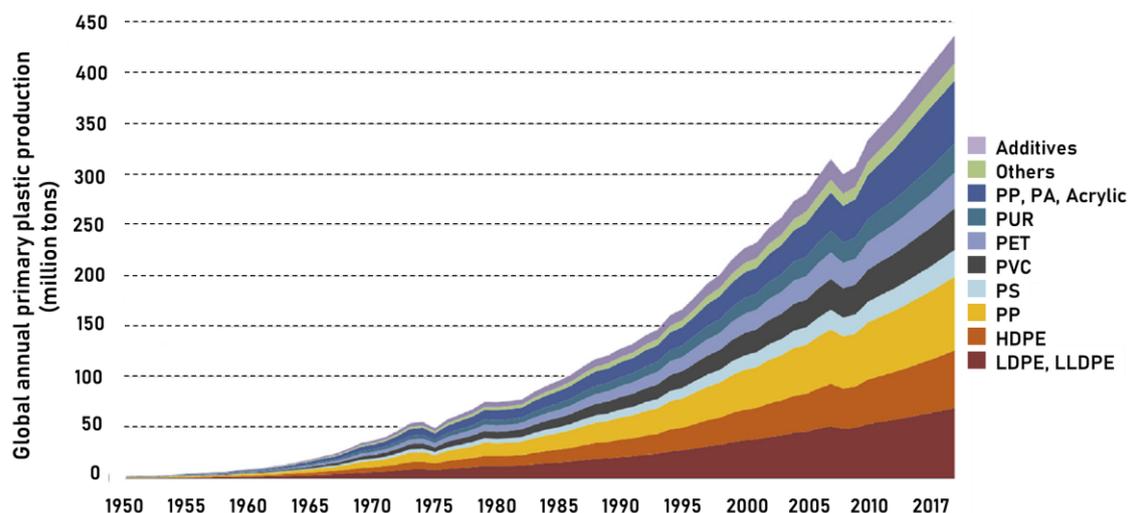


Figure 1-7. Global annual primary plastic production from 1950 to 2017 [2] .

1.2. Plastic Wastes and Environmental Impact of Plastic Pollution

Various plastic products have played an important role in our daily life and also convenient for current society. Since 1950, the fast pace of plastic development not only significantly raise the massive production of plastic but also change the using habits of single-use plastics. Our dependence on plastic things has been proven by all-around plastic products in many ways, which leads to our improved living standard. Though the plastic has many merits as we mentioned before, it also brings widespread environmental concern and irreversible harm to our circumstances. Many plastic items including straws, plastic bags, beverage cups, coffee cups or packaging materials are mostly discarded after only single use [15, 16]. Therefore, the huge amount of plastic wastes has become a severe environmental problem and been aware by people [17]. The decisive factor leads to such an issue is that the plastic itself cannot be naturally degraded, and results in microplastics and distribute in everywhere. Plastic waste is buried in the soil or dumped in the sea, which pollutes the biological food chain and causes a biological crisis, the biggest burden on the environment [18]. We'll never notice that the plastic improving the life quality of people someday turns out to be one of the environmental killers, namely we called the never-end plastic pollution as long as people keep using without any careful considerations.

1.2.1. Types of plastic wastes

The main resources of global plastic consumption are shown in figure 1-8, and it is obvious to see that primary plastic wastes are from packaging, textiles, and consumer and institutional products, respectively. Among them, the plastic materials we mentioned before such as PP (16%), LLDPE & LDPE (12%), PVC (11%), HDPE (10%), and PET (5%), which in total percentage is almost 54% of the total plastic usage [19].

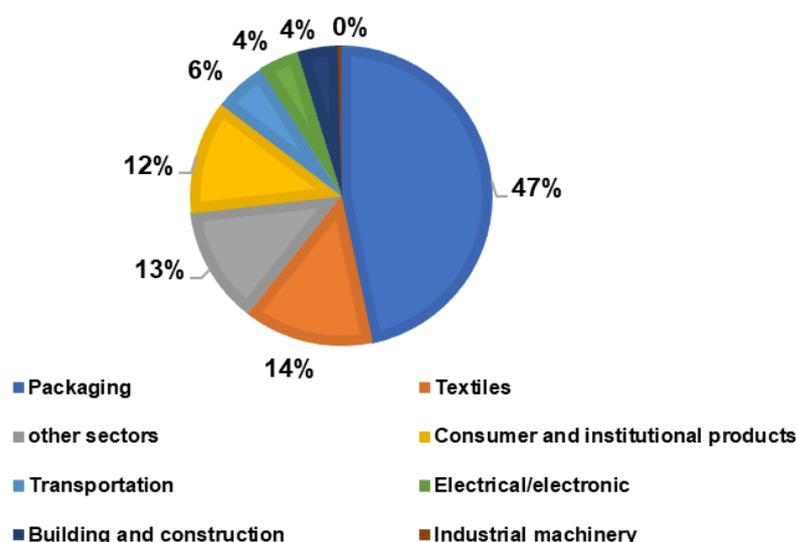


Figure 1-8. the global plastic consumption wastes [20].

Single-use plastics, namely disposable plastics, are the most widely used for packaging products in various fields including plastic bags, bottles, tableware, straws, and even food and drink containers. According to the report from the United Nations Environment Program in 2018, it is indicated that nearly 50% of plastic waste is generated from plastic packaging around the world [21]. Moreover, the raw materials that used to produce the single-use plastics are mostly from thermoplastics, and the main plastic materials come from HDPE (drink bottles, shampoo bottles), LDPE (plastic bags, food packaging film), PET (especially for water bottles), and PP (dishes and containers that can be used in a microwave oven, and caps for water bottles).

Apart from the daily necessities, textile waste also accounts for a very high proportion due to the rapid rise of fast fashion for clothes. The global population has enormously grown in the past decades, and so is the living standard. People have been pursuing better life quality in every aspect, neither the clothes nor other textiles. Hence, the global textile production increases up to 110 million tons annually, and also for the huge amount of consumption of textile wastes from factories and customers [22]. Most of the references and reports indicated that the plastic packaging material (for example, the wrapper or the packaging film) have become the main resource of the total plastic wastes all over the world [15].

1.2.2. Plastic production and plastic wastes

According to the annual report “Plastics- the Facts 2019,” it is clearly revealed that the entire plastic production of global has reached up to 359 million tons as shown in figure x, which Asia accounted for 51%, NAFTA (the US, Canada, and Mexico) for 18%, and Europe was 17%. Among the Asia regions, China accounted for 30%, Japan accounted for 4%, and the remaining regions accounted for 17% [5]. In 2017, Geyer, Jambeck, and Law et al. reported that nearly 47% of global plastic wastes is from packaging waste, which apparently generated from Asia in 2015[23]. Figure 1-9 shows the global plastics production and consumption from each region [19].

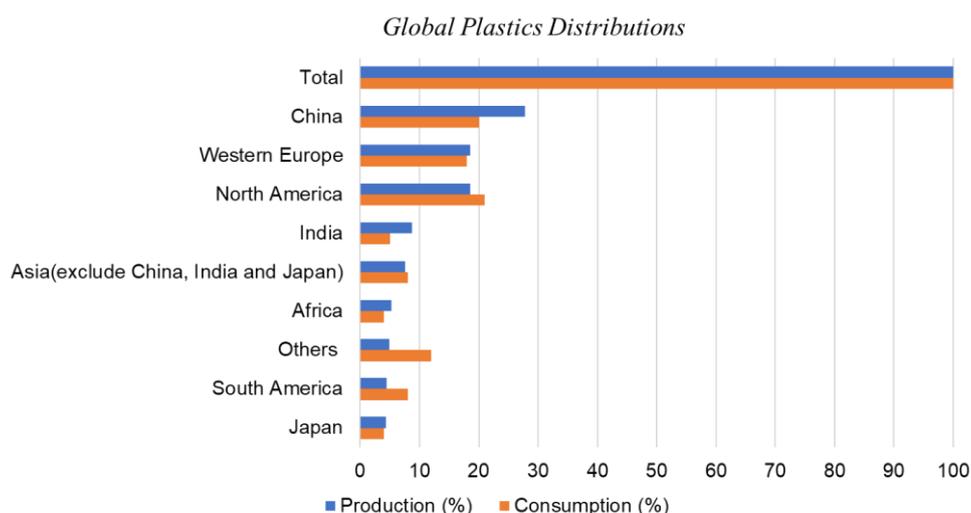


Figure 1-9. Global plastics production and consumption from each region [19].

1.2.3. Pollutions caused by plastic wastes in environment

An apparent increasing number of researches relevant to plastic waste problems has indicated that it is an urgent issue for people and the entire macro and micro circumstances. In the near decades, the apparent raising amount of plastic wastes result in severe plastic pollutions all over the world. It is predicted that there could be 1 ton of plastic for every 3 tons of fish in the ocean, and thus leads to serious marine ecological problems. Gradually, more and more shocking news about the negative effect and tragedies harming marine lives have been exposed by relevant organizations and scholars. The death of large mammal animals being entangled by plastic fishing net, sea turtles being suffocated by plastic bags or their noses being inserted by the straws, and the presence of microplastics found in the food chain of the ecological system are all evidences to prove that the plastic pollution has caused serious ecological catastrophe [24, 25].

The serious environmental problems caused by plastics have resulted from its

intrinsic characteristic – cannot be completely decomposed by itself, and thus the macroplastics and microplastics remain in our circumstance everywhere. With regard to macroplastic, it is indicated that most of the macroplastics are attributed to the various plastic packaging or consumer goods, especially single-use plastic products. In addition to macroplastic, microplastic also plays an important role that primarily found in the marine environment is usually produced from PP, HDPE, LDPE, and PET, which are the most common plastic materials used in the goods. For example, as shown in figure 1-10, it is apparent that the plastic wastes in marine circumstances mainly come from microplastics (microfiber from textile washing or industrial garbage) and macroplastic products (the abandoned fishing net in the ocean or mismanaged trashes).

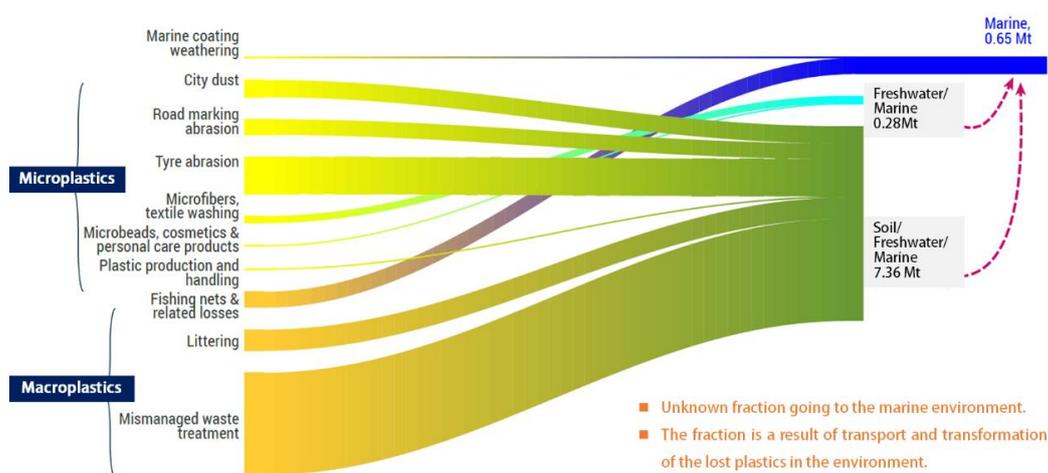


Figure 1-10. The sources of plastic wastes and the environmental part of plastic wastes [19, 21].

1.2.4. Current plastic restriction policies

As plastic pollution becomes more and more severe, countries and organizations have begun to promote plastic restriction policies all over world. The sustainable ecology issue has attracted people's attention, and thus not only the marine pollution but also the entire environmental pollutions require more positive responses. In April 2018, Boracay, the famous tourist spot in the Philippines, was closed, which due to the contamination resulted from the terrible amount of accumulated plastic wastes produced from the visitors. Moreover, in June 2018, Thailand's Maya Bay also closed because the corals are damaged and even died by plastic wastes and other pollutes in the ocean.

Early in 2002, Bangladesh bans plastic bags, and more than 60% of countries in Africa have already strictly enforced the ban on the use of plastic bags. The Association of Southeast Asian Nations (ASEAN) initiates to formulate regulations and laws to limit the use amount of plastics, and the European Union (EU) proposes a new law banning

single-use plastic goods such as plastic straws, plates, cups, plastic tableware, and even cotton buds sticks and will be carried out in 2021 [21, 26-28].

In 2019, according to the content of the United Nations Environment Assembly meeting held in Kenya, the 170 participating countries pledged to significantly reduce the amount of plastic by 2030. With the statistics collected from the United Nations, there are at least 8 million tons of plastic flows into the ocean every year, which seriously threatens the marine ecological system, including coral reefs that are endangered by extinction [29]. Moreover, Japan, as one of the leading countries in Asia, decides to ban providing free plastic bags in all retail stores and promises to reduce 25% plastic garbage before 2030. In Taiwan, the government approves to entirely ban using single-use disposable plastic goods such as plastic bags, straws, and tableware before 2030, and starts to conditionally limit the use of single-use plastics from now on. Hence, the sustainable development and long-term usage of plastic products are a new challenge for people. It is said that the only method to permanently eliminate the plastic wastes from the world is to incinerate or to melt, meanwhile, the release of toxic gas and global warming are also concerning issues for people. In my opinion, an appropriate recycling method is important but it is also necessary to maximize the use of existed plastic products rather than throw them away after a single-use.

1.3. Plastic Recycling

It has been estimated that only 9% of the used plastics are recycled, 12% of them are burned, and the rest of them are eventually discarded in soils, ocean, and landfills [15, 21, 30, 31]. In 2017, Geyer, Jambeck, and Law et al. mentioned that the recycle and incineration of plastic are almost negligible, most of them were buried in the land before 1980. For non-fiber types of plastic recycling rate, the global recycling rate has slowly increased up to 18% in 2014 [2].

There are several ways to recycle materials including mechanical, chemical, and thermal recycling methods [16, 32, 33]. Practically, these methods are often processed with others as required, consisting of a mix of the mentioned processes. In mechanical recycling, the solid species of plastic wastes usually progressing with crushing the wastes from large to small flakes or particles that can be applied as functional fillers or reinforced materials for subsequent reutilizations [34, 35]. Thermal recycling is another method to provide heat energy to help the materials transform into other statuses including solid, liquid, and gas. Moreover, thermal recycling often relates to the conversion of polymer materials, in which the species may be transformed from solid status to melting status. But the species usually produce from the polymer wastes such as flakes, chips, or pellets by mechanical recycling [36]. For instance, chemical recycling is usually selected when the polymer material requires depolymerization or

dissolving, but most materials undergo mechanical treatments before processing with chemical recycling. Therefore, it is hard to well recycle or reuse the plastic wastes by a single method, the combination of different processing techniques is required.

As we mentioned before, there are two types of plastic materials, one is thermoplastics and the other one is thermosets. Based on their different intrinsic characteristics, thermoplastics are prone to be recycled than thermosets. Currently, the primary wastes come from plastic packaging materials including food & drink containers and thin film, and most of them are composed of thermoplastic materials such as polypropylene (PP), polyethylene (PE), polystyrene (PS), thermoplastic polyurethane, etc. On the other hand, the cross-linking structure of the thermosets such as epoxy resins, phenolic resins, and unsaturated polyesters makes them hard to remelt and reform under heat treatments. In 2017, Geyer et al. stated that there are nearly 91 billion tons of plastic wastes worldwide, but only 12% of them are incinerated and 9% are recycled and reused [23]. In the meantime, it is also pointed out that recycling cannot prevent plastic wastes from affecting the entire circumstances. Recycling only delays the wastes entering into the ocean or being buried in landfills. Hence, how to well use the existed plastic product or extend the life span of plastics are also important issues for people who have been relied on plastic products around the world.

1.3.1. Potential Strategy of Plastic Problems

In recent years, people's environmental awareness has gradually increased due to the rapidly increasing amount of pollution problems. Hence, to recycle plastic waste or to well use existed plastic products are both major issues for current society. Though the recycling issues have gained lots of attention from people and relevant scholars, there are still some to-be-solved problems. For instance, poor performance of plastic materials after recycling, complicated cleaning process (ex: clean, separation, reusing, and reforming), high cost on separating the different component in one plastic product, and bad using habits of single-use plastic products (ex: straw, table wares, and cups) [34, 37]. Among the plastic problems, the products that simultaneously composed of multiple component are hard to be recycled and reused. Based on my opinions and relevant news, reports, studies, etc., several points are listed as follows:

1. Though the thermoplastics are possible to be recycled, the complicated process and different intrinsic characteristics of materials make the recycling become difficult to practically implement, and thus recycling rate is still lower than other treatments including bury or incineration.
2. Currently, the recycling method is primarily for single-composition plastic, but there are many plastic products are made of multiple compositions. Thus, the recycling process is hard to implement the policies thoroughly, it costs higher

labor and much time to classify the recycling wastes before the next utilization. Hence, incineration is another method to eliminate plastic trashes but also comes with the release of toxic gas led to air pollution and health issue[18].

3. We should not refer recycling to as the only solution for severe plastic pollution but try to solve the problems of excessive amounts of plastics from the original using habits.
4. In order to increase the utilization efficiency of existed plastics and plastic wastes, the polarity difference resulted from the different intrinsic polar structures of each plastic material that causes significant incompatible or immiscible situation among the plastic materials [38].
5. For sustainable development of plastic recycling, the lack of long-term policies limit the sustainability and employment of plastics. Also, relevant contamination caused by plastic wastes may also happen during the recycling process.

1.3.2. Polarity difference issues among the plastic materials

As we previously mentioned, it is difficult to well recycle and reuse the multi-composition plastic materials, the reason is that the intrinsic structures of plastic materials are totally different. It is well known that polymer materials are composed of molecules with different atoms joined by covalent bonds. Essentially, the positively charged atom will share the negative electrons with others, but the polarity caused by the unbalanced charge distribution [8]. Therefore, the polymer can be mainly divided into two types including polar and non-polar polymers. In general, the molecules only contain C and H atoms belong to the non-polar family; on the other hand, the molecules construct with Cl, F, O, N, and S are for the polar family. The electronegativity arrangements of the previously mentioned atoms are $F > O > Cl$ and $N > Br > C$ and H[8]. The common non-polar plastic materials are polypropylene (PP) and polyethylene (PE), and for polar plastic materials are polyester (PET) and thermoplastic polyurethane (TTPU).

To increase the second utilization of each plastic polymer, blending is a nice choice to combine the advantages of different polymers and make up for the shortcomings of each other. Polymer blending is a mature method that used for polymer processing, it possesses many advantages such as easy processability, tailorable performance and short processing time that is broadly employed in industrial domains to develop functional polymer materials [39]. Hence, it is also another pathway for single-composition plastic after recycling. They can cooperate with other plastic material to broaden their application fields, namely the property of blends can be modified or controlled by blending process to obtain better mechanical, thermal, and physical

properties.

However, a typical serious problem for blends is the incompatibility and immiscibility between the polymer materials resulted from the polarity significance of each plastic polymer, which often leads to poor performance and defects in the resulting samples [40]. In this study, we aim to use a common method to solve the problem in an easy way, and thus a common maleic-anhydride-contained compatibilizer is selected and employed.

1.3.3. Compatibilizer and reactive mechanism

Early in 2003, compatibilizers played an important role between the materials that incompatible or immiscible problems, which caused poor performance and defects after blending. The function of compatibilizer is to reduce the negative effect brought by an extremely immiscible material system and also can improve the properties we expected. In general, the hybrid polymers containing the functional groups such as acrylic acid, maleic anhydride, and glycidyl methacrylate can be grafted onto the polymer chain of the polyolefin family, and then connected to other polymers by forming new hydrogen or covalent bonding [41].

The utilization of compatibilizer has been focused on improving the various performance of specific abilities of the blends. Here, in this study, we change the viewpoint of “compatibilizer” to a different perspective – to help improve recyclability of multi-composition plastics and extend the life span of existed plastics. Some scholars have been focused on developing biodegradable polymers to solve the non-degradable problem of most synthetic materials including plastics. Others have reduced the proportion of plastic materials in products and replaced them with natural and eco-friendly material that prone to be decomposed in environments. However, I think the most important issue is not to develop materials that can replace plastic materials or biodegradable materials, but to make good use of these plastic materials that have been produced, extend their service life, and achieve maximum utilization benefits. Also, using compatibilizer is a mature method in various fields. It can be applied as a bridge to different materials according to the different functional groups contained in the compatibilizer, and thus reducing the interfacial tension and phase separation, and increasing the compatibility at the interphase of materials.

There are various compositions of multi-composition plastic materials that we cannot comprehensively discuss in this study. The materials we choose in this study are polypropylene (PP) and thermoplastic polyurethane (TTPU). The main reason is that polypropylene is a commonly used polyolefin-based material and has many advantages, while thermoplastic polyurethane is another general elastic material as we mentioned in the 1.1.3 section. There are some reasons listed as follows:

- (1) Polypropylene has poor impact resistance at lower temperatures, while thermoplastic polyurethane has good impact resistance [9].
- (2) Polypropylene has good rigidity and tensile strength that can be applied in a product that requires good mechanical performance, and the addition of thermoplastic polyurethane can improve its shortcoming including flexibility and impact resistance.
- (3) Thermoplastic polyurethane has relative high cost, poor thermal stability and vulnerable to high temperature, while polypropylene has reasonable cost and good thermal stability [13, 42]. Due to the presence of low-thermally-stable urethane groups, polyurethane is usually recognized with low thermal stability [43]. Hence, the incorporation of polypropylene can help increase the thermal stability of thermoplastic polyurethane [38].
- (4) Polypropylene and thermoplastic polyurethane are both common packaging materials. The former PP is commonly used as food and drink containers and the latter TTPU is widely employed as the packaging film and elastic materials. Both of them are suitable for recycling and reusing studies, especially their processing temperatures are very close, 160 and 180 °C, respectively.

Therefore, the compatibilizer used in this study is polypropylene grafted maleic anhydride (PP-g-MA), in which the end of PP can contact the polypropylene and the end of maleic anhydride can react with the thermoplastic polyurethane under thermal treatment. During the thermal treatments, the PP segments of PP-g-MA co-crystallize with the origin PP, and the MA segments of PP-g-MA react with the urethane bond of TTPU to form isocyanate group and then form the grafting polymer at the interphase of polypropylene and thermoplastic polyurethane [44]. Hence, at the interphase, a bridging effect would lead to lower interfacial tension and mitigate the phase separation and thus improve the incompatibility and immiscibility among the blends. The results are positive for the recycling process that can increase the possibility of sustainable utilization of plastics with different intrinsic polar nature but can help improve each other's shortcomings.

1.4. Constitution of the dissertation

It is indicated that recycling is an important concept from the ecological and economical points of view, and the mechanical and thermal behaviors of materials themselves are also critical for recycling processes. To be honest, the repeated thermal treatments (melting and cooling) and mechanical ruptures during the recycling process may result in contamination (water or gas) and poor property performance. Therefore, recycling seems to be a nice solution for plastic wastes and plastic pollution, we still need to consider the specific characteristics of plastic materials and thus to obtain the

most suitable for the existed plastic wastes or extend the long-term utilization of plastic materials [45].

In this dissertation, the main purpose is to investigate the sustainable development of used plastic materials composed of multiple components, which could have positive influence on entire circumstances and mitigate the negative effect of plastic wastes. Furthermore, thermoplastic material has been chosen as the primary materials due to its specific characteristic – can be reshaped and reformed after proper thermal treatment. As one of the most commonly used plastic material employed in various domains, polypropylene (PP) is selected as one of the raw materials, while another experiment material is thermoplastic polyurethane (TTPU). Both of them are thermoplastic materials, namely can be recycled and reused after single-use based on proper conditions.

Moreover, the main text can be divided into two main sections, one of which is polypropylene as the major material, while the other is thermoplastic polyurethane. It is well known that PP is a thermally stable material while TTPU has poor thermal stability under high temperatures and prone to be damaged and decomposed. However, thermal treatments are often employed in recycling routes, and thus good thermal stability is a decisive factor. On the other hand, the mechanical performance of each material is also another important reason that may affect the subsequent applications. It is said that PP has good mechanical strength but poor impact strength at a lower temperature, while TTPU has good flexibility, toughness, and excellent impact strength. Thus, they can preserve their own advantages and simultaneously make up for their disadvantages. Furthermore, the incompatibility and immiscibility resulted from their different intrinsic polar nature are also important issues to be discussed and investigated. A common compatibilizer that can properly act as the bridging role to react between PP and TTPU is applied and expected to solve or mitigate the incompatible effect. Several processing techniques such as melt-blending, injection molding, and hot-pressing method are employed with regards to various conditions of materials in this dissertation, and also propose to find an easy and convenient method to reach the goals of recycling multiple-composition plastics and prolonging the sustainability of plastics.

1.4.1. Mechanical performances of multi-composition thermoplastic materials after interphase modification treatment

In Chapter 2, multi-composition thermoplastic materials composed of polypropylene (PP) and thermoplastic polyurethane (TTPU) are melt-blended for two cycles, which a small amount of compatibilizer (i.e. polypropylene grafted maleic anhydride, PP-g-MA) is added during the process in order to mitigate the polar difference between PP and TTPU. Besides the recycling efficiency, the influence of

various ratios of blends and different amount of compatibilizer are also investigated. The specified ratios of PP/TTPU blends are 90/10, 80/20, and 70/30, respectively. The morphology and mechanical properties of the PP/MA/TTPU blends are then measured and investigated. SEM images show that without the compatibilizer, TTPU particles demonstrate a dispersive phase in PP matrix. The presence of compatibilizer improves the incompatible situation between TTPU and PP. The impact test results have proven that the incorporation of 20 wt% of TTPU and 5 wt% of compatibilizer helps to improve the interphase problem, thereby yielding the impact strength of 63.01 J/ g. The tensile strength test results show that the presence of PP compensates for the insufficient rigidity and high production cost of TTPU. The flexural strength test results show that PP with high stiffness synergizes to the softness and flexural performance of TTPU. It is expected that using the secondary recovery process obtains the added value and sustainable use of plastic products, which is helpful to the sustainable development of the earth.

1.4.2. Thermal performance and morphology observation of multi-composition thermoplastic materials after interphase modification treatment

In Chapter 3, the multi-composition thermoplastic materials are as same as in Chapter 2 - polypropylene (PP) and thermoplastic polyurethane (TTPU) that can be properly heated to reform and reuse due to the inherent characteristics of thermoplastic materials. This chapter focused on investigating thermal behaviors of multi-composition thermoplastic materials, and the reason is that the using efficacy may be compromised as the waste may be overheating and thus damaged during the reheating process. Hence, this study also goals to investigate the synergistic effect between these materials and also discuss the compatibilized effect caused by MA. The thermal degradation behavior, melting and crystallization behaviors, and surface morphology of PP/MA/TTPU blends are evaluated under appropriate considerations. In light of the thermal degradation, the presence of thermally stable PP improves the thermal stability of TTPU accordingly. From TGA and DTG results, the addition of MA is also helpful, and therefore the third thermal degradation temperature (T_{3max}) is increased by 5 °C averagely when compare to neat PP. T_{1max} and T_{3max} of PP/MA/TTPU are postponed about 2 and 4 °C when TTPU content varied from 10 to 30 wt%. SEM images show that the employment of TTPU strengthens the toughness of the surface, and with the aid of 5 wt% MA, PP and TTPU exhibit greater interfacial compatibility and better adhesion. Above all, this study aims to investigate the feasibility of using thermoplastic based on the consideration of how to sustain the excess plastic products and develop the measure to melt-blend diverse thermoplastics for reclamation. The excessive plastics via an easy and convenient melt extrusion process is expected to be regarded

as an eco-friendly method for green development on mother earth.

1.4.3. The cycling effect of mechanical fractures and thermal treatment on the recycled multi-composition thermoplastic materials

In Chapter 4, as we commonly known that with appropriate conditions, thermoplastic materials possess a good reversible ability. They are prone to exceed the reversibility range when being repeatedly processed as they cannot bear high temperatures. Therefore, this study aims to explore the impacts of the melting–recycling cycles (as simulating thermal treatments) and the presence of a compatibilizer on the omnipresent multi-composition thermoplastic materials. It is predicted that the multi-composition thermoplastic materials are prone to be damaged than single-composition ones due to the inherent difference between different plastic materials in cycling use though thermoplastics are easily recycled. Additionally, the tensile properties, morphology, and thermal properties are studied, which tensile test simulates the mechanical fractures and hot-pressing process simulates thermal treatments. The feasibility of multiple utilizations and differentiation effects are examined afterward. In this study, recycled or mechanically damaged multi-composition thermoplastic wastes composed of TTPU/PP are used as the raw materials for the cycling treatments, while another group contained maleic anhydride grafted polypropylene (MA) – TTPU/PP/MA is used as experiment group, thereby simulating the waste compounds. Next, the both TTPU/PP and TTPU/PP/MA wastes that undergo post-2nd and post-3rd recycling are evaluated for comprehensive change. The test results indicate that without MA, TTPU/PP blends exhibit significant differentiation effects due to an increase in the polypropylene content and multiple mechanical and thermal cycles. By contrast, the presence of MA mitigates the overall differentiation effect of TTPU/PP blends. The ultimate purpose of this study is to treat waste compounds via a simple hot-pressing approach to produce useful materials that can be used again. As a result, this study attenuates the negative influences of plastic waste on the environment while achieving sustainable development.

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Part I – Performance Improvement of Recycled Multi- composition Thermoplastic Materials

Chapter 2 – Improving Mechanical Properties of Multi-composition Thermoplastic Materials by Enhancing Interphase Performance

2.1. INTRODUCTION

Plastic has been one of the common raw materials in our everyday products. Greene has reported that from 1950 to 2015, the global consumption of plastics from 2 million tons to 440 million tons, and plastic is one of the most used man-made materials other than steel and cement [1]. Unlike natural materials, plastic cannot be decomposed by itself. Therefore, the severe plastic pollution problems resulted from a rapid increase in the plastic wasted are mentioned in Chapter 1.2. Jimenez et al. and Navarro et al. have revealed that during the last decades, plastic waste has become a serious concern of environmental burden around the world since the complicated elimination process and long lifespan of itself polluted the biological food chains of entire circumstances[2, 3]. Due to the severe environmental issues, there are many countries and institutions around the world have started to face the problems and developed relevant strategies, which listed in the Table 2-1. Therefore, a substantial use of plastic products becomes a new challenge to people. The only method to eliminate the plastic products is to burn and melt them, but the release of toxic gas and subsequent global warming will be two severe issues. The most effective improvement on the reduction of plastic products is to take the most advantage of them, instead of disposal after one-time use.

Table 2-1. Current restriction strategies against to the plastic problems.

Country/ Institution	Strategies
Bangladesh and 60% Africa countries	Bangladesh bans plastic bags, and others strictly enforced the ban on the use of plastic bags.
European Union (EU)	A new law banning single-use plastic goods such as plastic straws, plates, cups, plastic tableware and will be carried out in 2021 [4].
Philippine	In April 2018, Boracay was closed and opened to tourists with specified conditions in October of 2018.
Thailand	80% of coral in the Maya bay was damaged due to marine plastic wastes, and it was closed in June 2018 for infinite limit of time until the ecological environment recovered.
Association of Southeast Asian Nations (ASEAN)	Formulate regulations and laws to limit the use amount of plastics [5].
Japan	The government decides to ban providing free plastic bags in retail stores and to reduce 25% plastic garbage before 2030.
Taiwan	The government entirely ban using single-use disposable plastic goods before 2030, and starts to conditionally limit the use of single-use plastics.

There are many types of plastic materials as we mentioned before, and the main purpose of this study is to increase the utilization of plastic materials whether the existed plastic products or plastic wastes. Furthermore, we start the experiment from one of the common plastic materials – polypropylene, which has been broadly employed in various domains. In 2018, Lopez et al. mentioned that the steady grown-up plastic waste has become a huge problem and also described that polyolefin-type materials account for over half of the plastic production, especially polypropylene standing for 19.2% in diverse fields [6, 7]. Lazim et al. and Li et al. have described that polypropylene possesses several advantages as we mentioned before in Chapter 1.1.3, the most important of all is that polypropylene is recyclable to environmental concerns and can be reformed by injection, extrusion, or pressing processes [8, 9]. However, Chen et al. describe that the polypropylene becomes brittle at low temperature and has low impact resistance [10].

In order to simultaneously help improve the toughness of polypropylene (PP) and reach the recycling goal, we choose thermoplastic polyurethane (TPU) as another experiment material. In 2003, Jimenez et al. have presented that the results of blends composed of recycled polypropylene and elastomers can improve the impact behavior of the blend [2]. Matei et al. mention that PP compounds with elastomer can obtain ideal properties [11]. Hence, TPU and PP can be blended in order to combine good elasticity and toughness of TPU and rigidity of PP, thereby obtaining the synergistic effect.

Nonetheless, recycling diverse materials demands to be classified according to different characteristics, otherwise the subsequent procedure would cost extra charge. As a result, it becomes challenging to recycle multi-composition materials. It is indicated that the most serious issue is the interphase problems between the different polymer materials, which usually lead to poor performance and other defects [12]. If we want to increase the recycling efficiency of polymer materials, we must face this critical problem – interphase problem.

Yang et al. revealed that polypropylene and thermoplastic polyurethane are separately non-polar and polar polymers and they have problems of phase dispersion and poor adhesion at interphase [13]. In 2018, Chen and Zhang have indicated that the compatibilizer plays an important role to solve the interfacial problem between two incompatible material ABS and PETG [14]. Bajsic et al. have proven that the surface of talc filler can be modified by silane coupling agent and thus to improve the polymer-filler interface interaction between polypropylene and thermoplastic polyurethane [15]. Therefore, it is said that “compatibilizer” can properly improve the shortage of poor interface of two different incompatible polymers [16].

The aim of this study is to increase the reuse probability of plastic materials whether the materials have been used or not, and also investigates the sustainable development

of materials and the feasibility of multi-composition polymers for secondary or subsequent use. Hence, in Chapter 2, the recycling efficiency of the plastics are evaluated by diverse aspects including mechanical tests (tensile, impact, and flexural properties) and morphology observations (SEM) of the recycled blends.

2.2. EXPERIMENTS

2.2.1. Materials

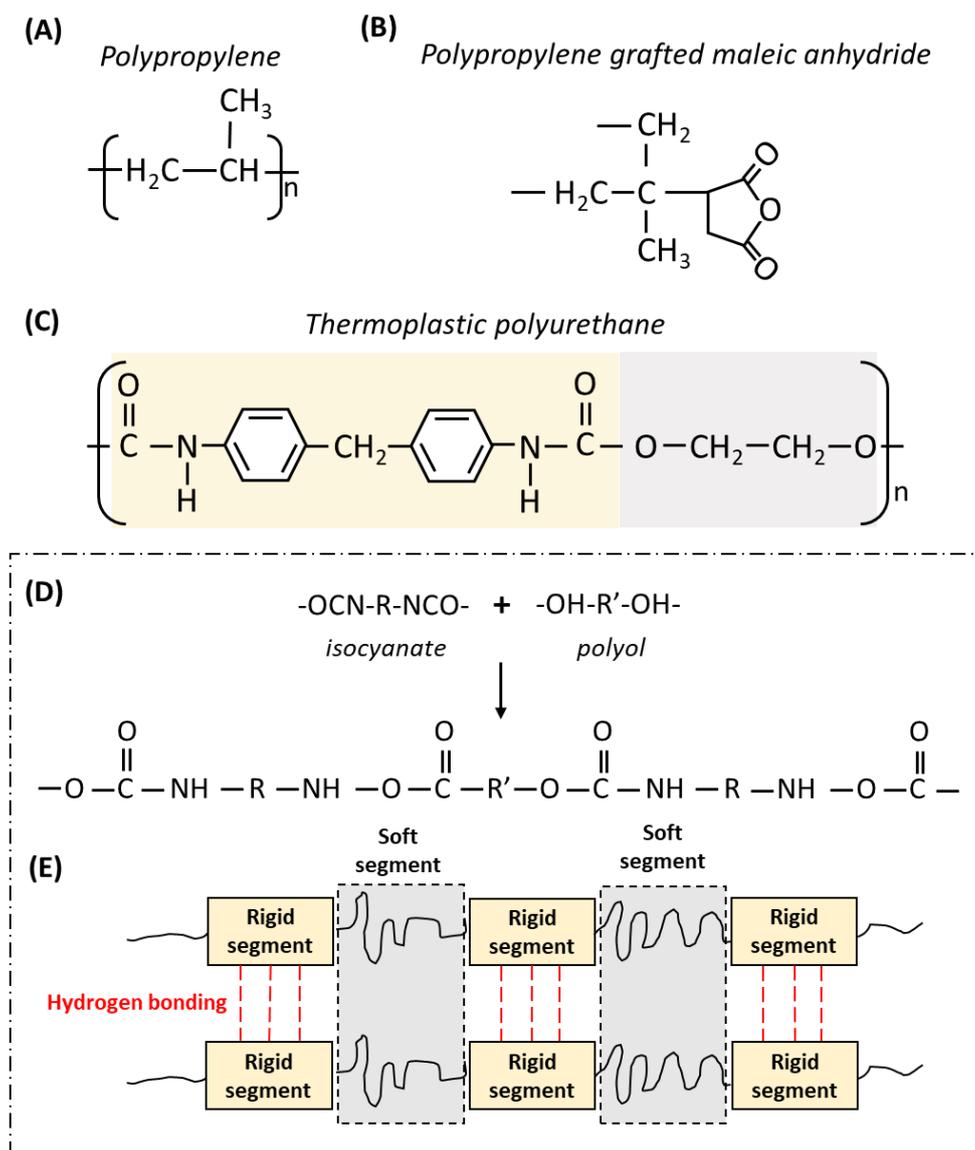


Figure 2-1. (A)(B)(C) the chemical structure of PP, MA, and TTPU, (D) chemical reaction and (E) composition of thermoplastic polyurethane.

As early mentioned in the Introduction, polypropylene (PP) and thermoplastic polyurethane (TTPU) are selected as the materials in Chapter 2. In this study, we don't only aim to focus on the plastic groups composed of PP and TTPU. It can be regarded as one of the multi-composition plastic groups among the various groups. As shown in Figure 2-1(A), polypropylene is constructed in a long and ordered polymer chain.

Furthermore, the main reason that TTPU is chosen as supplemented material is because it has both soft and hard structures, the former of which provides elasticity while the latter improves the mechanical properties as presented in Figure 2-1(C) [17]. Lastly, the polypropylene grafted maleic anhydride (PP-g-MA) is an important bridging role between PP and TTPU as shown in Figure 2-1(B). The following information listed the intrinsic characteristics of each materials. PP (YUNGSOX 1080, Formosa Plastics Co., Taiwan) is a homopolymer and has a melt flow index (MFI) of 10g/ 10min. TTPU is a copolymer (HE-3285ALE, Headway Polyurethane Co., Ltd., Taiwan) has an MFI of 7.03g/ 10min (175 °C). The chemical structure and composition of raw materials are shown in Figure 2-1[18-20]. PP-g-MA (DuPontTM® Fusabond P353, Dupont, US) is maleic anhydride grafted PP with an MFI of 22.4g/ 10min (190°C). The practical images of materials are shown in Figure 2-2 (B).

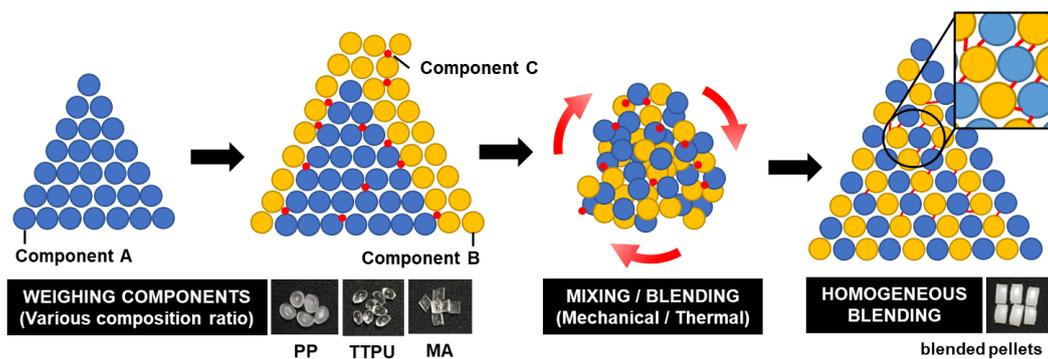
2.2.2. Experiment Methods

In Chapter 2, melt-blending and injection-molded extrusion processes are selected as the manufacturing process for blending pellets, which because the process has been commonly used processing techniques for polymer materials due to it possesses many advantages such as fast process, well processability for materials and large-scale production. In order to increase the recycling efficiency of plastic wastes, the manufacturing method is considered to be chosen under conditions containing fast and common after the recycling process. The experiment processes are divided into two sections, one is preparation of PP/MA/TTPU blending pellets, and the other is PP/MA/TTPU test samples for subsequent mechanical tests including tensile, flexural and impact properties.

Preparation of PP/MA/TTPU Blending Pellets

The processing principle and experimental diagram of melt-blending method to produce PP/MA/TTPU blending pellets are shown in Figure 2-2 and 2-3(A) [22]. A single-screw extruder is employed to manufacture the PP/MA/TTPU blending pellets with various ratios as revealed in Table 2-2. Before started the blending process, TTPU pellets were pre-dried in the oven at 70 °C for at least 24 hours to remove extra moisture. The PP and TTPU pellets were then mixed with ratios including 90:10, 80:20, and 70:30, and the extra addition amounts of PP-g-MA are 1, 3, and 5 wt%, respectively. From Figure 2-3 (B), the matrix material is polypropylene (PP), the reinforcement is thermoplastic polyurethane(TTPU), and the compatibilizer is polypropylene grafted maleic anhydride (MA), which aimed to solve the interfacial issue between PP and TTPU. Moreover, pure PP/TTPU blends without compatibilizer were served as the control group. The materials are blended at 25 rpm and four continuous heating temperatures of 200, 210, 210, and 210 °C using a single-screw extruder (SEVC-45, Re-Plast Extruder Corp., Miaoli, Taiwan). The polymer melts come out from the extruder

are then cooled and drawn in the water bath and granulated by a cutting machine. The resulting blending pellets are shown in Figure 2-3(B).



Reference from *Chungjin Tech* >> <http://www.cjtech.co.kr/Process%20Principles%20Blending.htm>

Figure 2-2. Processing principle of melt blending for PP/MA/TTPU blending pellets [22].

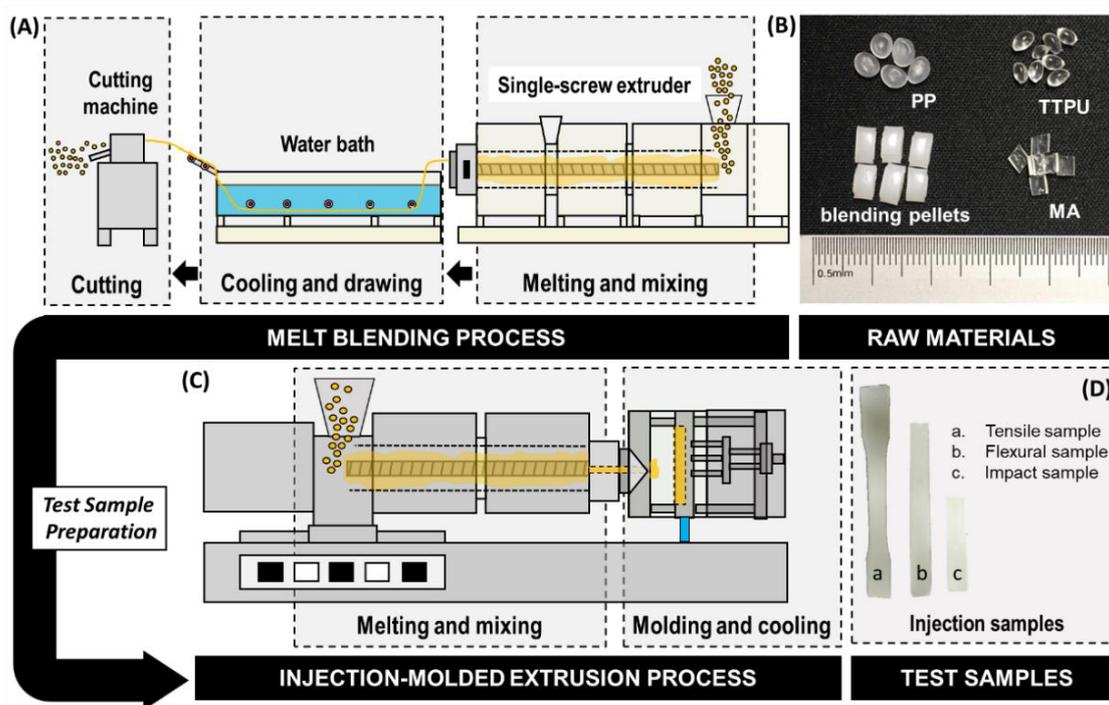


Figure 2-3. (A) Melt-blending process of PP/MA/TTPU blending pellets, (B) raw materials and resulting pellets, (C) injection-molded extrusion process, and (D) test samples of PP/MA/TTPU blends made by injection-molded extrusion process.

Table 2-2. Sample codes of PP/MA/TTPU blending groups.

PP (wt%)	TTPU(wt%)	MA (wt%)	Sample codes
90	10	0	PP90/MA0/TTPU10
		1	PP90/MA1/TTPU10
		3	PP90/MA3/TTPU10
		5	PP90/MA5/TTPU10

80	20	0	PP80/MA0/TTPU20
		1	PP80/MA1/TTPU20
		3	PP80/MA3/TTPU20
		5	PP80/MA5/TTPU20
70	30	0	PP70/MA0/TTPU30
		1	PP70/MA1/TTPU30
		3	PP70/MA3/TTPU30
		5	PP70/MA5/TTPU30

Preparation of PP/MA/TTPU Injection-Molded Samples

After the melt-blending process, PP/MA/TTPU blending pellets are placed in the oven at 70°C for 24 hours to completely remove extra moisture. As shown in Figure 2-3 (C), PP/MA/TTPU blending pellets are processed with an injection-molded extrusion process with four same heating temperatures of 200, 210, 210, and 210 °C as used in preparation blending pellets previously. In order to appropriately evaluate the mechanic properties among the PP/MA/TTPU blending pellets, the tensile, flexural and impact properties are comprehensively investigated in this chapter. Figure 2-3 (D) shows the practical samples for mechanical test made by injection-molded extrusion process.

2.2.3. Tests

Scanning Electron Microscopy (SEM) Observation

A scanning electron microscopy (SEM, Phenom Pure+, Phenom World, Jing Teng Tech, Taiwan) was used to observe the fractured cross-sectioned surface of samples at a low and high magnifications. Samples were collected after the impact test.

Tensile Properties

As specified in ASTM D639-10, PP/MA/TTPU injection-molded samples were tested for tensile properties using the Instron5566 universal tester (Instron, US). The distance between the upper and lower clamps was 115 mm. The test rate was 5mm/min. Five samples for each specification were used. The tensile stress and Young's modulus were averaged.

Flexural Properties

A sample was mounted on the mold of Instron5566 universal tester (Instron, US) in the three-point flexural test with a stress at 2mm/ min being exerted downward onto it as specified in ASTM D790-10. The span of clamps was 50 mm and five samples for each specification were used. This test indicated the average bending resistance of samples.

Impact Properties

As specified in ASTM D256-10, PP/MA/TTPU injection-molded samples were tested using Izod notch impact test. The 45° V-shaped notch had a depth of 0.25 mm, and five samples for each specification were used.

2.3. RESULTS AND DISCUSSION

2.3.1. Morphology Observation

The aim of the study is to investigate the recycle and reuse the probability of thermoplastic materials, the morphology for blending materials is also an important index for second-used characterization. Therefore, the blending morphology is observed by a scanning electron microscope (SEM). However, not only due to the wide variety of plastic products but also the types and morphology of constituent plastic materials, it is hard to precisely separate the plastic product. The reason why makes material incompatible is the polarity difference between materials. Therefore, this study investigates not only how polypropylene, thermoplastic polyurethane, and maleic anhydride grafted polypropylene react but also the incompatible interface between PP and TTPU. Moreover, this study also shows that the poor impact resistance of polypropylene can be improved by supplying thermoplastic polyurethane.

Figure 2-4 shows the influence of different contents of TTPU and MA on PP. When the content of TTPU increases, the fractured surface is composed of more cracked layers and crack counts. Thermoplastic polyurethane (TTPU) possesses elasticity which strengthens the impact performance of PP at a low temperature. When PP/MA/TTPU blends being exerted with an impact force, TTPU particles serve as the stress concentration to absorb the impact energy via the presence of deformation and numerous cracks. As a result, the energy is dissipated instantly, which prevents the blends being damaged on the spot. An increase in the number of cracked layers and cracks is also a supportive evidence that PP/MA/TTPU blends have better capacity to absorb an external impact force. In addition, Figure 2-4 (A/B) separately shows the fractured surface of PP90/MA0/TTPU10 and PP/MA5/TTPU10. When MA is added, TTPU particle size becomes smaller and cracks among layers also increase (Figure 2-4 (B)). Figure 2-4 (C-F) shows PP/MA/TTPU blends that are composed of specified 20 wt% of TTPU and different amounts of MA (0-5 wt%), and Figure 2-4 (D/F) are the insets of Figure 2-4 (C/E), respectively. In Figure 2-4 (D), TTPU exhibits distinct a falling phenomenon, which in turn causes the presence of voids. This result is ascribed to the poor adhesion between TTPU and PP that possess different polarities. When MA is added, the phenomenon is improved (Figure 2-4 (F)). Figure 2-4 (G and H) shows PP/MA/TTPU blends that are composed of specified 70 wt% of PP and 1 or 5 wt% of MA. In Figure 2-4 (G), TTPU particles have a large size and demonstrate distinct falling phenomenon. By contrast, in Figure 2-4 (H), TTPU particles have a smaller size, and the presence of more MA alleviates the falling of TTPU particles, which suggests that adding PP-g-MA is helpful to the combination of TTPU and PP.

In this study, MA plays the role of compatibilizer that improves the compatibility between MA and TTPU, and the required amount of MA is low. Therefore, the

incorporation of MA with PP/MA/TTPU blends contributes to a better recycling efficiency of plastic materials. Furthermore, this study also indicates that the melt-blending process can easily solve the separation issue of thermoplastic products based on suitable compatibilizer.

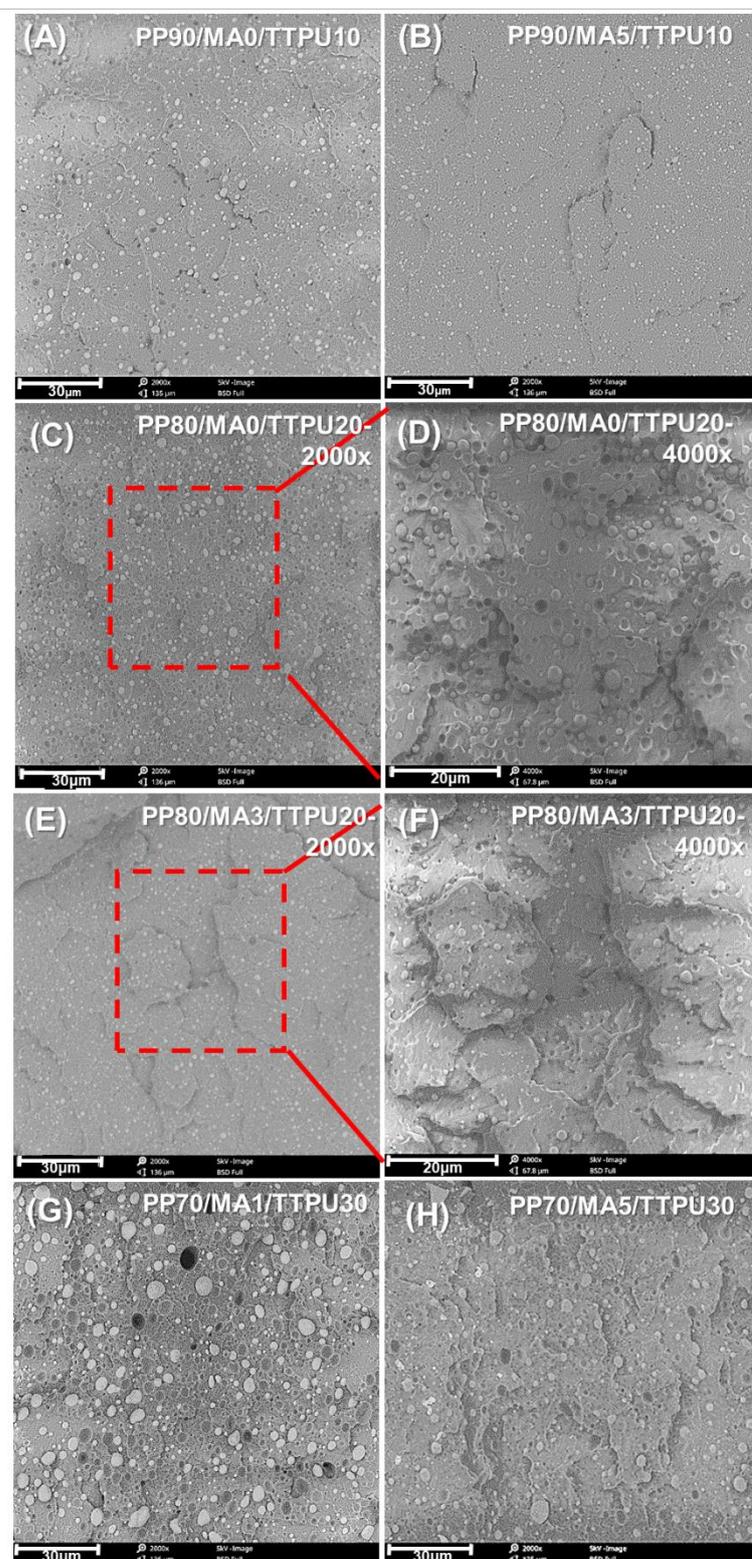


Figure 2-4. SEM images of PP/MA/TTPU blends.

2.3.2. Impact Properties

Currently, the most common method is thermal recycling, which employs high temperatures to melt plastic materials so as to re-form new products. Nevertheless, the properties of recyclable thermoplastic materials are undermined due to the second melting. Hence, this study aims to investigate how to improve the property performance of recyclable materials during the second-cycle use. Not only aim to provide the additional functional value after first using cycle but also solve the inherent weakness of polypropylene. A recyclable thermoplastic elastomer is chosen to improve the low impact resistance of PP, so as, a thermoplastic polyurethane (TTPU) is used as reinforcement. Figure 2-5 shows that PP/MA/TTPU blends with 0wt% of MA demonstrate a descending trend on the impact strength as a result of increasing the content of TTPU. PP is non-polar polymer whereas TTPU is polar polymer, and thus the interphase tension in between makes them incompatible and immiscible. The resulting phase dispersion is responsible for the decrease in the impact strength [21]. Noticeably, an increase in the content of MA can overcome the conflict between PP and TTPU for PP-g-MA is used as compatibilizer that helps with morphological stability. In particular, with 5 wt% of MA, PP80/MA5/TTPU20 exhibits the maximum impact resistance of 63.10 J/g. Conversely, for PP90/TTPU10 group, 5 wt% of MA does not complete react with only 10 wt% of TTPU, yet for PP70/TTPU30 group, it seems that it demands a more amount of MA for a full reaction. In light of Figure 2-4, the SEM image shows that PP and TTPU construct a sea-island structure where TTPU is dispersed as islands in the sea of PP matrix. For MA-free blends, TTPU exhibits clear silhouette, and for MA-contained blends, TTPU has blurry silhouette. Namely, an appropriate amount of MA decreases the interphase tension and incompatibility between MA and TTPU, which subsequently strengthens the impact resistance of the blends.

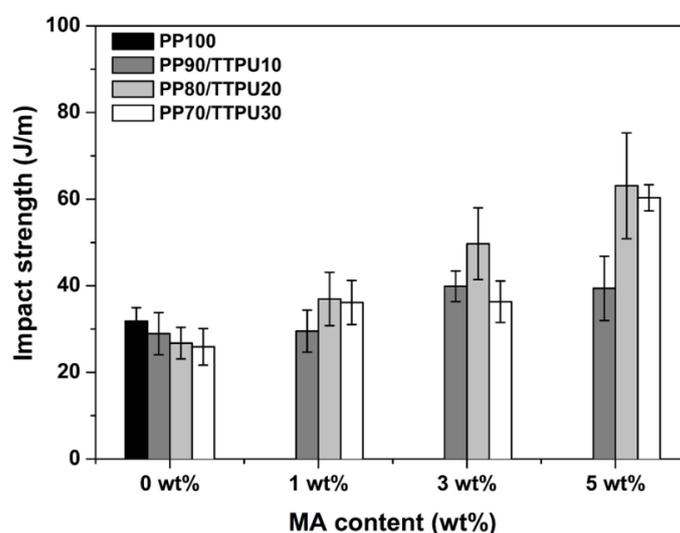


Figure 2-5. Impact strength of PP/MA/TTPU blends.

2.3.3. Tensile Properties

From the perspective of inherent characteristic, both of PP and TTPU are thermoplastic polymer materials, the former of which features low-temperature brittleness while the latter is an elastic polymer. Namely, PP has high strength and low elasticity, but the opposite is the case for TTPU. Although the properties of PP and TTPU are compromised due to the recycling process, they still maintain a certain level of intrinsic performances. Hence, this study combines both materials to have a synergistic effect and fulfills the recycling purpose. In previous discussion on impact resistance, the toughness of PP is strengthened by the presence of TTPU, so in this section, the mechanical properties of TTPU as related to the presence of PP is discussed.

Figure 2-6 shows that the tensile strength and Young's modulus of blends increase as a result of increasing the content of PP. Although it is slightly higher than that of pure TTPU, it is still slightly lower than that of pure PP. In other words, the presence of PP mechanically strengthens TTPU. Figure 2-6 (A) shows the MA-free blends, PP90/TTPU10, PP80/TTPU20, and PP70/TTPU30 have comparable tensile strength, but PP70/TTPU30 has the lowest tensile modulus (Figure 2-6 (E)), which indicates that excessive TTPU makes the blends softer. To sum up, the mechanical properties of the blends are dependent on the adhesion and compatibility of two-phase materials. Furthermore, at the strain range between 0 - 0.2%, there are several slopes indicating the characteristic of elastic behaviors among thermoplastic materials. Subsequently, over the elastic yield domain, the recovery ability of plastic materials become inefficient. Figure 2-6 (B-D) shows that with the addition of MA, both of PP90/TTPU10 and PP80/TTPU20 have similar tensile curves to that of PP100, which suggests that the presence of MA does not affect the failure mode of the blends. The employment of the compatibilizer of MA improves the drawback of the low tensile strength of the blends made of incompatible PP and TTPU, which the compatible reaction happens as Figure 2-7 shows. Regardless of the content of MA, the PP70/TTPU30 group exhibits comparatively unstable tensile properties because this group has more equivalent amounts of two materials, which in turn heightens the poor compatibility and miscibility distinctively, and eventually has comparatively lower tensile stress. With the premise of recycling cost, TTPU has a high cost so the employment of PP with low cost can compensate for this disadvantage while strengthening mechanical performances.

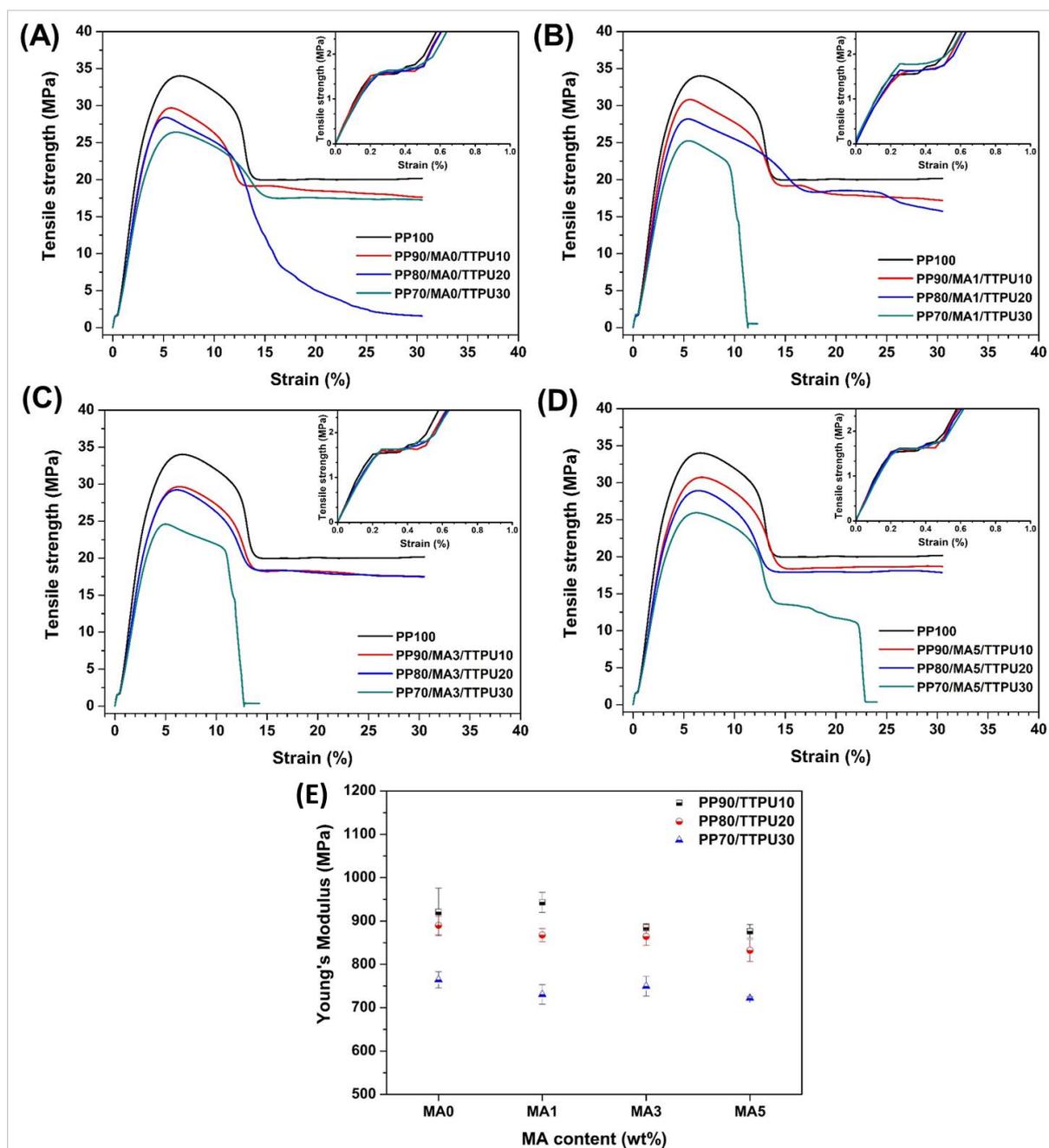


Figure 2-6. Tensile properties of PP/MA/TTPU blends.

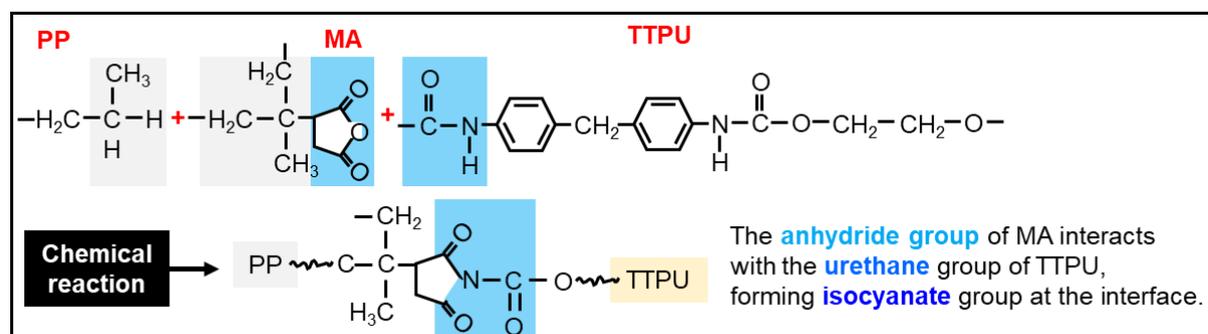


Figure 2-7. Chemical reaction among the PP/MA/TTPU blends.

2.3.4. Flexural Properties

Based on the test standard, when a sample is bent with 5% of strain and not broken, the maximum stress it withstands is recorded as flexural stress. Within the elastic deformation limit, when a sample is exerted by an external force, the deformation level it generates is called flexural modulus (*i.e.* flexural stress/strain). Figure 2-8 shows that in a flexural state, PP/MA/TTPU blends have stress-strain curve that appears the fracture mode of ductile material. With a strain being 0-2%, there are 1-2 peaks, which is presumed to be due to the fact that when the impactor moves downwards and touches the thermoplastic blends, they exhibit elastic deformation, after which it exceeds the yield strength, samples exhibit plastic deformation and can never retrieve their original state. Figure 2-8 (A) shows the flexural strength of MA-free blends, the addition of TTPU slightly increases the flexural strength. However, Figure 2-8 (B, C) also demonstrates the same trend where the majority of the blends have a marginal increase in the flexural strength comparing to the pure PP group. TTPU is a copolymer that consists of interlaced soft and hard segments. The soft segment of TTPU provides the blends with softness and flexibility. As a result, when TTPU is added to PP, its softness helps to modify the rigidness of PP and eventually contributes to a greater flexural performance.

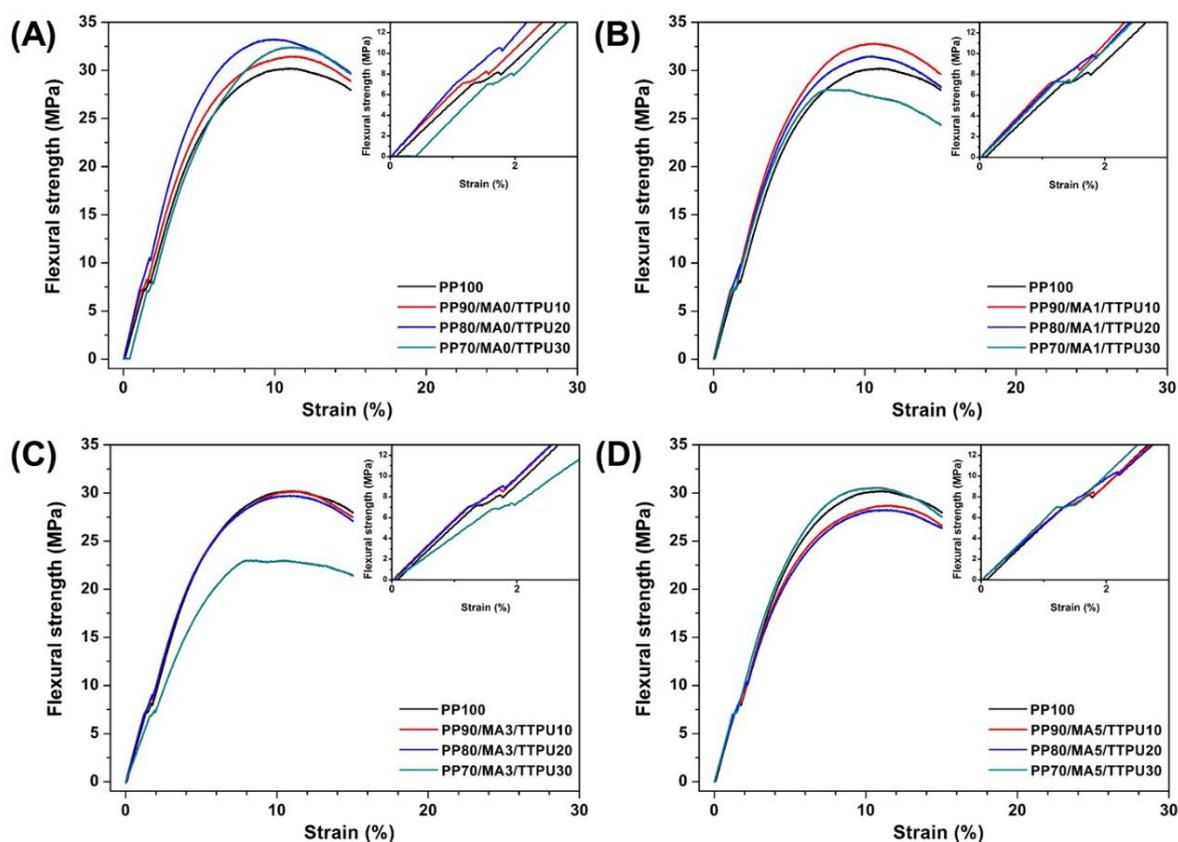


Figure 2-8. Flexural strength of PP/MA/TTPU blends.

2.4. CONCLUSION

This study successfully and efficiently produced and evaluated thermoplastic PP/TTPU blends using the melt extrusion process and injection molded process. Moreover, it is indicated that a trivial amount of PP-g-MA as a compatibilizer, which efficiently improves the poor interface between PP and TTPU as well as the impact performance of the blends. PP/TTPU blends demonstrated similar impact and flexural properties, which also proved that the intrinsic properties of PP and TTPU did not compromise as a result of recycling the polymers by melt-blending. Hence, the reclamation and sustainability of plastic waste were achieved. On top of that, the PP's high rigidity and TTPU's high resilience and tensile properties can be combined to yield the most beneficial reinforcement, thereby providing plastic products with greater added value and protecting the ecological environment. It is expected to recycle and reuse thermoplastic products via a convenient manufacturing process in order to mitigate the pollution harm to natural environment.

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Chapter 3 – Maintaining Thermal Performance of Multi-composition Thermoplastic Materials by Stabilizing Thermal Status

3.1. INTRODUCTION

In previous Chapter 2, the mechanical properties of multi-composition blends have been investigated, and also discussed the effect of compatibilizer and various blending ratio on each groups. Moreover, in Chapter 3, we're going to investigate the another important behavior of multi-composition blending materials – thermal behaviors. It is commonly known that thermal treatment is a general method to apply on thermoplastic materials due to its inherent reversible characteristic. Hence, in order to recycle and reuse thermoplastics, thermal treatment is a common method used to melt and reform it to satisfy the requirements of the customers subsequent users. The recycling effectiveness is easily reduced as a result of overheating damage due to the unfamiliarity of the inherent characteristics of thermoplastic materials. In addition, different materials cannot be recycled at the same time due to their different intrinsic properties.

As aforementioned in Chapter 1 and Chapter 2, people start to give attention to plastic issues including severe pollution, unnecessary consumption, excessive wastes, potential substitutes and sustainable development [1-5]. Moreover, it is obviously indicated that the rapidly increasing amount of plastic wastes requires efficient disposal to reduce plastic pollution. Geyer et al. (2017) indicated that there were almost 910 billion tons of plastic waste, 12% of which was burned while 9% of which was recycled and reclaimed [6]. Meanwhile, the study showed that only focusing on recycling and reusing plastic waste were inefficient to mitigate the environmental impact, but only delayed the waste from being disposed to the ocean or buried in soils. Based on the results, we should also consider other possible solution - to prolong and effectively use plastic products [6, 7].

Moreover, different thermoplastic materials should be recycled separately due to different intrinsic characteristic (polarity or chemical composition), and this become a problem that needs to be solved [8]. To reduce the difference between multi-composition plastic materials, compatibilizer is one of the possible solutions for the blending materials that are incompatible and immiscible. Compatibilizer is usually employed to reduce the negative effect brought by a immiscible or incompatible system of polymer materials aiming at improving the specific properties [9-12]. However, there are few articles have focused on the discussion of thermal behaviors of thermoplastic materials, which aim at excess plastic products and increase the possible usability of plastics. Hence, the viewpoint of compatibilizer is changed to a different perspective – to help improve the recyclability and extend the life span of existed plastic.

In Chapter 3, it aims to investigate the feasibility of using thermoplastic based on the consideration of how to sustain the excess plastic products and develop the measure to melt-blend diverse thermoplastics for reclamation. Furthermore, thermal behaviors

including differential scanning calorimetry and thermogravimetric analysis of multi-composition thermoplastic materials are were investigated. The results can be referred to as consultation for future studies with an attempt to fulfill the requirements of the user end and satisfy the goal of sustainability.

3.2. EXPERIMENTAL

3.2.1. Materials

As same as in Chapter 2, polypropylene (PP), thermoplastic polyurethane (TTPU), and polypropylene grafted maleic anhydride (PP-g-MA) are also employed, which individually served as the matrix material, reinforcing material and the compatible agent. To produce PP/MA/TTPU pellets, each group of pellets is mixed with specified PP/TTPU ratios (90:10, 80:20, and 70:30) and MAs (1, 3, and 5 wt%). The control group is MA-free groups. Samples were denoted according to the content of the constituent materials. Furthermore, for instance, PP70MA5TTPU30 is composed of 70wt% of PP, 30wt% of TTPU, and 5wt% of MA. The characteristics of raw materials are listed as follows in Table 3-1.

Table 3-1. Characteristics and resources of raw materials.

Raw Materials	Density	Melting flow index	Resources
Polypropylene (PP)	0.90 (g/cm ³)	10g/ 10min (230 °C)	YUNGSOX 1080, Formosa Plastics, Taiwan
Thermoplastic Polyurethane (TTPU)	1.23 (g/cm ³)	7.03g/ 10min (175 °C)	HE-3285ALE, Headway Polyurethane, Taiwan
Polypropylene grafted Maleic Anhydride (MA)	0.903 (g/cm ³)	49g/ 10min (190 °C)	Fusabond [®] P613, DuPont [™] , US

3.2.2. Manufacturing Processes

Preparation of PP/MA/TTPU blending pellets and multi-composition materials

In this chapter, there are three main processes for PP/MA/TTPU blends as simulating multi-composition plastic materials, first of all, it is the melt blending extrusion process and the others are the injection molding extrusion process and plate-type hot pressing process as presented in Figure 3-1. The details for each process are described in subsequent sections. As same as the previous experimental processes in Chapter 2, the different section is plate-type hot pressing process, which also widely applied in industrial field.

PP/MA/TTPU blending pellets

As shown in Figure 3-1, the melt-blending processes is mainly separated into 4

sections containing melting, extruding, cooling & extending, and cutting steps. The process starts from the feeding part of the single-screw extruder with different setting temperatures at 200, 210, 210, and 210 °C in melting zone, respectively. Furthermore, the blending polymer melt is cooled and extended in water bath and trimmed by a cutting machine in cutting zone. The blending pellets are also used for DSC and TGA analysis.

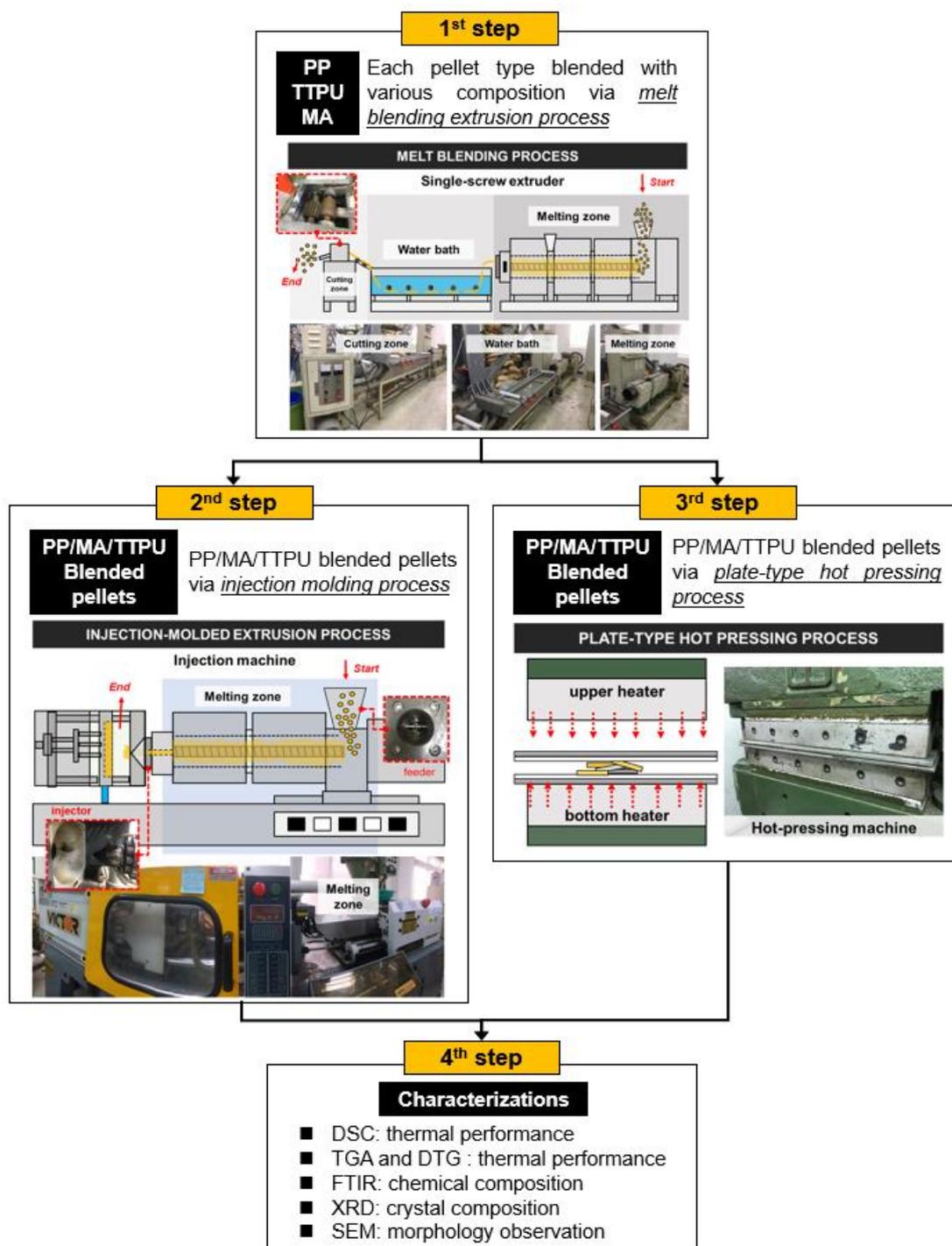


Figure 3-1. The flow chart of the experiment for PP/MA/TTPU multi-composition materials.

PP/MA/TTPU multi-composition samples for tests

Using injection-molded extrusion process and plate-type hot pressing process, PP/MA/TTPU blending pellets are made into PP/MA/TTPU multi-composition samples for each test. In the injection molding process, the diagram shows that there is also a melting zone to melt blending pellets and samples are processed with four processing temperatures being 200, 210, 210, and 210 °C, and then cooled by water system. The samples are generally used for tensile, flexural, and impact tests. In this Chapter 3, the SEM images are obtained by the fracture section of samples after tensile test.

From the plate-type hot pressing process, the thickness, temperature, pressure, and length of processing time for each group are set at 0.5mm, 200 °C, 20 MPa, and 10 minutes. Between the aluminum (Al) plates, the polytetrafluoroethylene (PTFE) film and aluminum foil were used to make the whole blending system evenly heat. The sample are used to undergo XRD and FTIR analysis.

3.2.3. Tests

Thermal Analysis

In this study, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) are applied to evaluate the thermal behaviors of PP/MA/TTPU blended materials.

According to DSC test, the experimental and control groups of pellets are placed in an aluminum plate in the heating system at a specified rate, and compared in terms of the enthalpy. DSC analyses are used to examine the influence of the presence of TPU on the crystallization and melting behavior of PP matrices. The melting enthalpy of 100% crystalline PP (ΔH_m^0) is 165 (J/g) [13].

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

TGA can estimate the association between the sample weight and the processing temperature. Samples are set in a ceramic plate and heated in an oven with N₂ gas at increments of 10°C/ min until the temperature reaches 600 °C. Hence, TGA is used to evaluate the influence of the content of TTPU on the thermal stability of PP. TGA is coupled with DTG to further examine the variation in the weight of PP/MA/TTPU blends. Hence, the first order of differential TGA curves is computed and as such obtains DTG curves. In this case, the inflection point of TGA equivalently means the peak of DTG curves.

Fourier Transform Infrared Spectrometry (FTIR)

Samples are scanned 600-4000cm⁻¹ using FT-IR(L160000A Perkin Elmer). For starters, the tester scans air as background before the composites are scanned. Next, samples are scanned at the same frequencies, during which moist is removed

simultaneously in order to obtain the accurate data.

X-Ray Diffraction (XRD)

Samples that are trimmed into 1 cm × 1 cm are examined at a range of 10°-30° and a scan rate of 2°/ min using a X-ray diffractometer. The diffraction peaks are recorded, thereby examining whether amorphous TTPU affects the crystalline-phase structure of PP.

Scanning Electron Microscopy (SEM)

A SEM (HITACHI, S4800, Japan) is used to observe the fracture surface morphology of samples with different magnifications. Moreover, samples that were evaluated using the impact test were collected, after which the fractured surface morphology was observed using an SEM. The morphology and particle size of PP/MA/TTPU blended multi-composition samples as related to the distribution of TTPU in the PP matrices are observed.

3.3. RESULTS AND DISCUSSION

3.3.1. Thermal Behaviors – DSC, TGA, and DTG

PP and TTPU are polymers, both of which are classified into thermoplastics and they can be melted by heat to reform produces used in the daily life and a variety of industries. For fear of compromising the application efficacy, we conduct the DSC analyses for a purpose of setting the temperature and time of melt-extrusion for PP and TTPU accurately as well as observing the melting and crystallization behaviors[14].

TGA and DTG are conducted in order to investigate the thermal stability of PP/MA/TTPU pellets. TGA is performed to observe the difference in weight of samples as related to the heating time and temperature. Furthermore, DTG is conducted primarily to determine the difference in weight of samples as related to the temperature. Afterward, the first order of differential of TGA is computed in order to obtain the DTG curves, and the inflection point of TGA is equivalently the peak of DTG curves.

Melting and Crystallization Behaviors - DSC

Figure 3-2 and Table 3-2 show the DSC results of PP/MA/TTPU pellets, indicating the melting and crystallization behaviors. Out of two heating cycles, the crystallization curve in the first cycle and the melting curve in the second cycle are adopted for analyses. This design is to ensure that the collected data involves the changes after samples are totally melted and cooled in two melting cycles. The T_c/T_m for neat TTPU and neat PP are 62.46°C /145.81 °C and 114.63°C/162.79°C, respectively. Besides, neat TTPU and neat PP exhibit considerable differences in ΔH_c and ΔH_m , which are 6.15J/g and 9.71 J/ g for neat TTPU and 107.9J/g and 115.40 J/g for neat PP. The significant differences in enthalpy is ascribed to the fact that TTPU is amorphous material whereas PP is semi-crystalline material. Figure 3-2 (A-C) coupled with Table 3-2 show that the

incorporation of TTPU and MA with the PP system provides the majority of pellet groups (*e.g.* PP90/TTPU10, PP80/TTPU20, and PP70/TTPU30) with a crystallization temperature which is 0.7 - 4.5 °C higher than that of neat PP. Conversely, the crystallization temperature of PP80/MA5/TTPU20 and PP70/MA5/TTPU30 pellets is individually 0.9 °C and 0.3 °C lower than that of neat PP. The existence of TTPU enhances the crystallization temperature of PP. With TTPU being as a nucleating agent, crystallization mechanism of PP converts from being homogeneous nucleation to being heterogeneous nucleation. The addition of a nucleation agent markedly reduces the free energy of the whole system, which provides a supportive nucleating environment. Particularly, heterogeneous nucleation mechanism facilitates the molecular chains to attach to the nucleation agent in an orderly alignment, which enables the formation of crystallization at a high temperature.

PP/MA/TTPU pellets exhibit a greater crystallization temperature when being composed of 30wt% of TTPU rather than 10wt% of TTPU. When more TTPU is added, TTPU molecular chains enter the PP system and impact the mobility of PP molecular chains. The crystallization temperature slightly decreases as a result of the occurring of polymer chain entanglement. Also, the crystallization enthalpy of PP/MA/TTPU pellets shows a declining trend when there is more TTPU because neat TTPU has a lower crystallization enthalpy. Figure 3-2 (D-F) and Table 3-2 show that the melting temperature of PP/MA/TTPU pellets falls between 164.17 °C and 166.34 °C. The melting temperature of PP is not dependent on the presence of TTPU, suggesting that the addition of TTPU does not change the crystalline structure of PP [15]. Apart from PP90/MA5/TTPU10, PP80/MA5/TTPU20, and PP70/TTPU30, all of the rest pellet groups exhibit a greater crystallinity than neat PP. The results can be ascribed to two factors. One factor is that TTPU is amorphous material, a greater content of TTPU adversely affects the crystalline structure and bonding behavior of the continuous phase PP. During the melt-blending process, TTPU's soft segments enter PP's amorphous domain as a result of the dynamic flow. The intermolecular/intramolecular interaction of PP are compromised and PP thus exhibits a lower crystallinity. The other factor is that maleic anhydride (MA) is proven to be an effective compatibilizer that can undermine the polarity difference and interfacial tension between PP and TTPU, which in turn mitigates phase separation between PP and TTPU while jeopardizing the orderly alignment of PP molecular chains. The crystallinity of PP is then decreased accordingly.

Table 3-2. Crystallization and melting behaviors of PP/MA/TTPU blended pellets.

	T_C	ΔH_C	T_m	ΔH_m	X_{cPP}
	(°C)	(J/g)	(°C)	(J/g)	(%)
Pure PP	118.11	91.29	164.48	92.29	44.16
Pure TTPU	62.46	6.15	145.81	9.71	-
MA	-	-	124.06	64.55	-
PP90/MA0/TTPU10	122.66	92.81	165.30	96.03	45.95
PP90/MA1/TTPU10	122.06	93.98	164.75	102.1	48.85
PP90/MA3/TTPU10	120.91	91.50	166.06	96.67	46.25
PP90/MA5/TTPU10	120.46	87.30	165.11	91.76	43.90
PP80/MA0/TTPU20	121.45	85.93	166.34	92.31	44.17
PP80/MA1/TTPU20	121.93	90.36	164.17	96.00	45.93
PP80/MA3/TTPU20	120.15	88.69	164.28	98.44	47.10
PP80/MA5/TTPU20	117.25	76.03	162.81	83.01	39.72
PP70/MA0/TTPU30	122.40	75.97	164.35	80.23	38.39
PP70/MA1/TTPU30	119.14	67.04	165.33	70.67	33.81
PP70/MA3/TTPU30	118.82	70.73	164.65	78.67	37.64
PP70/MA5/TTPU30	117.84	70.62	163.59	74.76	35.77

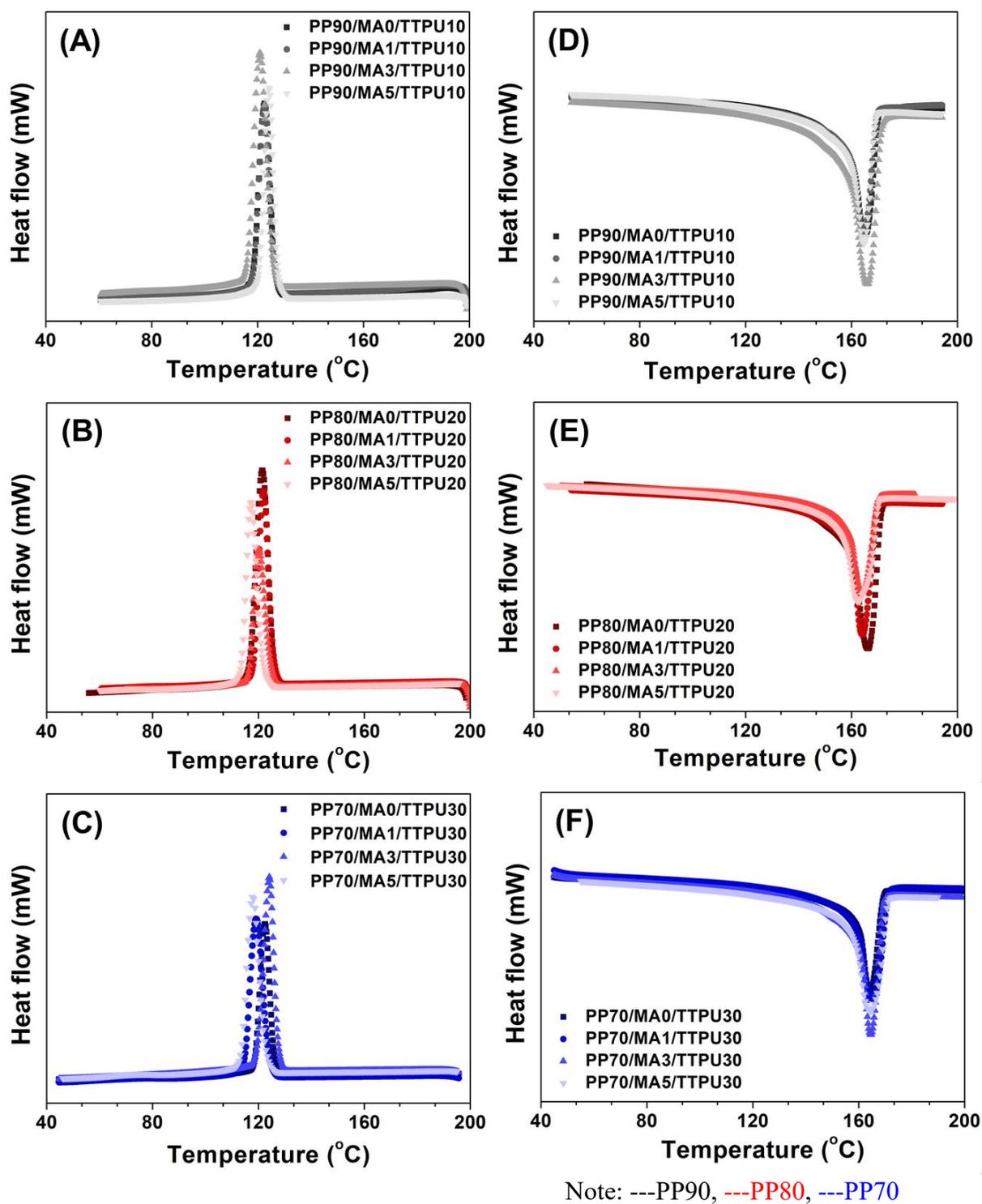


Figure 3-2. (A-C) Crystallization and (D-F) melting behaviors of PP/MA/TPPU pellets.

Degradable Behaviors – TGA and DTG

Figure 3-3 shows the thermal degradation of neat PP and neat TTPU. PP exhibits one-step degradation behavior resulted from long-chain breakage, while TTPU exhibits two-step degradation behaviors caused by the rigid and soft segments, respectively[16]. The first and second degradation of TTPU occurs individually at 305.7°C with a weight

loss of 16.2% and at 395.6°C with a weight loss of 65.5%. With a comparison to TTPU, PP has better thermal stability under high temperatures. Not until 446.1°C does PP lose weight significantly, and the remaining weight is only 39.2wt%. This result indicates that although PP thermally decomposes at a greater rate than TTPU, it has well remained its original state until the degradation temperature comes [16].

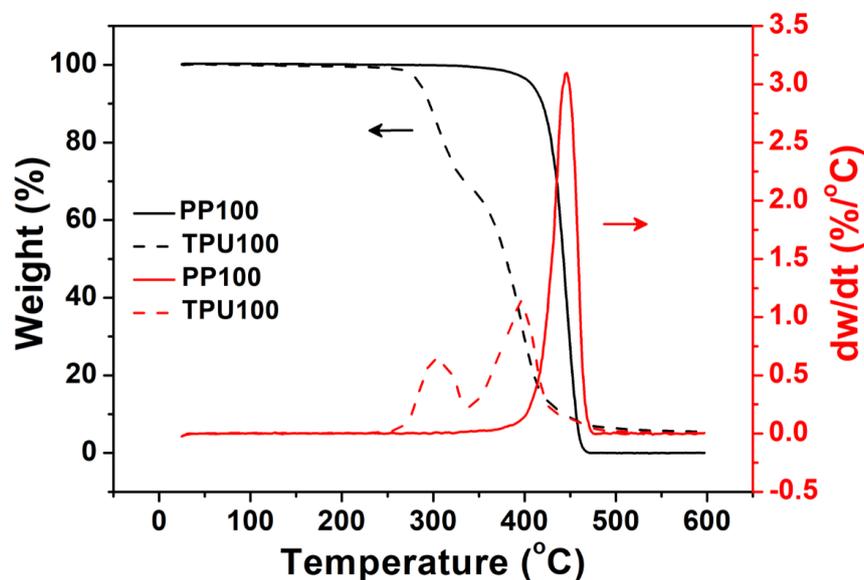


Figure 3-3. Thermal degradation of neat PP and neat TTPU. Black lines are for TGA analysis, and blue lines are for DTG analysis.

Figure 3-4 and Table 3-3 show the TGA and DTG results of PP/MA/TTPU blends. From Figure 3-4, it is clearly revealed that the thermal degradation of PP/MA/TTPU blends have three stages where T_{1max} occurs at 315-332 °C, T_{2max} at 356 °C-399 °C, and T_{3max} at 446 °C-455 °C with Δm_1 , Δm_2 , and Δm_3 being 1.9%-4.7%, 3.4%-21.1%, and 59.4%-69.1%. The continuous degradation behaviors for each stage are attributed to the degradation of rigid segments and soft segments on TTPU, and the degradation of free radicals in PP molecular chains, respectively. TTPU has rigid segments consisting of interlocked diisocyanate and diols via covalent bonding, and the molecular chains of diisocyanate are longer than those of diols. Nonetheless, both of diisocyanate and diols are incompatible and immiscible so they display phase separation easily. In addition, TTPU's rigid segments consist of comparatively more rigid diisocyanate via hydrogen bonding that is fragile at low temperatures. By contrast, TTPU's soft segments consist of comparatively softer polyols molecules. It demands more energy to damage the longer molecular chains of polyols and the thermal degradation temperature is high.

Figure 3-4 (A) and Figure 3-4 (B) show that the presence of TTPU expedites the thermal degradation of PP/MA/TTPU pellets distinctively. The weight loss of PP70/MA0/TTPU30 pellets is 30 wt% at 425°C, but the weight loss of PP90/MA0/TTPU10 pellets is merely 10wt% at the same temperature. The results are due to the low thermal stability of TTPU, which can be compensated for by using

thermally stabilized PP [17]. Figure 3-4 (C-H) show that a greater content of PP heightens the temperature of maximum thermal degradation of PP/MA/TTPU blends in the first and third stage, indicating that both of the decomposition of TTPU's rigid segments and the breakage of PP's molecular chains are delayed. Comparatively, TTPU's soft segments are decomposed at a lower temperature, which may be due to the addition of PP. The orderly arranged PP's polymer chains interfere with the TTPU's molecular structure of soft segments, which results in a decrease in the thermal stability of soft segments. In spite of being immiscible and incompatible, PP still improves TTPU in terms of thermal stability.

Table 3-3. Thermal degradation behaviors of PP/MA/TTPU multi-composition samples.

	T_{95}	T_{1max}	Δm_1	T_{2max}	Δm_2	T_{3max}	Δm_3	T_5
	(°C)	(°C)	(wt%)	(°C)	(wt%)	(°C)	(wt%)	(°C)
Pure PP	407.7	-	-	-	-	446.1	39.2	459.4
Pure TTPU	285.8	305.7	83.8	395.6	34.5	-	-	$T_{10}=443.8$
PP90/MA0/TTPU10	347.2	319.6	97.2	356.9	93.8	450.8	38.1	462.8
PP90/MA1/TTPU10	352.6	332.6	96.7	369.5	93.2	450.1	38.5	462.3
PP90/MA3/TTPU10	355.1	325.6	97.6	367.5	93.5	449.3	40.6	462.0
PP90/MA5/TTPU10	366.6	321.1	98.1	359.9	95.6	446.5	39.7	458.6
PP80/MA0/TTPU20	325.4	317.4	95.6	379.3	86.4	451.2	35.9	463.5
PP80/MA1/TTPU20	327.5	317.4	96.6	373.7	88.6	451.5	39.0	464.5
PP80/MA3/TTPU20	325.7	317.6	96.3	375.9	88.1	452.2	36.1	464.9
PP80/MA5/TTPU20	322.2	313.6	96.5	368.2	88.6	450.9	39.8	463.9
PP70/MA0/TTPU30	324.9	321.9	95.5	399.4	79.9	454.7	31.9	467.0
PP70/MA1/TTPU30	317.9	315.9	95.3	392.3	80.9	452.5	33.2	465.5
PP70/MA3/TTPU30	319.9	317.2	95.6	395.9	80.4	453.1	33.4	466.2
PP70/MA5/TTPU30	316.3	315.6	95.3	394.6	79.9	453.1	32.4	465.5

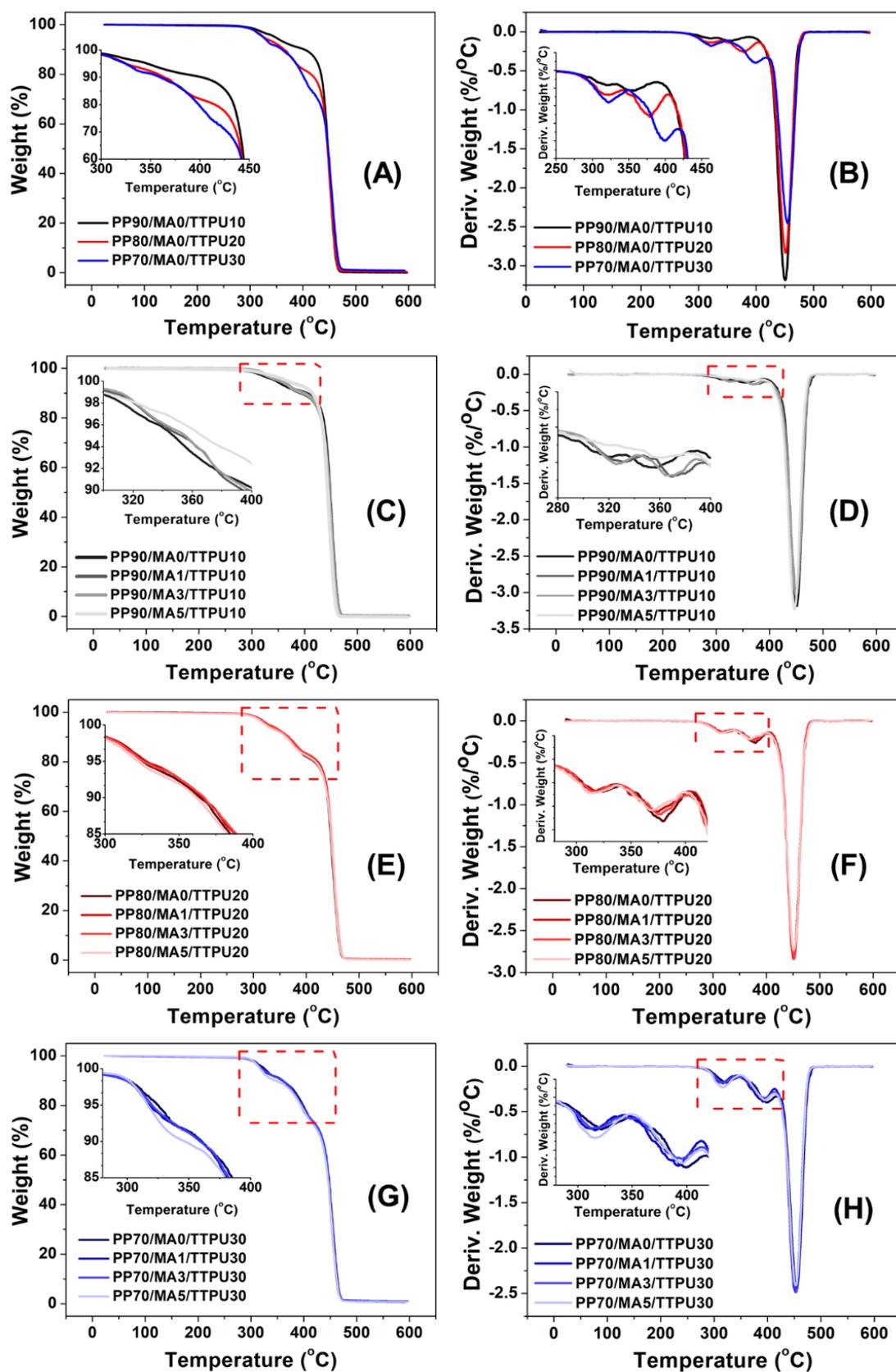
Notes:

T_{95} = temperature that causes the remaining weight to be 95 wt%.

T_5 = temperature that causes the remaining weight to be 5wt%.

T_{1max} , T_{2max} , and T_{3max} =The maximum degradation temperature at each stages.

Δm_1 , Δm_2 , and Δm_3 = the remaining weight percent in the three stages.



Note: ---PP90, ---PP80, ---PP70

Figure 3-4. TGA and DTG analyses of (A)(B) MA-free group, (C)(D) PP90/MA/TTPU10, (E)(F) PP80/MA/TTPU20, and (G)(H) PP70/MA/TTPU30 pellets.

Table 3-3 shows that PP/MA/TTPU pellets have greater Δm_3 than neat PP and neat TTPU, which means a greater content of residue at T_{3max} . Moreover, the addition of a compatibilizer slightly increases the content of residue, indicating that MA has a positive influence on the thermal stability of the blends. To sum up, two incompatible and immiscible materials commonly exhibit a greater interfacial tension and a lower interfacial tension, which can be improved by adding MA[17]. The anhydride group of MA interacts with the urethane group of TTPU, forming isocyanate in the interface and reducing the interfacial tension between PP and TTPU. The interfacial adhesion is enhanced and the compatibility is improved accordingly.

3.3.2. Chemical Composition – Fourier Transform Infrared Spectrometry (FTIR)

Figure 3-5 shows the FTIR analyses of neat PP and neat TTPU, and the chemical functional groups of PP and TTPU functional groups are presented. Figure 3-5 (A) shows that between $4000-500\text{cm}^{-1}$, PP demonstrates the relative characteristic peaks caused by CH, CH₂, and CH₃ vibration frequencies because PP are mainly composed of carbon atoms and hydrogen atoms. Figure 3-5 (B) shows that the characteristic peaks of TTPU caused by CH₂ and CH₃ stretching, NH stretching vibration, C=O stretching vibration and N-H-C=O bonding [18]. Figure 3-5(C)-5(F) show the FTIR analyses of PP/MA/TTPU composites, which is similar to that of neat PP. Moreover, the characteristic peaks of PP are attenuated due to an increase in TTPU, which proves that TTPU is blended in the PP matrices. As being a compatibilizer, MA exerts a marginal influence on the PP/MA/TTPU composites. The interaction between diisocyanate group of TTPU and anhydride group of MA generates the urethane group. Nevertheless, MA used in this study is MA-g-PP with a grafting rate of 1.5%, which makes it difficult to display its complete reaction.

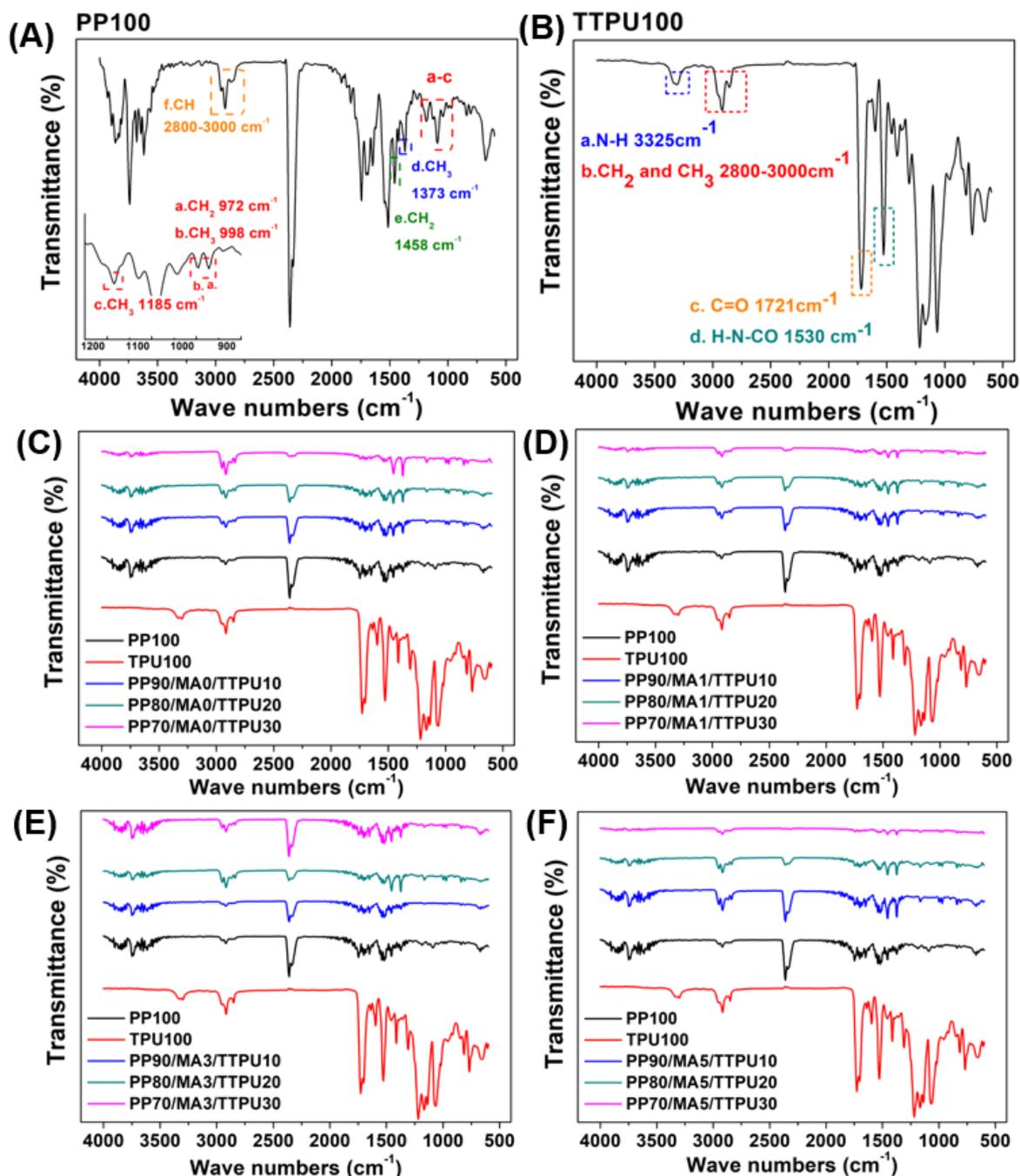


Figure 3-5. FTIR analyses of (A) neat PP and (B) neat TTPU; PP/MA/TTPU composites made of (C) 0 wt%, (D) 1 wt%, (E) 3 wt%, and (F) 5 wt% of MA.

3.3.3. X-ray diffraction analysis of PP/MA/TTPU blends

Figure 3-6 shows the XRD analyses that indicate that the blends are composed of PP that is a semi-crystalline polymer and TTPU that is an amorphous polymer. PP is commonly a polymorphism-type polymer, including α -phase, β -phase, and γ -phase. Figure 3-8 (A) shows that the characteristic peaks of neat PP are noticeable and much stronger than those of neat TTPU, which is due to the fact that PP is polymer that possesses a relatively greater crystallinity than TTPU. Being an amorphous polymer,

TTPU has flatter diffraction characteristic peaks. When $2\theta=14.2^\circ$, 17° , 18.7° , 21.3° , 22° , and 25.5° , neat PP demonstrates Bragg diffraction characteristic peaks, corresponding to (110), (040), (130), (111), (131), and (060) crystal diffraction[19]. When 2θ is at $16-26^\circ$, neat TTPU shows a broad diffraction peak with a center being at 20.7° [18, 20]. Figure 3-6 (B) shows that an increase in TTPU has a negative influence on the characteristic peaks of (040), (130), (111), and (131) as shown in pale-yellow domain. Additionally, as being an amorphous polymer material, more TTPU influences the primitive crystalline structure of PP, the characteristic peak of which has a declining trend. Figure 3-6 (C-E) shows that the presence of MA does not affect the crystalline characteristic of PP/MA/TTPU blends yet undermines the strength of characteristic peaks. MA is referred as a compatibilizer that improves the incompatible phenomenon between PP and TTPU, and is proven to heighten the compatibility without changing the crystallization structure of the PP/MA/TTPU composites.

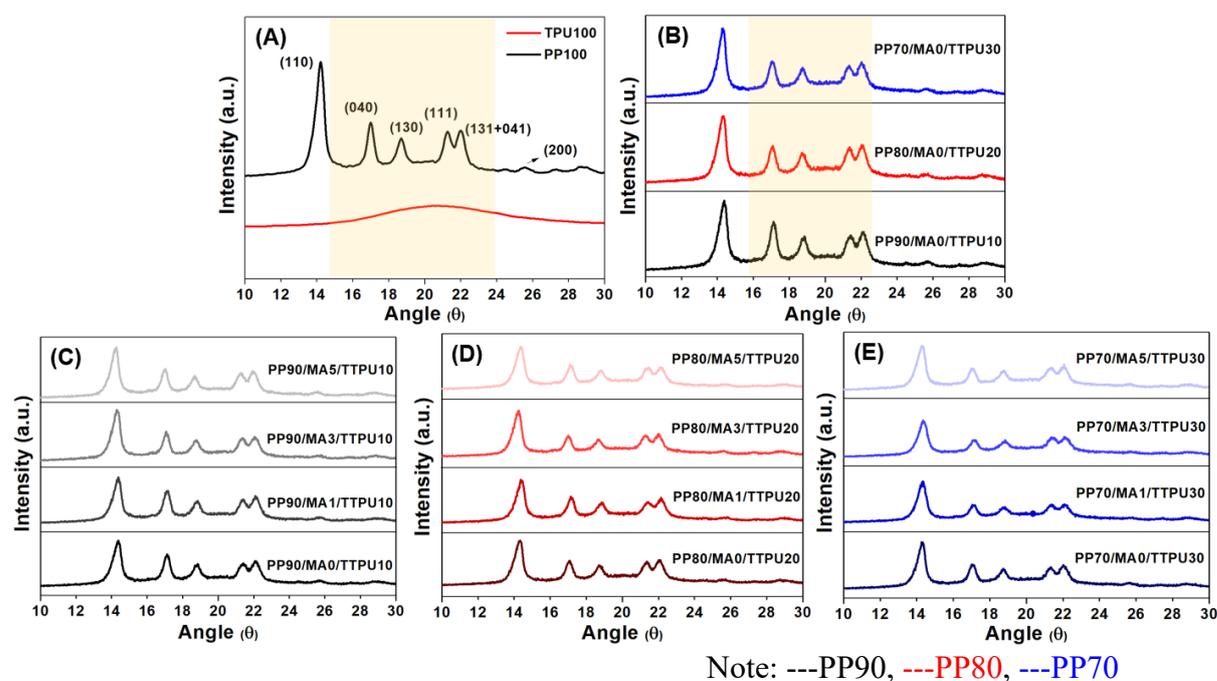


Figure 3-6. XRD analyses of A) neat PP and neat TTPU, B) MA-free, C) PP90/TTPU10, D) PP80/TTPU20, and E) PP80/TTPU20 composites.

3.3.4. Morphology Observation of PP/MA/TTPU blends

Figure 3-7 shows the SEM images of the fractured morphology of PP/MA/TTPU composites, which are composed of 0wt% of MA (A-C) and 5wt% of MA (a-c). Figure 3-7(A)-(C) show an increase in TTPU causes a larger size of TTPU particles in the PP matrices, which is attributed to the high polarity difference and high interfacial tension between PP and TTPU. Figure 3-7 (C) demonstrates the significant pores because TTPU particles coupled with PP matrices exhibit a low interfacial adhesion, which

leads to the detachment of TTPU particles [15, 21]. Furthermore, the effect of using a compatibilizer can be observed based on the variations in TTPU particle size and the roughness of fractured surface (Figure 3-7 (a-c)). In other words, with an improved compatibility between PP and TTPU, TTPU particle size is smaller and the fractured surface has a smooth morphology.

In Figure 3-7 (A) and 3-7 (a), PP90/TTPU10 group exhibits that TTPU particles have a smaller size indicated in the circles. Moreover, Figure 3-7 (B, b) show that the roughness of surface is decreased and there is a greater number of cracks, which suggests that the presence of compatibilizer is helpful to the toughness of the composites. Figure 3-7 (C, c) show that with a compatibilizer, TTPU's particle size is smaller, the fractured surface is smoother, and the number of cracks is increased. As a result, MA is an effective compatibilizer that improves the interfacial compatibility between PP and TTPU, providing PP and TTPU with greater adhesion and better stress transmission and eventually advancing the toughness of the composites. As far as the recycled materials are concerned, when a compatibilizer is used, PP can improve the mechanical properties of TTPU, and likewise TTPU can improve the toughness of PP to attain a reciprocal, synergistic effect while decreasing the consumption of sources.

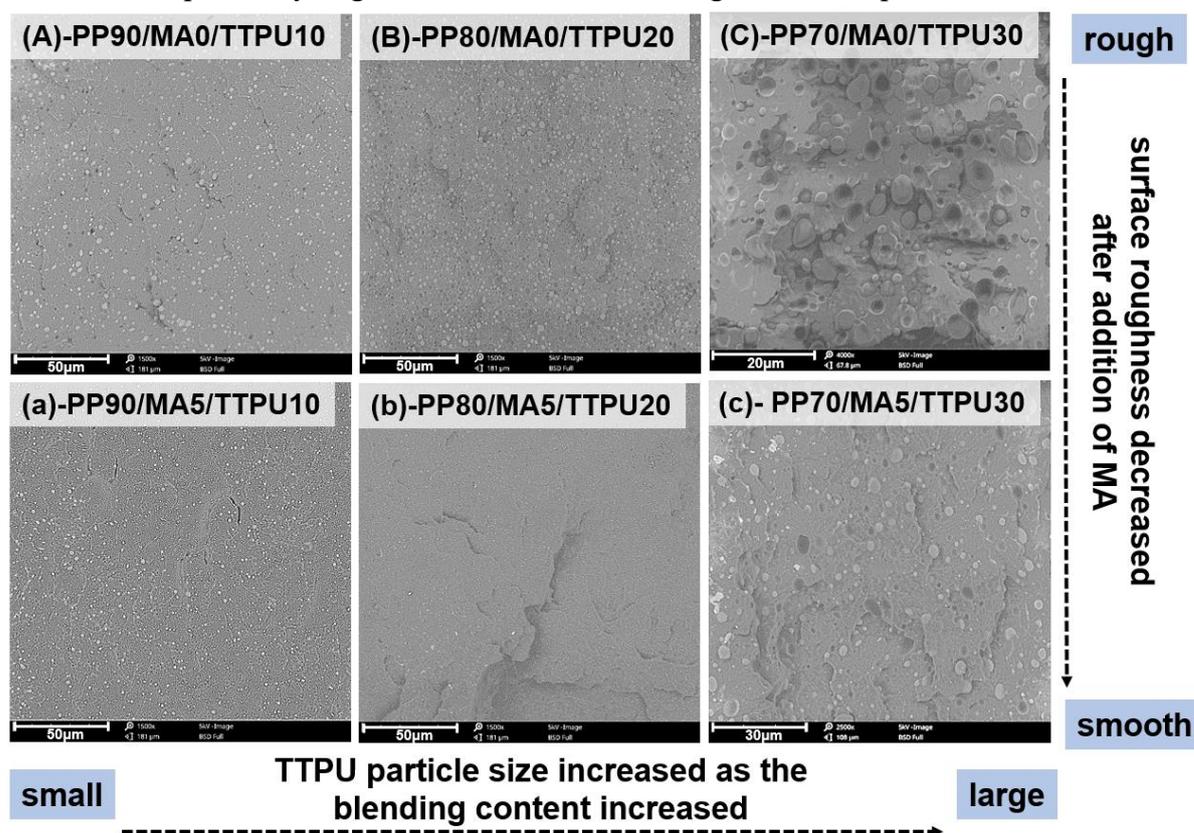


Figure 3-7. SEM images (1500x) of PP/MA/TTPU multi-composition samples composed of (A-C) 0wt% and (a-c) 5wt% of MA.

3.4. CONCLUSION

This study successfully applies an easy, efficient and convenient melt extrusion process to investigate the recycling possibility of PP/TTPU blends for remodeling excess plastic wastes. Also, a compatibilizer-MA is added aiming to improve the inherent weakness and have additional value of the recycled materials. The test results indicate that thermal behaviors, crystallization property, composition, and surface morphology of the composites are not compromised due to the usage of an appropriate amount of TTPU. Based on the results of thermal property tests, it is indicated that PP has reinforced the thermal stability of TTPU, which is also slightly improved when MA is added. Hence, the presence of MA also demonstrates a positive influence on the thermal stability. SEM results show that introducing TTPU causes rougher surface morphology while adding MA has been effectively improving the interfacial compatibility between PP and TTPU, contributing to a greater adhesion level and stress transmission. It is clearly indicated that separated thermoplastic can be assisted under appropriate conditions.

The main goal of the study is to enable the thermoplastics to demonstrate their properties once again and as such attain reciprocal reinforcement. In this case, more value-added can be yielded, thereby attains the extreme purposes of environmental protection and sustainable developments. Therefore, it is concluded that this easy and convenient process not only can reduce the waste probability of excess thermoplastic materials but also increase the utilization chance of them. Moreover, this study proves a positive effect on the cleaning aspect of our circumstances. In the future, the mechanical performance of the blending materials and to-be-recycled ones is also important targets, therefore, it is expected to implement in subsequent studies.

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**Part II – Performance Improvement of Recycled
Multi-composition Thermoplastic Materials after
Cycling Utilization**

Chapter 4 – Cycling Effects of Mechanical Fractures and Thermal Treatment on Recycled Multi- composition Thermoplastic Materials

4.1. Introduction

In previous Chapters 2 and 3, we discussed the mechanical properties and thermal behaviors of multi-composition thermoplastic materials and indicated that compatibilizer has helped to mitigate the interphase difference between different plastic materials, and thus improving the mechanical performance and stabilizing the thermal status of multi-composition thermoplastic materials. Moreover, in Chapter 4, the cycling effect of mechanical fractures and thermal treatments on the recycled multi-composition thermoplastic materials are discussed, and further investigated the difference between the groups with and without compatibilizer.

As we commonly know that plastic products have been commonly used in different regions in the late decades [1, 2]. Worldwide, the annual production of plastics is approaching more than 300 million tons, and it is predicted that the global growth of plastic products can be up to 400 million tons in 2020 [3-5]. The enormous amount of plastic derivatives and their disposal have become a global and important environmental issue [2, 4, 6, 7]. Based on their inherent characteristics, they can be divided into thermoset plastic and thermoplastic, of which the latter has a noticeable feature of reversibility and is thus suitable for reclamation [1, 8, 9]. Despite the amazing reversibility, thermoplastic materials may demonstrate compromised performances and lose its original advantages as a result of insufficient processing conditions or mistakes. Therefore, the thermal conditions of each polymer material are very important during the future processes. In 2009, Young-Hee et al. concluded that the processing conditions of hot-pressing/melt mixing methods strikingly influenced the various aspects of thermoplastic polyurethane and pointed out that the thermoplastic materials could not be retreated over two or three recycling times due to its poor thermal stability. Therefore, a strategy for thermoplastic polyurethane is to find a suitable polymer that can supplement the required properties [10].

As same as in previous chapters, the experiment materials used in Chapter 4 are thermoplastic polyurethane and polypropylene. Thermoplastic polyurethane consists of rigid segments and soft segments and it has good toughness and flexibility, yet, simultaneously, its expensive cost and low thermal stability also restrict the applications by end customers[11-19]. On the other hand, polypropylene with good rigidity, good thermal stability, and a low cost that is qualified to complement the disadvantages of thermoplastic polyurethane[20]. However, not all of the blending polymers have good compatibility due to their various origins and polarity, so a bridging element is required [1]. They are separately a polar polymer and a nonpolar polymer; therefore, phase separation and poor phase adhesion commonly inflict the performance of blends. With the assistance of a suitable compatibilizer, the compounds can be rid of interphase problems [21, 22]. Additionally, there is an imperative issue of how the blended

polymer compounds can be recycled [23]. There are several recycling methods, including mechanical recycling, thermal treatment, and chemical recycling [24-26]. Furthermore, Chen et al. mentioned that plastic waste can be reused by introducing functional fillers to obtain value-added polymer composites [27].

Therefore, in Chapter 4, the motivation is not only to effectively use recycled thermoplastic materials after first use but also to investigate the mechanical fractures and thermal conditions during the recycling steps. It is hard to recycle multiple-composition ones at the same time; therefore, the multiple-composition ones are commonly dealt with using combustion or landfill treatment [1, 28]. In this chapter, the samples composed of thermoplastic polyurethane and polypropylene undergone one-term tensile test and hot-pressing treatment simulate the mechanical fractures and thermal treatment, there are three cycles during the routes. Moreover, the existence of a compatibilizer—maleic anhydride grafted polypropylene (MA) — contained in the blend is also considered in the recycling effectiveness. Furthermore, the differentiation effect caused by various composition ratio of each group is discussed in results and discussion, which also can previously predict the polarity difference among the multiple compositions. Also, the morphological, tensile, and thermal properties of TTPU/PP and TTPU/PP/MA blends are examined and evaluated, thereby determining the influences of cycling effects containing mechanical fractures and thermal treatments.

4.2. Materials and Methods

4.2.1. Materials

In Chapter 4, the multi-composition thermoplastic materials are composed of used thermoplastic polyurethane and polypropylene, and divided into two main groups – TTPU/PP and TTPU/PP/MA blends. The waste materials originate from our laboratory; these are materials that have been used for mechanical tests in previous studies. It can be regarded as used materials that require suitable treatment. From Figure 4-1, following the recycling routes for these TTPU/PP and TTPU/PP/MA blends, the materials are first trimmed into small pieces, mixed, and hot-pressed to form the blends beforehand. The blending ratios of TTPU/PP and TTPU/PP/MA blends are 90/10/0, 90/10/5, 70/30/0, 70/30/5, 50/50/0, and 50/50/5, and TTPU 100 and PP100 are referred as control groups. Moreover, Table 4-1 displays the corresponding denotations of the samples, and in order to shorten the length of sample codes, the abbreviations are a little bit different than previous chapters, T representing TTPU and P representing PP. Based on the different blending ratios of each group, the hot-pressing temperatures are different. The more TTPU in the group, the lower the pressing temperatures it becomes.

4.2.2. Preparation

In this chapter, the damage that resulted from the mechanical fractures and melting–recycling cycles of used T/P and T/P/MA waste-blended samples is evaluated, in which the plate-type hot-pressing method and tensile tests are employed as thermal breakage and mechanical breakage, respectively.

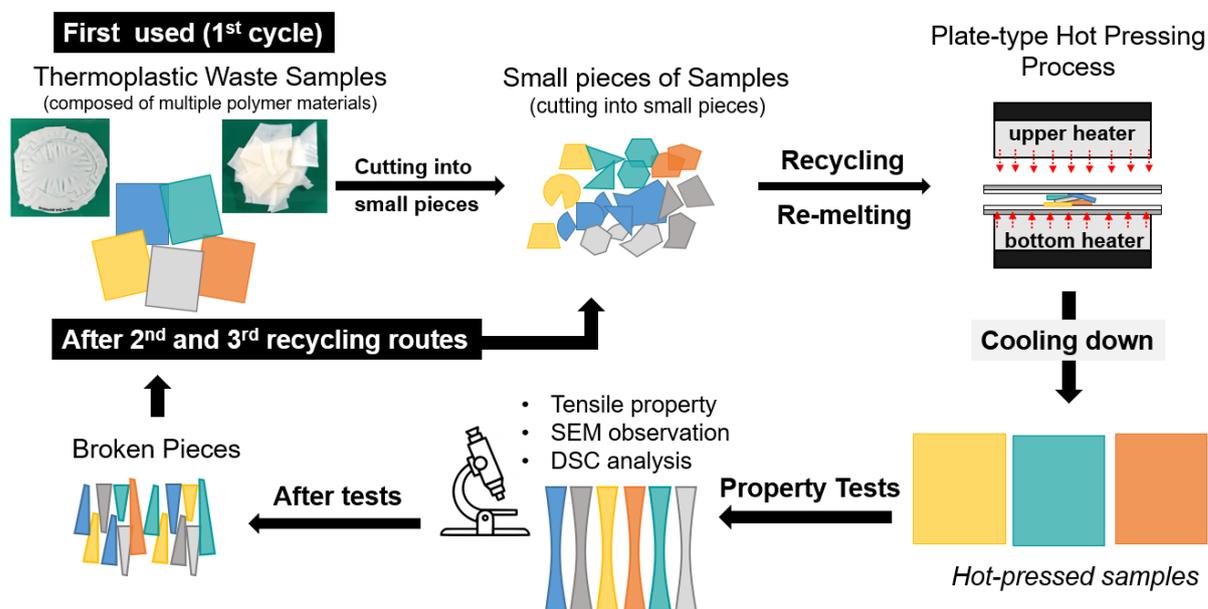


Figure 4-1. Sample preparation and recycling routes of TTPU/PP and TTPU/PP/MA waste-blended materials.

As shown in Figure 4-1, the given TTPU/PP and TTPU/PP/MA blended samples are one-off mechanically damaged and then hot-pressed again, and the new TTPU/PP samples are denoted as the *post-2nd-recycling group*. The new blended samples are denoted as the *post-3rd-recycling group* when undergoing the aforementioned route again. For these two groups, recycling means a process that combines hot-pressing and mechanical fracture.

Therefore, melt-recycling involves one-time hot-pressing, the post-2nd-recycling, and the post-3rd-recycling. Before conducting hot-pressing, six groups of samples were dried in an oven at 40 °C for 24 h in order to remove residual moisture. Next, the hot-pressing machine was preheated for one hour, and compounds were then placed on an aluminate plate and treated with a melting process for 3–5 min and then a pressing process for five minutes. Afterward, samples were cooled at room temperature (Figure 5-1). The blends were hot-pressed at a pressure of 20 MPa, and the specified thickness was 0.5 mm. Table 4-1 demonstrates the corresponding hot-pressing temperatures for different blending ratios. A greater PP content provides TTPU/PP/MA blends with a higher melting temperature. In contrast, the melting temperatures were 165 °C for PP100 and 145 °C for TTPU100.

Table 4-1. Parameters of TTPU/PP and TTPU/PP/MA blends in the hot-pressing process.

Sample Codes	Compositions			Hot-Pressing Parameters
	Thermoplastic Polyurethane (TTPU) (wt %)	Polypropylene (PP) (wt %)	Maleic Anhydride Grafted Polypropylene (MA) (wt %)	Temperature (°C)
PP100	-	100	-	185
TTPU100	100	-	-	160
T90	90	10	0	170
T90/MA	90	10	5	170
T70	70	30	0	170
T70/MA	70	30	5	170
T50	50	50	0	185
T50/MA	50	50	5	185

4.2.3. Tests

SEM Observation

In this study, the fracture morphology of TTPU/PP and TTPU/PP/MA waste-blended samples with various conditions (as related to the number of hot-pressing cycles and the number of mechanical fractures) was observed by a scanning electron microscope (SEM, S4800, HITACHI, Tokyo, Japan). To observe the morphology of both blended groups, the SEM equipment was set a 3-kV voltage, with various magnifications [29]. Moreover, the influence of TTPU/PP and TTPU/PP/MA waste-blended samples with the presence of a compatibilizer on morphology and particle size was also examined.

Tensile Properties

As specified in ASTM D638-14, type IV samples were prepared with a dog-bone shape. A universal tester (Instron 5566, Instron, Norwood, MA, USA) was used to measure the tensile properties of the 0.5-mm thick TTPU/PP and TTPU/PP/MA waste-blended samples. The speed of testing was based on the specifications of the specimen type, and TTPU/PP and TTPU/PP/MA groups were classified as rigid and semirigid groups. Moreover, type IV samples were chosen to be tested at a speed of 5 mm/min [30]. Five samples for each specification were used to obtain the average value.

DSC Analysis

DSC analysis is used to evaluate the thermal properties related to two factors (the number of melting cycles and the number of mechanical fractures). In Chapter 4, TTPU/PP and TTPU/PP/MA blends were heated from 40 to 180 °C at an increment of 5 °C per minute and kept isothermal for 5 min at 180 °C. Moreover, the environment temperature was decreased from 180 to 40 °C at a decrement of 5 °C every minute. The melting and cooling loops were repeated for two cycles to remove the thermal history of the TTPU/PP and TTPU/PP/MA blends. Furthermore, DSC analysis was also used to evaluate the crystallization performance, as related to the presence of a compatibilizer, after the TTPU/PP and TTPU/PP/MA blends had undergone multiple thermal cycles [30].

4.3. Results and Discussions

Recycled thermoplastic TTPU/PP and TTPU/PP/MA waste compounds were used in this study instead of individual thermoplastic polyurethane and polypropylene materials. The noticeable feature about thermoplastic materials is that they can be reshaped with an appropriate temperature. It is challenging to recycle thermoplastic waste compounds due to various intrinsic properties. This chapter mainly explores how to reuse polymer waste compounds and examines the reshaped materials in terms of morphological observation, thermal properties, and tensile properties. Additionally, the effect of the existence of a compatibilizer on the various aspects of TTPU/PP and TTPU/PP/MA waste blends will also be discussed after multiple melting–recycling cycles.

4.3.1. Surface Observation

Microscope Observation

Figure 4-2 (A and B) show the appearance variation of T/P blends and T/P/MA blends as related to the post-2nd and post-3rd recycling, respectively. In Figure 4-2(A), blends that are composed of a greater T content appear in dark yellow, while blends that are composed of a greater P content appear in lighter yellow, according to the comparison between the images of T90 and T70. The yellowing phenomena can be ascribed to the oxidation reaction of thermoplastic polyurethane during the recycling processes [31, 32]. Based on the results of melt-recycling, TTPU/PP/MA blends are more easily and efficiently hot-pressed than TTPU/PP blends (i.e., MA-free blends). As MA serves a bridging role that can improve the original interfacial property between T and P, it well attenuates the interfacial tension. It has been proven that a proper compatible agent for a multiple-polymer system is desirable, where the original system without a compatible agent was with poor performance and limited application [27]. Figure 4-2(B) shows that PP100 and TTPU100 waste-blended samples do not show

distinct defects in the post-3rd-recycling process and still maintain good formability. It is a good piece of evidence that the thermoplastic materials can be well reformed within an appropriate treatment. At the same time, the MA-containing blends also have stable formability and can be hot-pressed efficiently. With a greater number of melting–recycling cycles, MA provides TTPU/PP matrices with significant compatibility and stability. As for MA-free blends, the images of T90, T70, and T50 in Figure 4-2(B) exhibit distinctive pores and defects. The phenomenon results from melting–recycling cycles, in which the variation of thermal energy may escalate the incompatibility and immiscibility between T and P. Moreover, phase separation becomes apparent and forms larger defects on the T/P blends with increasing content of polypropylene. Furthermore, the larger the content value difference between T and P, the more significant the differentiation effect. On the other hand, the MA-containing groups (T90/MA, T70/MA, and T50/MA) show a reverse result, where the presence of MA makes a contribution to stable formability regardless of multiple melting–recycling cycles, which suggests that the feasibility of multiple utilization is increased considerably.

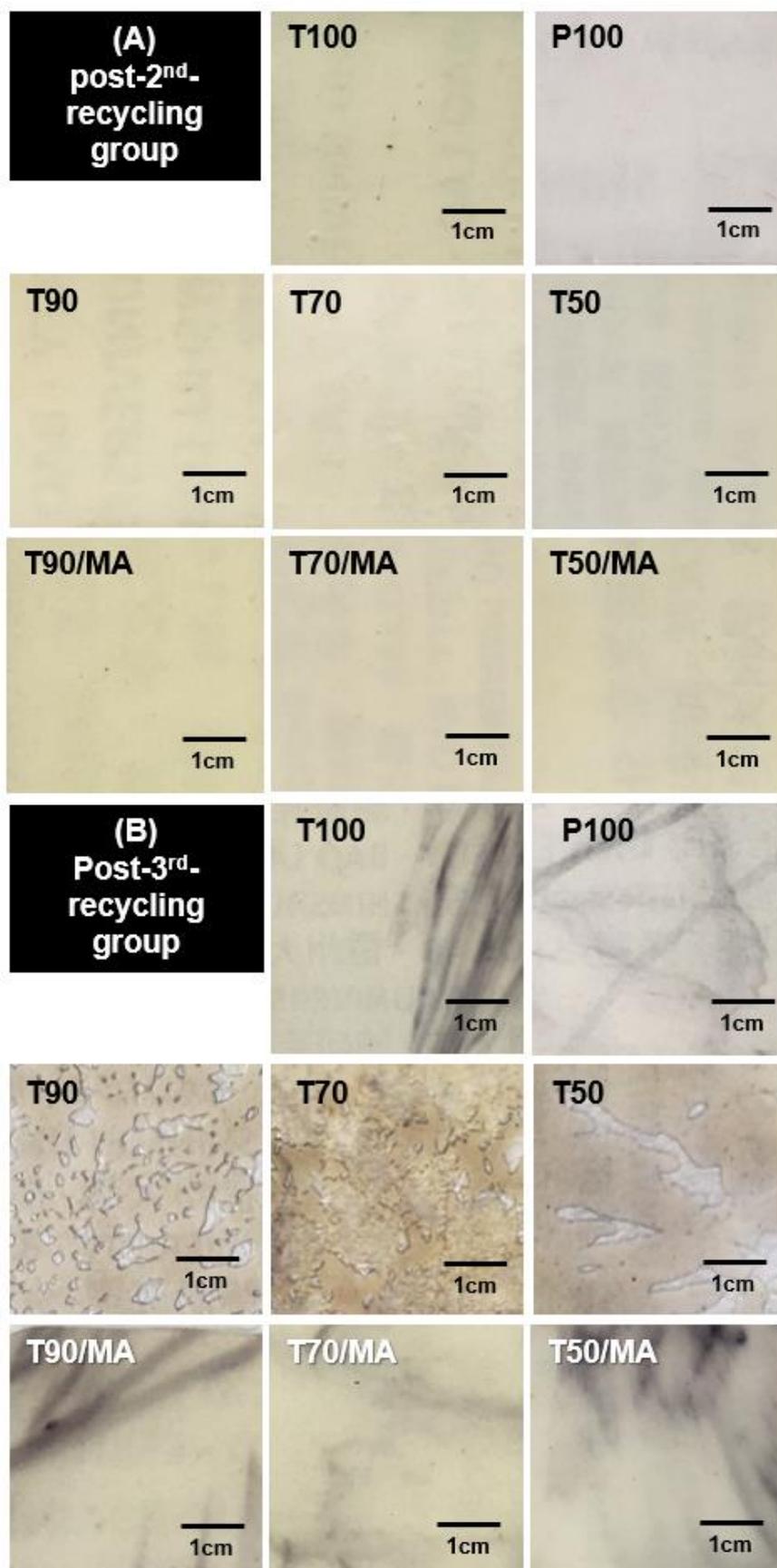


Figure 4-2. Surface observation of T/P and T/P/MA blends as related to post-2nd and post-3rd recycling. (A) Post-2nd-recycling group; (B) post-3rd-recycling group.

SEM Observation

Figure 4-3(A and B) show the fracture sections of post-2nd-recycling and post-3rd-recycling T/P/MA blends, respectively, after tensile tests. Figure 4-3(A) shows that T100 looks flatter and smoother than P100 because thermoplastic polyurethane is, comparatively, a more ductile material. Pure polypropylene reveals a homogeneous pattern, with a rough and flat surface that indicates a typical characteristic of tough fractures [33]. Figure 4-3(B) displays the surface roughness of PP100 and TTPU100 after the post-3rd-recycling process and further explains that thermoplastic materials require appropriate post-treatment when reforming. T100 shows an ascending trend on roughness, which is ascribed to the poor thermal stability of thermoplastic polyurethane. The multiple melting–recycling cycles result in damage on T100 to a certain extent, so the surface is no longer being sleek. Polar thermoplastic polyurethane and nonpolar polypropylene are incompatible and immiscible when blended with each other, and further lead to phase separation derived from high interfacial tension produced at interphase [34]. The Figure 4-3(A) group (T90, T70, and T50) shows that with greater polypropylene content, the blends yield more pores, which means, equivalently, that both the differentiation effect and incompatibility between thermoplastic polyurethane and polypropylene are strengthened. Figure 4-3(B) (T90, T70, and T50) demonstrates that with the employment of the post-3rd-recycling, thermoplastic polyurethane matrices are partially expanded, and polypropylene particles are wrapped in the matrices while the roughness is concurrently enhanced. Furthermore, the differentiation effect is clearly observed when comparing T70 and T50; the spherical particles in T50 blends appear prone to fall off from the pores due to enlarged interfacial tension and poor adhesion between thermoplastic polyurethane and polypropylene [33]. The Figure 4-3(A) group (T90/MA, T70/MA, and T50/MA) shows that the presence of MA stabilizes the morphology of all T/P/MA blends (i.e., MA-containing blends). Similarly, Figure 4-3(B) (T90/MA, T70/MA, and T50/MA) shows that MA improves the pores and defects triggered by the excessive interfacial tension between the thermoplastic polyurethane and polypropylene [33]. Moreover, the copolymer on the TPU/PP interfaces prevents the occurring of coalescence. Comparing the MA-containing and MA-free groups, the former shows an attenuated differentiation effect. The results indicate that a proper introduction of compatibilizer improves the defects and reduces the differentiation effect caused by the diversity or blending ratio of the constituent materials.

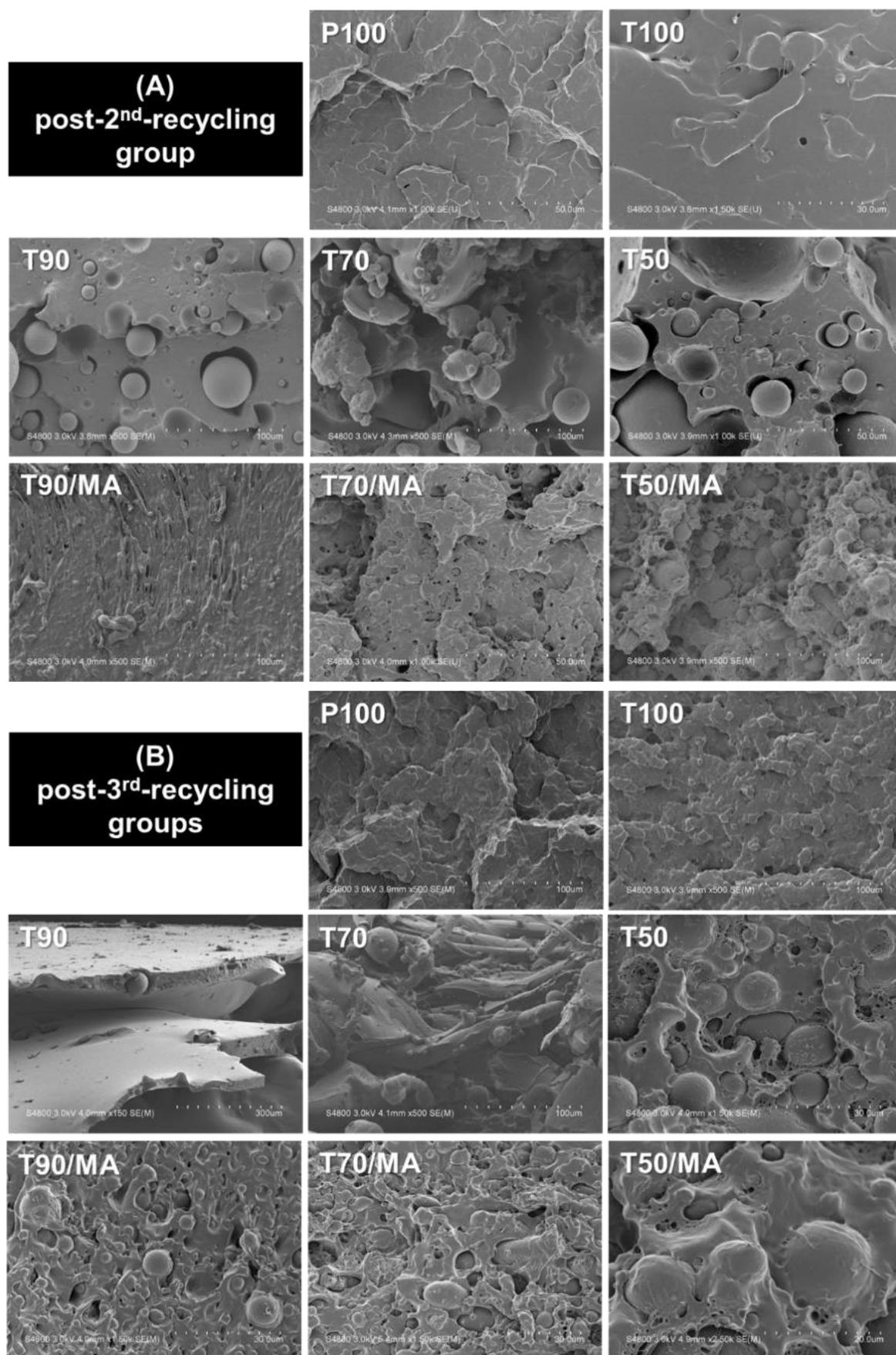


Figure 4-3. SEM images of post-2nd-recycling and post-3rd-recycling T/P and T/P/MA blends. (A) Post-2nd-recycling group; (B) post-3rd-recycling group.

4.3.2. Tensile Properties

Figure 4-4 shows the stress–strain curves and stereomicroscopic images of TTPU/PU and TTPU/PP/MA blends after tensile test and the corresponding denotations are listed in Table 4-1. Figure 4-4 (A to C) show the tensile properties of T90, T70, and T50, as related to whether MA is added, namely, T90/MA, T70/MA, and T50/MA. Figure 5-4(D) shows the stereomicroscopic image of the expanded T/P blends. In Figure 5-4(A to C), the black curve means samples are treated with one-off hot-pressing, while the red and blue curves, separately, mean samples are treated with post-2nd- and post-3rd-recycling and the resulting samples are compared, thereby examining the reclamation efficacy of TTPU/PP blends. Meanwhile, the solid lines represent the MA-free groups, while the dotted lines represent the 5 wt % MA-containing groups.

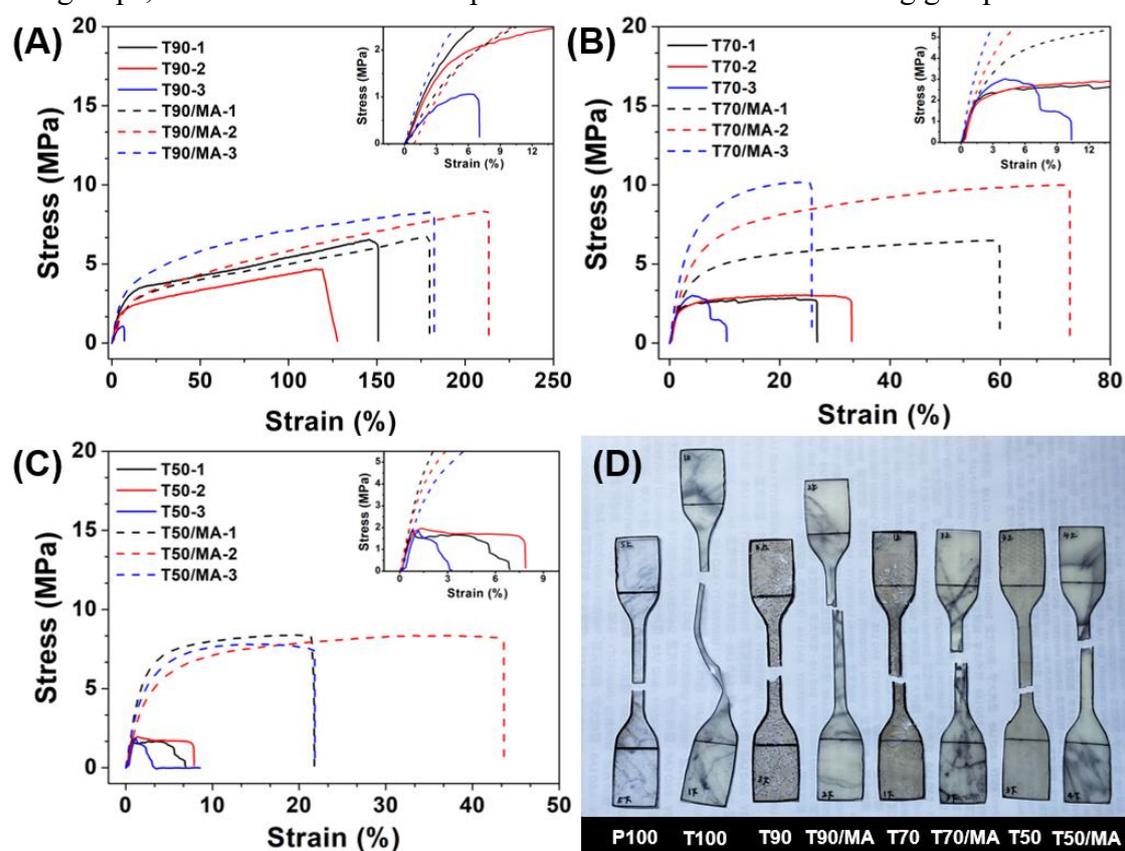


Figure 4-4. Tensile performance of TTPU/PP and TTPU/PP/MA groups as related to the melting–recycling cycles: (A)–(C) stress–strain curves; (D) practical samples after tensile property tests. ** 1: one-off hot-pressing, 2: the post-2nd-recycling, and 3: the post-3rd-recycling.

Figure 4-4(A) and Table 4-2 show that T90 has decreasing tensile strength and strain as a result of the number of melting–recycling cycles, which is opposite to the 5 wt % MA-containing group that shows higher tensile performances. Compared to the post-2nd-recycling group, the tensile strength of T90 in the post-3rd-recycling group decreased by 78.6%, while T90/MA increased by 80.5%. Figure 4-4(B and C) show

that T70 and T50 have a marginal increase in tensile stress and strain when processed with post-2nd-recycling when comparing to first use. The results also show an obvious decrease in tensile stress and strain when processed with post-3rd-recycling. It is surmised that post-2nd-recycling makes thermoplastic polyurethane and polypropylene more evenly blended, but the 3rd time may cause unrecoverable breakage to TPU/PP blends. The insets of Figure 4-4(A to C) show the tensile stress and strain of MA-free groups, which exhibit a drastic decrease as a result of the post-3rd-recycling. Moreover, increasing polypropylene content renders MA-free groups with a more significant differentiation effect that results from higher interfacial tension and poor adhesive performance. In particular, T50 displays the lowest tensile stress and strain, which is attributed to a rather low tensile strain of polypropylene, as well as the most remarkable differentiation effect between thermoplastic polyurethane and polypropylene. In sum, the presence of MA has a positive influence on the tensile properties of TPU/PP/MA blends. From Figure 4-4(B), the tensile strength of T70/MA-3 increased up to 9.2 MPa, and that of T70/MA-2 also reached 9.0 MPa. Figure 4-4(C) shows a slight decrease in tensile strength from T50/MA-2 to T50/MA-3, where maleic anhydride may have a lighter effect when the thermoplastic polyurethane and polypropylene are both half the content of the blends. Applying a maleic anhydride grafted copolymer as a compatibilizer is an efficient strategy in reactive compatibilization for incompatible polymer systems, where the diisocyanate group on the rigid segment of thermoplastic polyurethane reacts with the maleic anhydride group and forms a copolymer layer at the interphase of TTPU/PP during the melting and reheating process, as revealed in Figure 4-5 [4, 35]. It can be found that the mechanical properties of blended thermoplastic materials are improved, even enhanced, with the introduction of an appropriate compatibilizer of proper content [1].

Table 4-2. Tensile stress and tensile strain of post-2nd-recycling and post-3rd-recycling TTPU/PP and TTPU/PP/MA blends.

Post-2nd- Recycling (Groups)	Tensile Stress at Break (MPa)	Tensile Strain at Break (%)	Tensile Stress at Yield Point (MPa)	Tensile Strain at Yield Point (%)
PP100	29.3 ± 0.2	4.3 ± 0.9	31.1 ± 0.2	3.0 ± 0.2
TTPU100	13.7 ± 0.9	280.3 ± 27.3	14.0 ± 1.0	279.2 ± 28.4
T90	4.2 ± 0.5	144.1 ± 25.4	4.4 ± 0.5	139.8 ± 29.9
T90/MA	4.1 ± 0.3	212.4 ± 25.1	4.3 ± 0.3	210.7 ± 26.0
T70	2.2 ± 0.3	21.4 ± 10.2	-	-
T70/MA	9.0 ± 1.3	72.7 ± 7.7	9.3 ± 1.0	70.4 ± 6.2
T50	1.0 ± 0.3	8.9 ± 4.6	-	-

T50/MA	8.0 ± 0.9	39.9 ± 5.3	8.4 ± 0.9	31.2 ± 3.7
Post-3rd- Recycling (Groups)	Tensile Stress at Break (MPa)	Tensile Strain at Break (%)	Tensile Stress at Yield Point (MPa)	Tensile Strain at Yield Point (%)
PP100	23.6 ± 1.4	3.9 ± 0.1	25.1 ± 1.5	3.1 ± 0.2
TTPU100	10.8 ± 0.5	252.1 ± 24.7	11.1 ± 0.6	250.6 ± 26.2
T90	0.9 ± 0.2	7.0 ± 0.04	-	-
T90/MA	7.4 ± 0.5	170.0 ± 23.7	7.7 ± 0.3	167.5 ± 24.8
T70	1.7 ± 1.2	6.6 ± 3.4	-	-
T70/MA	9.2 ± 0.4	29.6 ± 5.2	9.8 ± 0.3	25.2 ± 3.1
T50	0.2 ± 0.2	7.00 ± 1.2	-	-
T50/MA	7.1 ± 0.3	20.9 ± 1.8	-	-

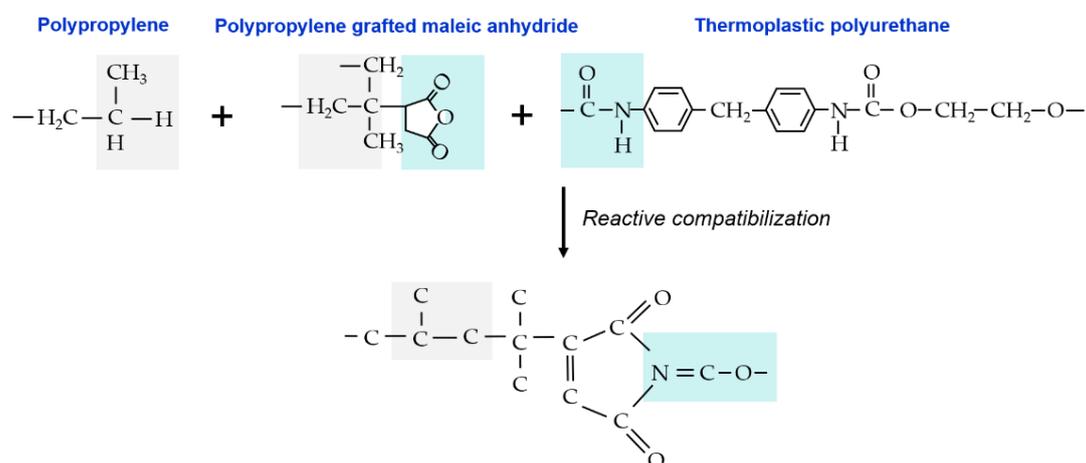


Figure 4-5. The reacted chemical groups in each material during recycling processes.

Table 4-2 summarizes the tensile stress at break, tensile strain at break, tensile stress at yield point, and tensile strain at yield point of the TTPU/PP blends. TTPU100 and PP100 both show a decreasing trend in tensile properties due to the conduct of post-3rd-recycling. PP100 and TTPU100 dropped by 19.4% and 21.2% in the post-3rd-recycling and post-2nd-recycling groups, respectively. Moreover, post-2nd-recycling TTPU/PP and TTPU/PP/MA blends have higher tensile properties than the post-3rd-recycling TTPU/PP and TTPU/PP/MA blends. It is indicated that although polypropylene has better thermal stability than thermoplastic polyurethane, less polypropylene content remains than thermally unstable thermoplastic polyurethane. Hence, the tensile performance of pure material groups become poor after multiple recycling cycles. At the same time, TTPU/PP/MA blends also demonstrate similar improvement. As MA improves the high interfacial tension and low compatibility between thermoplastic polyurethane and polypropylene, which are caused by a polarity

difference, TTPU/PP/MA blends exhibit better tensile properties.

4.3.3. DSC Analysis

With constant pressure, the heat flow (Q) is equal to the enthalpy change (ΔH) as Equation (1).

$$\Delta H = Q \quad (1)$$

The melting temperature (T_m) and melting enthalpy (ΔH_m) for thermoplastic polyurethane are 145.8 °C and 9.7 J/g and for polypropylene 164.5 °C and 92.7 J/g. On the other hand, the crystallization temperature (T_c) and crystallization enthalpy (ΔH_c) for thermoplastic polyurethane are 62.5 °C and 6.2 J/g, and for polypropylene 118.1 °C and 91.3 J/g.

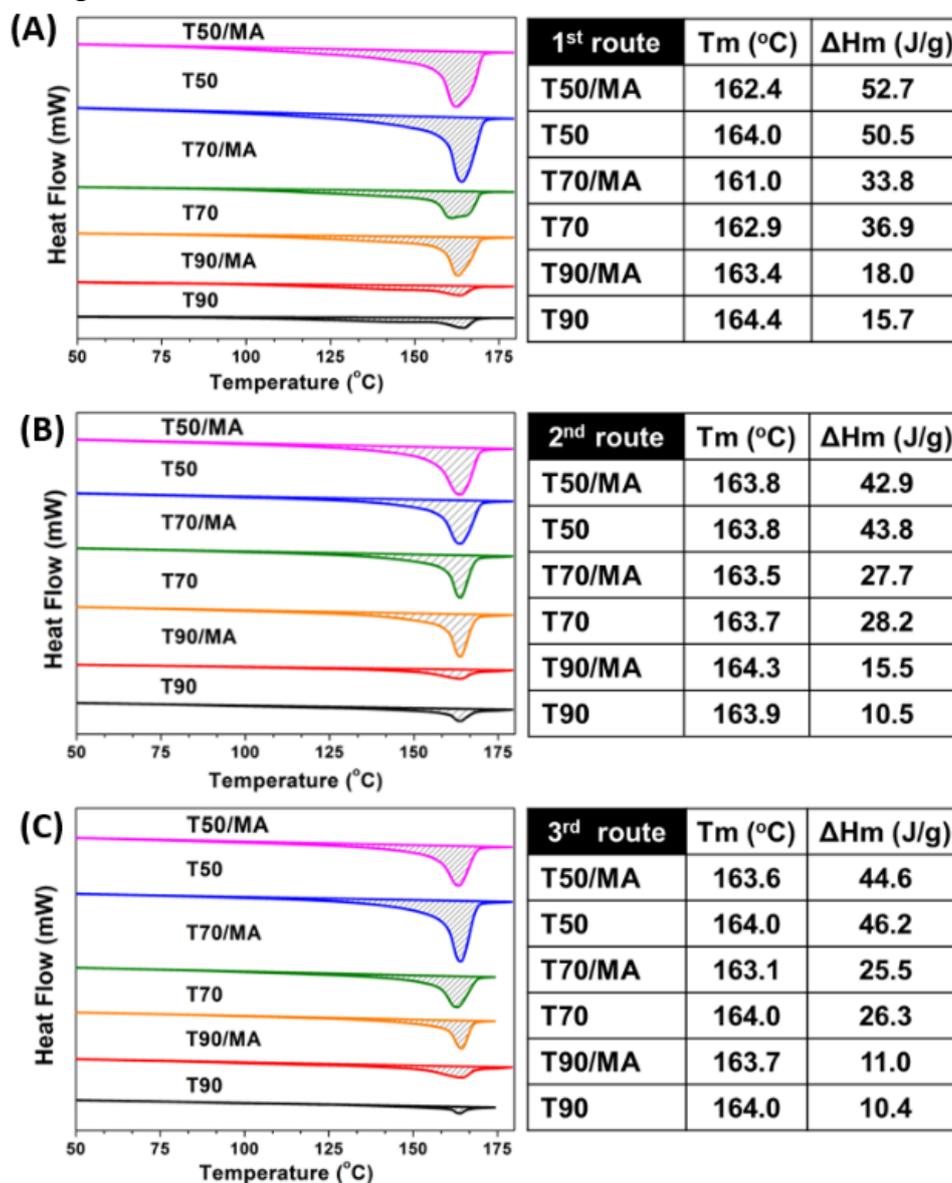


Figure 4-6. Melting behaviors in the differential scanning calorimetry (DSC) performance of T/P and T/P/MA blends as related to melt-recycling: (A) one-off hot-pressing, (B) the post-2nd-recycling, and (C) the post-3rd-recycling. ** T_m = melting temperature and ΔH_m = melting enthalpy.

Figure 4-6 shows the melting behaviors, including T_m and ΔH_m of T/P/MA blends, while Figure 4-7 shows the crystallization behaviors, including crystallization temperature (T_c) and crystallization enthalpy (ΔH_c). Figure 4-6(A to C) show that with a rise in polypropylene content, T50 has the maximal melting enthalpy for polypropylene, which is a semi-crystalline polymer. However, thermoplastic polyurethane is an amorphous polymer, and hence, the yielded maximal melting enthalpy is primarily attributed to the presence of polypropylene. Based on the employment of melt-recycling, the melting enthalpy of samples undergoing one-off hot-pressing (Figure 4-6(A)) is higher than the melting enthalpy of the two batches of samples undergoing post-2nd-recycling (Figure 4-6(B)) and post-3rd-recycling (Figure 4-6(C)). Despite being thermoplastic polymers, both TTPU and PP still trigger a greater number of interactions among molecular chains due to the enthalpy variation. Subsequently, the molecular chains are exerted with influences or even damage, which adversely affects the stability of the entire structure [36].

From Figure 4-7(A and B), the crystallization curves of the T90 and T90/MA groups show small exothermic peaks around 60–70 °C, which are related to the disordered arrangement of rigid segments in thermoplastic polyurethane block copolymers [14]. Figure 4-7(A to C) show that the T90 and T90/MA groups demonstrate insignificant crystallization peaks regardless of whether MA is added. On the other hand, increasing the polypropylene content provides the T70 and T50 groups with increasingly complete crystallization peaks, followed by a rise in crystallization enthalpy. Being an amorphous polymer, thermoplastic polyurethane has rather low intrinsic crystallization behavior. Thus, the deductive comparison confirms that the occurrence of the crystallization peak is owed to the presence of polypropylene. The interactions between polypropylene and thermoplastic polyurethane polymer chains lead to an increment in heat transition. Furthermore, as an increasing consequence of the presence of polypropylene crystallites in the thermoplastic polyurethane matrix, the crystallization rate of the TTPU/PP blended group increases [37]. Moreover, the addition of MA broadens the shapes of both melting peaks and crystallization peaks, which also suggests that either the heating process or cooling process demands more time to melt or generate crystals. In addition, MA-containing blends also have lower melting enthalpy or crystallization enthalpy than the MA-free blends. The urethane groups located in the rigid segment of thermoplastic polyurethane exhibit dissociation, and then have grafting reactions with the anhydride groups of MAs. As a result, the molecular chains from some crystal phases are entangled and, as such, limit the composition of the entire crystals, which eventually interferes with the difference in enthalpy.

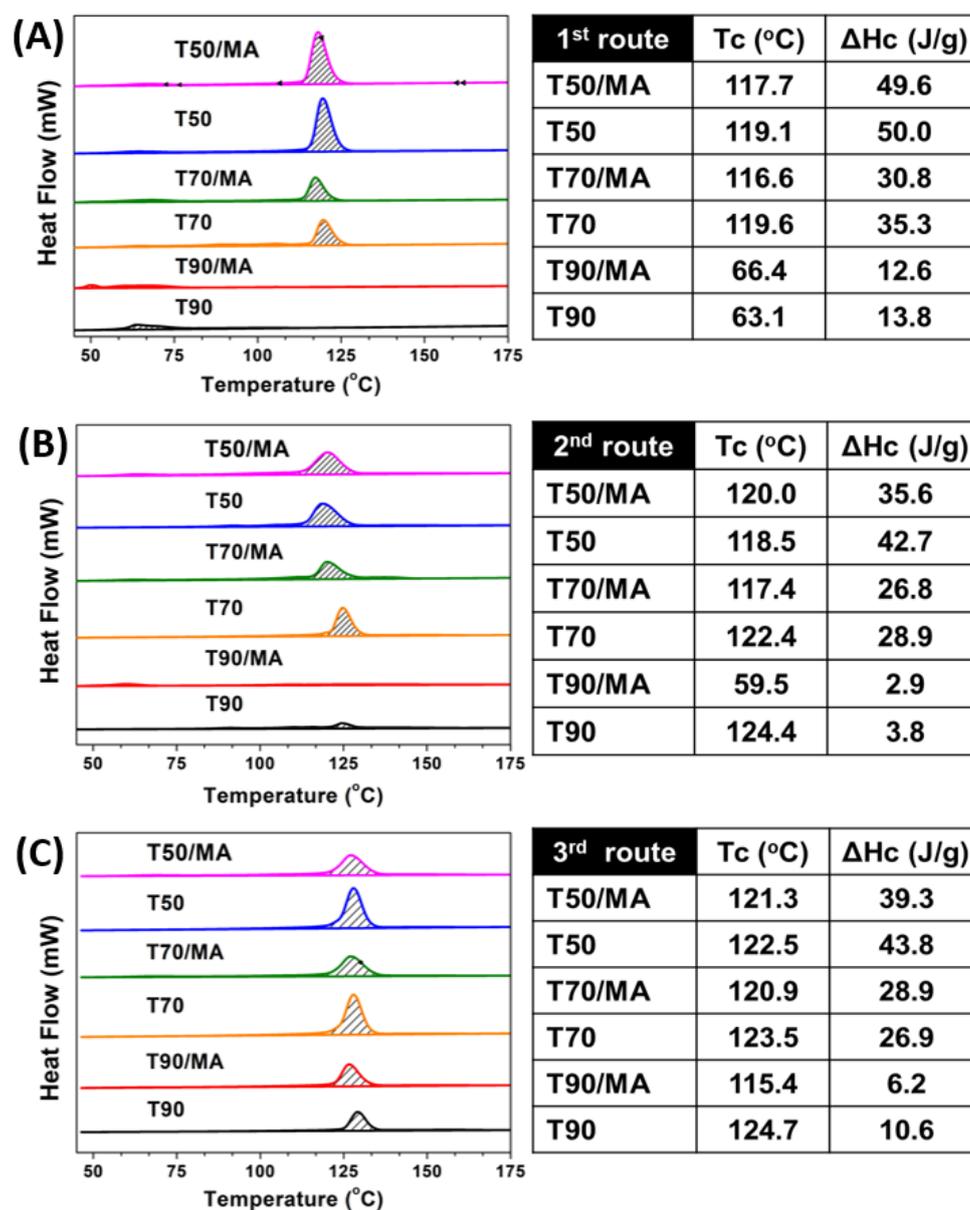


Figure 4-7. Crystallization behaviors in DSC performance of TTPU/PP and TTPU/PP/MA groups as related to melt-recycling: (A) one-off hot-pressing, (B) the post-2nd-recycling, and (C) the post-3rd-recycling. ** T_c is crystallization temperature and ΔH_c is crystallization enthalpy.

4.3.4. Differentiation Effect

The differentiation effect is a quick and easy reference to consider the difference between incompatible or immiscible materials, which is affected by the polarity of each material. In this study, the differentiation effect of TTPU/PP blends, as related to the blending ratios, is examined. Based on the discussion of Sections 4.3.1–4.3.3, a rise in the melting cycles exacerbates the phase separation between thermoplastic polyurethane and polypropylene. When the filler content is less than 50 wt %, that is, the ratio of filler to the total content is close to 0.5, the differentiation effect is

increasingly significant. Namely, the PP/(TTPU + PP) ratio can be used as a reference to determine the differentiation effect with corresponding variations in the ratio. The ratio can be computed with Equation (2).

$$\text{Differentiation effect} = \frac{\text{filler content (\%)}}{\text{total content (\%)}} \leq 0.5 \quad (2)$$

Based on the TTPU/PP ratios, samples can be divided into T90, T70, and T50. The incorporation of MA is precluded from the discussion on the differentiation effect. This equation is exclusively used for two incompatible and immiscible materials. MA is used in this study as a compatibilizer to attempt to mitigate the interfacial tension and phase separation. To sum up, the differentiation effect, from highest to lowest, can be ranked as T50, T70, and T90. Moreover, Figures 4-3, 4-4, and 4-6 indicate that with an increasing number of melting–recycling cycles, phase separation is more distinctive, which suggests that the differentiation effect is intensified.

From Figure 4-8, it is clear to see that the effects of cycling route numbers and composition ratios on each multi-composition group without MA are significant. As the cycling route number increases, T90, T70, and T50 have lower maximum tensile strength, in which T90 in the post-3rd-recycling group has the most obvious diminishment. The significant decreasing tensile strength of T90 results from the enlarging differentiation effect after several subsequent recycling routes, while T90/MA group in post-2nd and post-3rd route has a totally different results. Though T90 has the slightest differentiation effect at first cycle, it still faces some recycling challenges during recycling processes. On the other hand, it is indicated that the maximum tensile strength of T50 is the lowest in the first cycle and doesn't have much significant change in post-2nd and post-3rd cycling routes, in which we may confirm that the differentiation effect of T50 in the first cycle has the most obvious influence. Moreover, Figure 4-8 reveals that the maximum tensile strength of MA-contained groups are all better than these groups without MA, in which MA can mitigate the differentiation effect and improve the interphase problem between TTPU and PP. In the first cycle, the maximum tensile strength of T90 and T90/MA is 6.53 MPa and 6.73 MPa, respectively. In the post-3rd-recycling route, T90 and T90/MA become 1.1 MPa and 8.3 MPa, respectively. There is also the same trend in T70/MA and T50/MA groups. It is proven that the presence of MA has a positive effect during the recycling process.

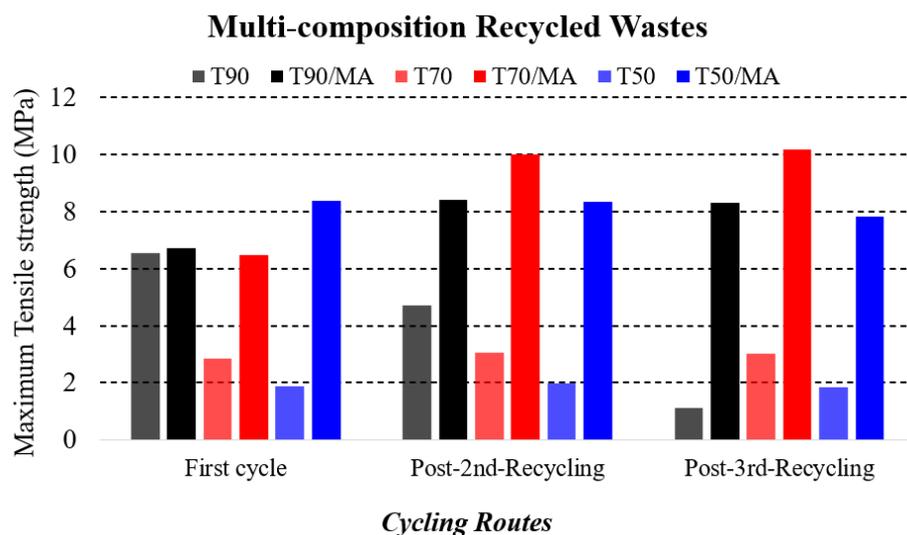


Figure 4-8. Maximum tensile strength of multi-composition recycled wastes in each cycling routes.

Figure 4-9 shows the individual comparing ratio to the 1st cycle of the maximum tensile strength of each group in each cycling route, which the basic comparing standard line is the first cycle set as 100% and the comparing ratio in each group can not be compared to other groups. As shown in Figure 4-9, the comparing ratio of the maximum tensile strength of T90 decreases as the cycling route number increases, which in the post-3rd-recycling group has a rapid decrease to only 17%. It is an unexpected result that T90 has a rapidly decreasing trend in the post-3rd-recycling route, which because T90 has the slightest differentiation effect among the groups without MA at first. As compared to the results of other groups, T90 has the most significant descend trend. It is clearly proven that T90 still has some challenges during the recycling process even it has the smallest differentiation effect value. Except that, T70 and T50 groups have similar results among the three cycles. The reason is that the differentiation effect of T90 becomes stronger after several recycling routes, which also indicates that the interphase problem becomes severe. On the other hand, the MA-contained groups have much more stable results than the MA-without groups. In the post-2nd-recycling route, T90/MA and T70/MA have higher results and T50/MA maintains the tensile performance. In the post-3rd-recycling route, T90/MA and T70/MA maintain the same trends as in the post-2nd-recycling route, while T50/MA has a little bit descend (-7%). It is proven that the presence of MA can help maintain the tensile performance after several recycling routes.

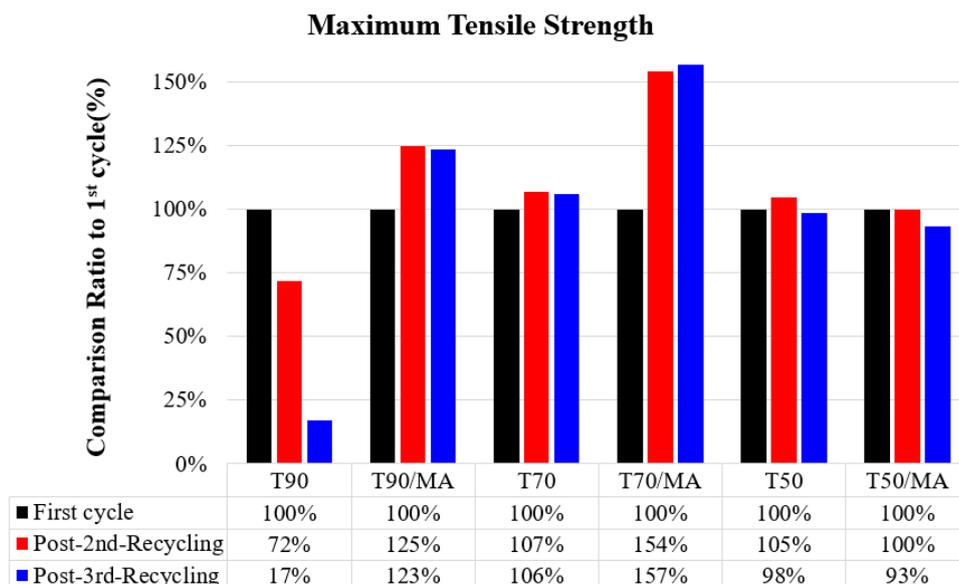


Figure 4-9. Individual comparing ratio to 1st cycle of multi-composition recycled wastes in each cycling routes.

4.4. Conclusions

In this chapter, the recycled TTPU/PP waste compounds are processed with one-off hot-pressing, post-2nd-recycling, and post-3rd-recycling to reform the blends. The TPU/PP/MA blends were tested for tensile properties and thermal performance, as well as observed for morphology, thereby investigating the influences of the number of melting–recycling cycles and the presence of a compatibilizer. In light of the stereomicroscopic images, TTPU/PP/MA blends exhibited a darker yellow shade as a result of increasing the T content. Moreover, on the same premise, with multiple melt-recycling, MA-containing TTPU/PP/MA blends exhibited better integral formability than MA-free TTPU/PP blends and did not have pores or defects. The SEM images showed that the post-3rd-recycling TTPU/PP/MA blends had a higher roughness level than the post-2nd-recycling TTPU/PP/MA blends. In addition, MA-free and MA-containing groups separately exhibited a distinctive and mild differentiation effect. Furthermore, the post-2nd-recycling TTPU/PP/MA blends had higher tensile properties than the post-3rd-recycling T/P/MA blends. The presence of MA addresses the high interfacial tension and low compatibility caused by the polarity difference between TTPU and PP and provides the blends with better tensile properties. The differentiation effect of MA-free blends can be ranked from highest to lowest as T50, T70, and T90, and an increase in the number of melting–recycling cycles concurrently deteriorates the phase separation, which means, equivalently, a worsened differentiation effect. The purpose of this study is to efficiently use considerable waste plastic materials in order to achieve recycling efficacy with added value while sustaining environment protection.

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Chapter 5 – Conclusions

In this dissertation, the main purpose is to investigate the increasing utilization and sustainable development of used plastic materials composed of *multiple components*, which could have positive influences on entire circumstances and mitigate the negative effect of plastic wastes. The study is mainly focused on two parts, one is “Performance Improvement of Recycled Multi-composition Thermoplastic Materials”, and the other is “Effects of Performance Improvement of Recycled Multi-composition Thermoplastic Materials after Cycling Utilization.” In Part I, the multi-composition plastic materials composed of polypropylene and thermoplastic polyurethane, in which the former is the matrix and the latter is as reinforced materials. The mechanical properties, morphology observation, and thermal behaviors of multi-composition materials are all investigated. In Part II, the aim is to further discuss the effect of mechanical fractures and thermal treatments on the recycled multi-composition materials and also investigate the influence of various composition ratios and the presence of compatibilizers on each group, in which the thermoplastic polyurethane is matrix and polypropylene is reinforced material.

In Chapter 1, it comprehensively introduces the background of plastics including the development, types, most-common used ones at first. Secondly, plastic production, plastic wastes, the environmental impact of plastic pollution, current plastic restricting policies are presented. Subsequently, the various recycling processes of plastics, problems, and potential strategies of plastic problems are discussed. At last, the constitutions of the dissertation are individually introduced. In addition, Chapter 2 and 3 are focusing on the performance improvement of recycled multi-composition thermoplastic materials; Chapter 4 is concentrated on investigating the cycling effect of mechanical fractures and thermal treatments on recycled multi-composition thermoplastic materials.

In Chapter 2, the mechanical performance (including tensile, flexural, and impact properties) and morphology observation of multi-composition thermoplastic materials are discussed. This study successfully and efficiently produced and evaluated multi-composition thermoplastic materials composed of polypropylene (PP) and thermoplastic polyurethane (TTPU) using the melt extrusion process and injection molded process. Moreover, it is indicated that a trivial amount of PP-g-MA as a compatibilizer, which efficiently improves the poor interface between PP and TTPU as well as the impact performance of the blends. PP/TTPU blends demonstrated similar impact and flexural properties, which also proved that the intrinsic properties of PP and TTPU did not compromise as a result of recycling the polymers by melt-blending. Hence, the reclamation and sustainability of plastic waste were achieved. On top of that, the PP’s high rigidity and TTPU’s high resilience and tensile properties can be combined to yield the most beneficial reinforcement, thereby providing plastic products

with greater added value and protecting the ecological environment. It is expected to recycle and reuse thermoplastic products via a convenient manufacturing process in order to mitigate the pollution harm to natural environment.

In Chapter 3, the multi-composition thermoplastic materials is as same as that in Chapter 2, which we abbreviated as PP/TTPU blends. The thermal behaviors including (thermogravimetric analysis and differential scanning calorimetry analysis) of PP/TTPU blends are investigated. This study successfully applies an easy, efficient and convenient melt extrusion process to investigate the recycling possibility of PP/TTPU blends for remodeling excess plastic wastes. Also, a compatibilizer-MA is added aiming to improve the inherent weakness and have additional value of the recycled materials. The test results indicate that thermal behaviors, crystallization property, composition, and surface morphology of the composites are not compromised due to the usage of an appropriate amount of TTPU. Based on the results of thermal property tests, it is indicated that PP has reinforced the thermal stability of TTPU, which is also slightly improved when MA is added. Hence, the presence of MA also demonstrates a positive influence on the thermal stability. SEM results show that introducing TTPU causes rougher surface morphology while adding MA has been effectively improving the interfacial compatibility between PP and TTPU, contributing to a greater adhesion level and stress transmission. It is clearly indicated that separated thermoplastic can be assisted under appropriate conditions. Therefore, it is concluded that this easy and convenient process not only can reduce the waste probability of excess thermoplastic materials but also increase the utilization chance of them. Moreover, this study proves a positive effect on the cleaning aspect of our circumstances.

In Chapter 4, the effect of multiple thermal cycles and mechanical fractures on the TTPU/PP blends are discussed. In this study, TTPU is thermoplastic polyurethane and uses T as sample code, and PP is polypropylene and uses P as sample code. Furthermore, the recycled TTPU/PP waste compounds are processed with one-off hot-pressing, post-2nd-recycling, and post-3rd-recycling to reform the blends. The TTPU/PP/MA blends were tested for tensile properties and thermal performance, as well as observed for morphology, thereby investigating the influences of the number of melting–recycling cycles and the presence of a compatibilizer. In light of the stereomicroscopic images, TTPU/PP/MA blends exhibited a darker yellow shade as a result of increasing the T content. Moreover, on the same premise, with multiple melt-recycling, MA-containing TTPU/PP/MA blends exhibited better integral formability than MA-free TTPU/PP blends and did not have pores or defects. The SEM images showed that the post-3rd-recycling TTPU/PP/MA blends had a higher roughness level than the post-2nd-recycling TTPU/PP/MA blends. In addition, MA-free and MA-containing groups separately exhibited a distinctive and mild differentiation effect. Furthermore, the post-

2nd-recycling TTPU/PP/MA blends had higher tensile properties than the post-3rd-recycling TTPU/PP/MA blends. The presence of MA addresses the high interfacial tension and low compatibility caused by the polarity difference between T and P and provides the blends with better tensile properties. The differentiation effect of MA-free blends can be ranked from highest to lowest as T50, T70, and T90, and an increase in the number of melting–recycling cycles concurrently deteriorates the phase separation, which means, equivalently, a worsened differentiation effect. The purpose of this study is to efficiently use considerable waste plastic materials in order to achieve recycling efficacy with added value while sustaining environment protection.

Besides, it is concluded that the addition of compatibilizer significantly helps solve the typical issues – interphase problems resulted from incompatibility and immiscibility between the different plastic materials and thus have a positive contribution to the sustainable development of existed plastic materials and plastic wastes. Not only for the existed plastic materials but also for plastic wastes, the results have indicated the reusing efficiency and possibility in the subsequent recycling process and future applications.

List of Publications

1. Chapter 2 –
Ting An Lin, Jia-Horng Lin, Limin Bao*, Polypropylene/thermoplastic polyurethane blends: mechanical characterizations, recyclability and sustainable development of thermoplastic materials. *Journal of Materials Research and Technology*, 2020, 9(3):5304-5312, <https://doi.org/10.1016/j.jmrt.2020.03.056>
2. Chapter 3 –
Ting An Lin, Jia-Horng Lin, Limin Bao*, A Study of Reusability Assessment and Thermal Behaviors for Thermoplastic Composite Materials After Melting Process: Polypropylene/ Thermoplastic Polyurethane Blends. *Journal of Cleaner Production*, <https://doi.org/10.1016/j.jclepro.2020.123473>. Accept on 2020.07.26.
3. Chapter 4 –
Ting An Lin, Jia-Horng Lin, Limin Bao*, Effect of Melting–Recycling Cycles and Mechanical Fracture on the Thermoplastic Materials Composed of Thermoplastic Polyurethane and Polypropylene Waste Blends. *Applied Sciences-Basel*, 2020, 10(17), 5810; <https://doi.org/10.3390/app10175810> .

Oral Presentations and Award

Oral presentations

1. Ting An Lin, Ching-Wen Lou, Jia-Horng Lin and Limin Bao, Woven Fabric Reinforced Polypropylene/ Maleic Anhydride/ Thermoplastic Polyurethane Composite Boards Made by Sheet Extrusion and Hot Pressing Methods. The Second International Forum on Textiles for Graduate Students (IFTGS), Tianjin China, 2018.09.08-2018.09.11.
2. Ting An Lin and Limin Bao, The Effects of Thermoplastic Polyurethane on the Structure and Mechanical Properties of Modified Polypropylene Blends. 3rd Japan-China Textile & Composite Symposium(JCTCS-3), Wuhan, Wuhan Textile University, China, 2019.09.11-2019.09.13.
3. Ting An Lin and Limin Bao, The effect of different manufacturing processes on tensile properties of metal fabric reinforced thermoplastic composites.. 2019 年度纖維学会秋季研究発表会, Ueda, Shinshu University, Japan, 2019.11.09-2019.11.10.

Award

1. Ting An Lin, Ching-Wen Lou, Jia-Horng Lin and Limin Bao, Presentation award, Woven Fabric Reinforced Polypropylene/ Maleic Anhydride/ Thermoplastic Polyurethane Composite Boards Made by Sheet Extrusion and Hot Pressing Methods. 2018, The Second International Forum on Textiles for Graduate Students (IFTGS), Tianjin China.

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