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POLYMER DEGRADATION AND ENVIRONMENT

TITTLE

RECYCLING PROCESS OF POLYOLEFIN (POLYPROPYLENE)

PREPARED FOR

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1.0 Introduction

Polyolefins are macromolecules formed by the polymerization of olefin monomer units. Polyolefins are the largest class of commodity thermoplastics. They are polymers of simple alkenes such as ethylene, propylene, butenes, and pentenes. Fig.1 shows the two most important polyolefins are polyethylene (PE) and polypropylene (PP). PE are the largest volume polyolefin and have variety of grades. HDPE, LDPE, and LLDPE are few grades of PE. These differ in term of molecular weight, crystallinity (density), and branching. Degree of branching and the polymer molecular weight and its distribution determine the mechanical properties and the melt flow behavior of polyethylene. High molecular weight polyethylene without branching is rather brittle.

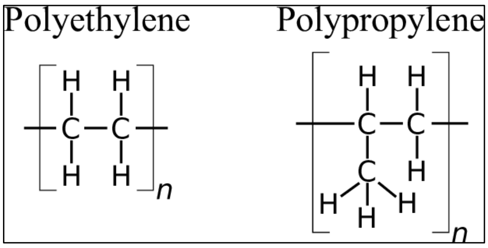

Figure 1 Chemical structure of polyethylene (PE) and polypropylene (PP).

PP is the second largest sales volume commodity thermoplastic. They often have a level of crystallinity between that of LDPE and HDPE. PP's elongation at break is similar to that of LDPE, whereas its impact strength and tensile modulus is closer to that of HDPE. Despite its semicrystalline nature, it is relatively easy to mould. Polypropylene has a lower density than most of the polyethylenes (0.905 g/cm^3) and a significantly higher melting temperature (160 - 180°C) which makes it more suitable for higher temperature applications such as retortable plastic products. However, isotactic-PP has lower impact resistance. To reduce its brittleness, it is sometimes copolymerized with ethylene, which leads to improved toughness and flexibility. Table 1 shows the chemical and physical properties of PP.

Atactic polypropylene is a soft, rubbery polymer, while isotactic polypropylene is strong and hard with excellent resistance to stress, cracking, and chemical reaction. Syndiotactic polypropylene has only recently been made on a large scale. It is somewhat softer than the isotactic polymer, but also tough and clear. Syndiotactic polypropylene is produced on a much smaller scale. It is often less crystalline but has greater clarity, elasticity, and impact toughness. If all the methyl groups lie on the same side of the chain, the polymer is called isotactic. If the methyl groups alternate in a regular fashion from one side of the chain to the other, the polymer is syndiotactic. Finally, if the orientation of the methyl groups is random, the polymer is given the name atactic.

Figure 2 shows waste of PP caps are known for good impact strength, cost effectiveness, light weight among all commodity plastic, pliability, autoclavable and are suitable for many dry products.

Figure 3 Cap of cosmetic product and drinking bottle.

Property	**Polypropylene**
Density	0.895-0.905g/cm^3
Elastic modulus	1.5 – 3 GPa
Impact strength, Charpy notched	2 – 6 kJ/m^2 at 20 °C
Coefficient of thermal expansion	6*10^{-5} – 1*10^{-4} 1/K at 20 °C
Max. service temperature, short	140°C
Melting point	160 – 168 °C
Specific heat capacity	1520 J/(kg.K) at 20 °C
Thermal conductivity	0.41 W/(m.K) at 20 °C
Flammability	UL 94 HB
Dielectric constant	2.8 at 20 °C
Electrical resistivity	1

Table 1 Properties of PP

2.0 Problems on environment that contribute to the waste accumulation of bottle cap

#	Type waste product	Number of items found
1	Plastic & paper: cigarette butts	63.355.828
2	Plastic: sweet, crisps & snack packaging	20.799.315
3	Plastic: caps & lids	20.262.369
4	Plastic: drinking bottles	14.624.693
5	Plastic: cutlery, plates and cups	14.283.883
6	Plastic: bags	12.449.384
7	Glass: bottles	9.265.944
8	Plastic: straws & stirrers	8.858.112
9	Metal: tins	8.576.292
10	Plastic: nets, rope	4.062.673

Table 2 Top 10 items found between 1985 – 2015 during the International Coastal Clean-up.

Plastic caps are used all over the world in all sorts of sectors. Those plastics discarded inland may face burial in terrestrial habitats, whereas those entering wastewater may be transported into aquatic environments. Moreover, despite the fact of increasing cost for landfill, polypropylene cap required a significant amount of time, approximately up to hundreds of year to be fully decomposed (to be determined because polypropylene cap have not existed for long enough) due to its very slow degradation rate. Few effects and problems that causes on the environment that contribute to the waste accumulation of the plastic caps:

2.1 Plastic caps cause harm to marine life

The enormous quantity of plastic in our oceans is hazardous for many species of marine animals. Some of the bottle caps will wash up on beaches, but many will remain floating at sea. Marine mammals, sea turtles, birds and fish can mistake this plastic material for food. More than 690 species ranging from microscopic plankton to whales suffer the negative effects of plastic pollution. Plastic caps are among the top five most deadly ocean trash items (Ocean Conservancy, 2015).

Figure 4 A dead albatross with plastic caps in its stomach.

2.2 The plastic society

Plastic production has skyrocketed over the last few decades, and there is no predicted decrease of this production in the foreseeable future. Plastic has become a part of almost every consumer product. About 311 million tons of plastic is produced worldwide every year. A quarter of this is for packaging purposes. Only 14% of packaging materials are recycled and almost a third leaks into the environment and pollutes our cities, beaches and oceans.

2.3 The costs of cleaning up are not only high, but also hidden

It is difficult to estimate the economic impact of litter in the sea and on beaches because these are made up of direct costs, such as cleaning, and indirect costs, such as damage to ecosystems and the loss of cultural values such as recreation and landscape aesthetics.

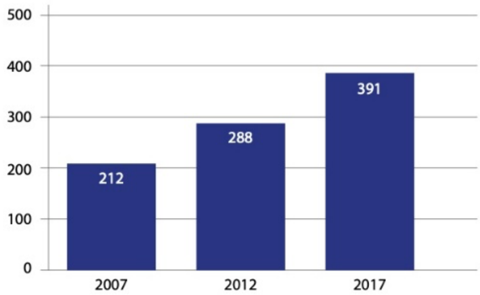

Figure 5 The worldwide consumption of bottled water in billions of litres (Statista, 2016).

In 2012, more than 250 billion litres of bottled water were consumed worldwide. Based on the data in Fig. 5, the forecast is that consumption will exceed 350 billion this year. This will result in an increase of both bottle and bottle cap production.

3.0 Issues arising from the recycling process

The aspects addressed below highlight some issues which may require further consideration and more profound analysis prior to using them as a solid argument to demand for industry action or even novel regulatory acts. They are rather meant to provide additional input for discussion and a new perspective on the role of legacy substances that are of no particular (health) concern but give rise to a number of other consequences for processing and product performance.

3.1 Melting Point

Plastic bottle cap which is made of polypropylene (PP) is one of the plastic product also known as low modulus synthesis fibers that are effectual in controlling shrinkage cracking (Foti, 2011). Polypropylene cap is a hard but flexible plastic while the body of plastic bottle is made from polyethylene terephathalate (PET), a clear tough plastic (Siddique et al, 2008). Unlikely to PET, the polypropylene cap is excluded in the process of recycling bottle due to its high melting point. The difference of polypropylene cap versus polyethylene terephathalate bottle in melting point is approximately 100℃, which dramatically increases the cost of processing polypropylene cap.

3.2 Material Complexity

Colorants and pigments are another important group of additives in plastic bottle caps, as in most other plastic products. However, coloration is a separate processing step that is typically not performed by the resin manufacturer. Color master batches are added to the polymer resins by other members of the bottle cap value chain such as a plastics converter or the brand owner. In short, contrary to the situation of the PET bottle body, it can be argued that there seems to be a material complexity issue with the caps of these bottles. Besides the difference in waste stream magnitude (a typical screw cap of a PET bottle may have a mass of 2 to 3 g, very roughly about a tenth of the respective bottle body), this material's complexity is an additional obstacle hindering effective high-quality recycling of screw caps.

3.3 Cross Contamination

Polyolefin cross-contamination is a common phenomenon in post-consumer plastics recycling, which is by now well documented through analytical work on both waste fractions and actual recyclates. Despite their apparent chemical similarity, PE and PP are immiscible polymers. When mixed together, they develop a heterogeneous morphology characterized by phase separation. As long as the contaminating minor component is present at a relatively low concentration, the effects on thermal behavior (such as crystallization) and simple mechanical properties such as stiffness (E-modulus) are moderate or even negligible. However, the presence of PP in PE-HD was found to influence the deformation behavior and to promote brittle failure.

At higher amounts of cross-contamination, a negative deviation from additive property changes was observed. This means that the blend of PE-HD and PP performs worse than expected from simply adding up the properties of both components multiplied with their respective mass fractions (simple additivity). This could be a major obstacle to utilization in caps and closure applications where toughness is often required. Furthermore, a negative impact on deformation behaviour might lead to significantly reduced performance in more complex and especially long-term mechanical loading cases such as environmental stress crack resistance (ESCR) testing, which is of high relevance for carbonated beverage caps. The presence of polyolefin cross-contamination can hence be regarded as a severe challenge in the pursuit of high-quality and high-value recycling paths for plastic bottle cap materials.

4.0 Recycling process

PP bottle caps go through the recycling process to be reused to produce new products. Caps are usually made of a different type of plastic compare to bottles. Generally, caps are made out of polypropylene (PP) whereas bottles are made out of PET material. There are many recycling methods that can be used to convert the waste PP bottle caps into valuable and useful products. There are four main types of recycling processes: Primary Recycling, Secondary Recycling, Tertiary Recycling and Quaternary Recycling. Before recycling, plastic wastes could be retrieved in two ways: these methods consist of collecting plastics before and after they enter the municipal waste stream. However, most post-consumer wastes end up in the municipal waste stream and usually contaminated and are difficult to recycle economically. Therefore, the wastes are either disposed in landfills or underwent incineration. On the other hand, plastic wastes collected outside the municipal waste stream are relatively clean and can be recycled after undergoing separation, sizing and washing processes (Saddique et al., 2008). Even though bottle caps made with a different type of plastic than the bottles, the caps should be put back on bottles before tossing them in recycling bins or taking them to the recycling center. There are issue arises whether people should have kept the caps on the bottle or not when recycling since it may impose safety risk to recycling workers but this also should depends on the local recycling center.

4.1 Primary recycling

Primary recycling is the simplest, low cost and rapid recycling method for PP bottle cap wastes where used drinking bottle is washed and reused again to approximately the same function as the original product. This recycling process also refers to the reuse of products in their original structure. In addition, this PP bottle cap with variety of colours can be reused and crafted to become beautiful home decorative items.

4.2 Secondary recycling

Secondary recycling which is also called mechanical recycling is the most common method used in the recycling industry. Mechanical recycling of plastics refers to processes which involve sorting, size reduction, washing, melting or granulation of plastics wastes. In this recycling process, only thermoplastic polymers like polypropylene, polyethylene, etc can be used because they can be re-melted and reprocessed into end products unlike thermoset polymers. The mechanical recycling does not involve the alteration of the polymer during the process. As mentioned earlier, this process is a physical method in which plastic flakes, pellets or granules is formed and then melted to form new product by either extrusion, injection molding, etc. Normally, the reprocessed plastic material is blended with virgin material to obtain good product properties. Generally, the stages of the recycling process are as follow; collecting, sorting, shredding, washing, and drying the plastic waste to be reprocessed into recycled plastic pellets, granules or flakes. It is applicable for the mechanical recycling of polyolefin (PP) and most of the thermoplastics.

4.2.1 Collecting

The drinking bottle wastes can be collected through various ways such as landfill, curbside collection and local recycling center. These are then sent to the recycling plant for identification and sorting. Bale opening might have needed if bales are collected.

4.2.2 Shredding

Shredding is one of the mechanical size reduction techniques in which the size of the plastics waste is reduced using a cutting action so that it can be fed into extruder, for reprocessing. The size of shredded plastics is from 5 to 10 mm. Plastics are shredded by the mechanical action produced between the rotor knives and a fixed counter knife in the presence of water. Wet shredding is preferred as the water in the washing granulator can reduce friction and heat generated during cutting which act as a direct cooling agent to prevent thermal stress and thermal degradation from experienced by the plastic wastes. At the same time, this method also helps to prevent any contaminants and dirt from adhering to the plastic. Wet shredding also can increase blade service life since water is washing and flushing the contaminants away from the product before granulating (Noel et al., 2017).

4.2.3 Sorting

The shredded plastics are then taken for sorting. Plastic wastes identification and sorting process is important to prevent any contamination in the recycled PP. The resin identification code on the plastic waste (PP bottle cap) is very useful when manual sorting is carried out. Besides that, more efficient identification and sorting techniques of plastics is density separation method. In float-sink separation method, it's based on the density of polymer; PP (0.90-0.91g/cm^3) and PE (0.91-0.94g/cm^3 for LDPE and 0.94-0.97 g/$cm^3$for HDPE) will float while other polymers such as PET (1.38-1.41 g/cm^3) will sink when water with density of 1.00 g/cm^3 is used as density separation fluid. The mixture of floating PP and PE wastes are further separated by using low density separation fluid of ethanol or water mixtures. PP will float since its density is lower than that of the mixture whereas PE will sink. Float-sink density method is used because it's a simple and direct method. However, density is the critical element and has to be determined precisely in this method.

4.2.4 Cleaning

After the sorting process, the shredded PP bottle cap waste which previously might have been contaminated will then enter the washing line for cleaning process. The shredded PP wastes are conveyed through a friction washer for cold water cleansing to remove light contaminants. Furthermore, the PP flakes are soaked in a mixture of hot water washing solution followed by a friction washer where the material is rinsed to ensure optimum cleaning effect.

4.2.5 Drying

The next step is followed by drying the material by hot air using a thermal dryer. The PP flakes must dry thoroughly since reprocessed PP flakes with water content inside will leave defect of air bubbles in the final product which is not desirable.

4.2.6 Melting and pelletizing

PP flakes are then reprocessed by melting at temperature above 250°C in an extruder to get rid of contamination molecules or substances through melt filtration process. The extruded or filtered PP material then passes through a series of screens or pelletizer to form pellets. Recycled PP normally mixed with virgin PP at certain proportion to produce new products such as car battery casing, storage container and bottle caps by using injection moulding process.

4.3 Tertiary recycling

Tertiary recycling is a widely used recycling process and produces chemical and fuels from waste plastics by means of chemical treatment or also called chemical recycling. Chemical recycling is defined as the process in which polymers are chemically converted to monomers or partially depolymerized to oligomers through a chemical reaction (a change occurs to the chemical structure of the polymer). The resulted monomers can be used for new polymerizations to reproduce the original or a related polymeric product. This method can transform the plastic material into smaller molecules, suitable for use as feedstock material starting with monomers, oligomers, or mixtures of other hydrocarbon compounds (Francis, 2016; Olah et al., 2008). The chemical reactions used for decomposition of polymers into monomers are hydrogenation, glycolysis, gasification, hydrolysis, pyrolysis, methanolysis, chemical depolymerization, thermal cracking, catalytic cracking and reforming, photodegradation, ultrasound degradation, and degradation in microwave reactor (Grigore, 2017).

Thermal cracking of PP is usually carried out either in high temperatures (>700 ^{o}C), to produce an olefin mixture (C_1–C_4) and aromatic compounds (mainly benzene, toluene and xylene) or in low temperature (400–500^{o}C) (thermolysis) where three fractions are received: a high-calorific value gas, condensable hydrocarbon oil and waxes. The aim of this method are mainly to maximize the gas fraction and to receive the olefins, which could be used after separation as monomers for the reproduction of the corresponding polyolefins. The gaseous fraction can be used for the supply of the energy required for the pyrolysis after burning. The liquid fraction mainly consists of linear olefins and paraffins with C_{11}–C_{14} carbon atoms with only traces of aromatic compounds (Aguado, 1999). Thermal cracking of PP proceeds through a random scission mechanism in four steps: initiation, depropagation, inter- or intra-molecular hydrogen transfer followed by b-scission and termination. In general, thermal cracking is more difficult in HDPE followed by LDPE and finally by PP (Aguado, 1999). However, due to the low thermal conductivity of polyolefins together with the endotherm of cracking, thermal pyrolysis consumes large amounts of energy. Thus, catalytic technologies have been proposed to promote cracking at lower temperatures, resulting in reduced energy consumption and higher conversion rates.

4.4 Quaternary recycling

Quaternary recycling or energy recovery process refers to the recovery of the plastic's energy content. The most effective way to reduce the volume of organic materials which involves the recovery of energy which is represented by incineration. This process involves incineration of plastic wastes at very high temperatures of up to 900 to 1000^{o}C. The leftover materials from this recycling process are sent to landfills. This method is a good solution because it generates considerable energy from polymers, but it's not ecologically acceptable because of the health risk from airborne toxic substances. These processes are highly toxic and environmentally unsafe. They lead to high levels of air pollution and emission of harmful gases. For example, dioxins in the case of heavy metals, chlorine-containing polymers, toxic carbon, and oxygen-based free radicals. Moreover, burning of plastics are banned in most of the developed countries. Thus, this type of recycling process is very rare and aren't considered as true recycling.

Among all the recycling processes mentioned above, the most attractive recycling method is secondary recycling or mechanical recycling as this recycling technique is in accordance with the principles of sustainable development, practical and cost-effective compared to the tertiary recycling and quaternary recycling method. According to this method, waste polymers in which PP bottle caps are collected, shredded, sorted using float-sink separation method, cleaned, dried, reprocessed and pelletized to form pellets. These pellets are then re-melted and reprocessed to form new end products as such vehicle battery casing. Others recycling techniques are unfavourable due to the following reasons. Quaternary recycling or incineration meets with strong societal opposition and not ecologically acceptable whereby tertiary recycling or chemical recycling are not worth the trouble since it needs extra labour and quite expensive in terms of cost since the desired new end products are only vehicle battery casing.

5.0 Final product and environmental analysis

One of the most significant advantages of recycling polypropylene is that it reduces the demand for plastics production. Fig. 6 shows the percentage of energy saved by recycling compared with raw material usage. When recycled polypropylene are used to produce goods that would otherwise have been made from new (virgin) polymer, it will reduce the oil usage and emissions of greenhouse gases associated with the production of the virgin polymer. These avoid the environmental damage caused by drilling for petroleum. Recycling and remanufacturing are 194 times more effective in reducing green-house gas emissions than landfilling and virgin manufacturing.

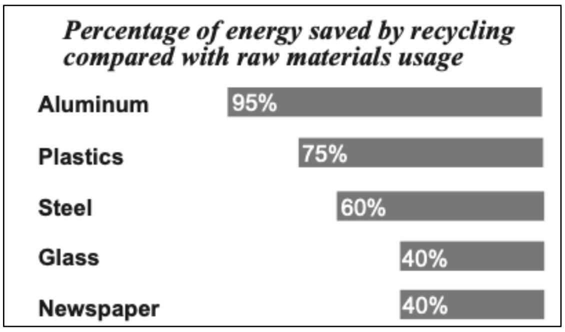

Figure 6 Percentage of energy saved by recycling compared with raw materials usage.

However, each piece of recycled plastic represents a variety of possible environmental concerns, which we must not overlook. During the melting and recycling of plastic, volatile organic compounds (VOCs) are created, and these gases can harm plant and animal life near the industrial site. Although we mentioned that recycled polypropylene can reduce the emission of greenhouse gases. The heat required to melt plastic will still emits carbon dioxide, a greenhouse gas that contributes to global warming. The same VOCs that cause plastic recycling to harm the environment can also present health threats to the people who come into contact with recycled plastics. Plastic resin, which is will be use as a part of the manufacturing and recycling process, derived from petroleum, can leach into foods stored in recycled plastic containers.

Much plastic recycling is actually downcycling due to the potential health threats recycled plastic poses. This means that instead of becoming another new bottle caps, the recycled polypropylene will become a different, less useful product. However, it is possible to make the original product using recycled materials, provided there is a mix of recycled plastics with new, virgin materials. The limited utilisation of recycled plastic places it at a disadvantage compared to new plastics and other recycled materials.

Polypropylene is strong than polyethylene and is used for packaging medicine, yogurt, ketchup, beverage, etc. Plastics made of polypropylene have no harmful substances and like polyethylene, polypropylene are considered safe for humans as packages for food and beverages is one of the biggest culprits. As it is difficult and expensive to rid recycled polypropylene of the smell of the product it housed in its first life. Some scents are particularly offensive and the recycled polypropylene ends up black or grey, which makes it tough to reuse in packaging. As a result, it frequently ends up hidden away from the consumer's eye inside park benches and auto parts.

In order to optimise the quantity of recycled plastic we can utilise and to assure the safety and cleanliness of our products for our customers, we cannot sell packaging product that is in grey or black. During the recycling, the molten polypropylene will forced through an extruder, which produces small, homogeneous plastic pellets. The recycled polypropylene pellets will be repurposed into vehicle battery cases (as shown in Fig 7). Polypropylene are frequently used in the production of vehicle battery cases due to its light weight, excellent impact strength, chemical resistance, and quick moulding capabilities.

Figure 7 Vehicle battery cases.

6.0 Conclusion

In conclusion, polypropylene is an economical material, which can be seen in every industrial and commercial application area today. Those include the automotive sector, textiles, medical sector, consumer goods, flexible packaging, rigid packaging, piping, food containers and industrial applications. Polypropylene's unique qualities and ability to adapt make it suitable for an extremely wide range of applications. Its chemical resistance makes it useful as a material for solvent containers.

7.0 Reference

Francis, R. (2016). Recycling of Polymers: Methods, Characterization and Applications; John Wiley & Sons: Hoboken, NJ, USA,.

Grigore, M. E. (2017). Methods of recycling, properties and applications of recycled thermoplastic polymers. *Recycling*, *2*(4), 24.

J. Aguado, D.P. Serrano, in: J.H. Clark (Ed.), (1999). Feedstock Recycling of Plastic Wastes, The Royal Society of Chemistry, Cambridge.

Noel, D. S., Gedricj, P., Amith, A., Joshwin, S., Dean, F., Joshua, F., Gilson, F. & Glen, . (2017) Fabrication of a Washing and Shredding Machine for Processing of Commingled Waste Plastics. Journal of Mechanical Engineering and Automation, 7(4), 119-123.

Olah, G.A.; Goeppert, A.; Prakash, G.S. (2008). Chemical recycling of carbon dioxide to methanol and dimethyl ether: From greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons. J. Org. Chem. 74, 487–498.

Saddique, R., Khatib, J. & Inderpreet, K. (2008) Use of recycled plastic in concrete: A review. Waste Management, 28, 1835-1852.