Multi Client Study Presentation

Plastics Recycling and the Circular Economy: Catalytic and Compatibilization Solutions

Study Completed: June 2020
Some Background Provides Justification for Study Subscription…

An intense global R&D effort is being undertaken by plastics producers, industry consortia and academia to understand and appreciate the hurdles to overcome and to economically resolve a serious challenge in the recyclability of plastics, which has taken center stage in a global debate on plastic waste.

This TCGR Multi Client Study is designed to assist the plastics and polyolefins industries to identify new pipeline technologies and strategic commercial directions which will help speed up the resolutions to these challenges in an economical way.

- This 156 page study was launched in December of 2019 and completed in June 2020. The study’s scope and specific contents reflect inputs from a group of “charter” subscribers who, prior to study launch, indicated their priorities for coverage, areas to be expanded/deepened and focal points for emphasis in opportunity identification.
- TCGR’s study allows plastic resin and technology developers, as well as the industries and customers served by them, to make an independent judgement on the options going forward and what is needed in order to maintain long-term viability in these increasingly competitive times.

We estimate that in the year 2020 the annual production of all plastics will be 435 million metric tons (MMT), and by 2050 will reach one billion metric tons
The Study is Unique in Its Objectives, Scope and Methodology…

- **Background**
  - This TCGR Multi Client Study is designed to document the need for optimization in plastics recycling today which represents a tremendous amount of value that local economies fail to capture, globally estimated to be $100 billion.
  - In many countries, both in the developed and developing world, recycling rates of plastic are too low, and the processes used are too uneconomic to make increased use of recycled plastic.

- **Objective**
  - Address the current state-of-art (SoA) in technology and commercial development, identify and address progress towards viability in two promising approaches — catalytic and compatibilizer technologies — and provide strategic guidance on the competitive landscape and future investment.

- **Scope**
  - Three main technology thrusts that are part of the solution to this challenge: process, catalysis and compatibilizers in commercial activities and early stage R&D endeavors.
  - A visionary, industrial oriented Technology Roadmap for the next 5-10 years that concentrates R&D and commercial development efforts to speed up deployment, improving both efficiency and effectiveness of implementation, particularly in mixed plastic waste.

- **Methodology**
  - TCGR utilized publicly available and in-house information and expertise collected over 35+ years in the plastics industry to assist plastic resin and polyolefin technology developers.

The study’s scope/TofC, on the following two pages, reflects inputs from “charter” subscribers, industry leaders in plastics recycling, process development and resins supply.
The Study’s Table of Contents Provides an Indication of Areas of Focus/Detail

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The quality of the recycled plastic will determine its use. Primary and secondary (mostly mechanical) methods produce generally lower quality material than the virgin plastic.

Certain applications, especially packaging in the beverage, food, and pharmaceutical industry demand quality nearing that of the virgin plastic.

The most attractive method currently is chemical depolymerization, since it produces virgin material, but today it can only be applied to limited types of plastics like polyethylene terephthalate (PET) and polystyrene (PS).

There are four types of plastics waste recycling:

- Primary (reuse for the same purpose)
- Secondary (use other than the original)
- Tertiary, Chemical or Thermal Depolymerization (recovery of starting materials/monomers)
- Quaternary or Energy Recovery (pyrolysis, hydrocracking, gasification)

As the production and application of plastics accelerated at an astonishing cumulative annual rate of 8.5%, so did the accumulation of plastic waste, creating a universal pollution problem for mankind.
An Indication of the Study’s Value Can Be Seen in Sustainability & Circularity…

All stakeholders are starting now to concentrate on some broad, interdependent action areas to create a circular economy, starting from plastic packaging. Drivers of this change are the wide plastics waste concern, the regulatory pressure, the brands commitment to use incremental amounts of recycled plastics in their produced goods, and the 2018 China ban on polymer waste import. Plastics stakeholders have directed their efforts to find solutions in:

- Rethinking plastics design & use by industrializing new compatibilization solutions or reducing complicated multi-layered structures into simpler ones; brands try to use less plastic, more PCR or alternative materials
- Exploring radical and innovative approaches to circular economy by applying new business models (e.g. plastic producers sell PCR grades in cooperation with recyclers; brands experiment reusable packages and refill/re-use containers), and developing new recycling technologies (e.g. producers cooperate with recyclers and technology enablers to industrialize chemical recycling technologies/infrastructures)
- Driving a systemic change in circular thinking at industry level by working with the Ellen MacArthur Foundation, UN and other platforms and governments to create an environment that enables the creation of a circular economy, including the necessary infrastructures and regulations.
An Indication of the Study’s Value Can Be Seen in Impacts from Regulatory Approaches

The current management of plastic wastes is a complex mosaic: waste management is extremely variable from country to country.

- Developed countries with regulations (e.g. Western Europe and Japan) can attain recycling rates in the order of 30% while the rest go to incineration or landfills.
- Developed economies without regulatory incitement (e.g. USA and Australia) possess similar characteristics, but less than 10% of plastic waste are recycled locally.
- U.S. State legislatures have considered a number of measures to reduce the plastic bags at grocery stores and other businesses. Some states are focusing on implementing effective recycling programs, others are imposing bans or fees to discourage the use of plastic bags altogether.
- In industrialized developing economies (e.g. China, India and Brazil) waste collection is not systematic, a large portion of household and industrial waste continues to be dumped at numerous informal and unregulated sites and recycling rates are in the order of 20%.
- The European Union (EU), in addition to the previous ban of non-degradable carrier bags, implemented in March 2019 a ban on single-use plastics such as cotton bud sticks, cutlery, straws, stirrers and plates by 2021.
- India announced at the beginning of 2020 a plan to eliminate single-use plastics within three years.
- Japan has committed to a less ambitious 25% reduction in single-use plastic by 2030.
Technological Advances, both Thermal and Catalytic, are Yielding Improvements in Polymer Recycling

- Chemical recycling of polymer waste via depolymerization of polymers to monomers or other small molecules such as BTX aromatics is already being piloted using known catalysts and infrastructures. These processes generate chemical feedstocks and/or liquid fuels that can be used as direct replacements in existing downstream processes.
- Some innovative processes combine thermal and catalytic steps, or multiple catalytic steps, to improve yields and obtain new reaction products. Since polyolefins are not naturally biodegradable, biological transformations tend to be very slow but new enzyme development is underway.
- Pyrolysis is today the most common approach to chemical recycling of polymers, with companies such as GreenMantra, Plastic Energy, SABIC, and Nestlé, as well as many others, proposing solutions.
- These solutions range from relatively simple, one-stream processes like those proposed by GreenMantra, to complex, multi-stream/multi-product processed like those proposed by SABIC.

Mechanisms of waste HD-PE plastic using pyrolysis-catalytic cracking over CuCO3. Source: Singh et al., 2018

Catalytic pyrolysis is the most widely investigated chemical depolymerization approach and the least sensitive to impurities, but catalyst stability, product separation, and process economics are on-going challenges.
Advances in Catalysis for Plastics Recycling Apply to Established Processes…

- **Hydrocracking**: conversion of PE to liquid n-alkanes in high yield (>99%) and a relatively narrow weight molecular weight distribution (Đ ≈ 1.1) by hydrocracking with 170 psi H₂ at 300 °C under solvent-free conditions by PtSrTiO₃ catalysts. The SrTiO₃ support was proposed to stabilize the dispersed Pt via nanoparticle-support interactions that minimize sintering under the reaction conditions.

- **Alkane Metathesis**: Low-value short alkanes (for example, petroleum ether) were used as cross-metathesis partners to decrease the molecular weight of polyethylene and to convert it into useful liquid fuels and waxes via tandem catalytic cross-alkane metathesis under mild conditions, the process uses an Ir-pincer complex as the alkane dehydrogenation catalyst and Re₂O₇/Al₂O₃ as the olefin metathesis catalyst.

- **Oxidative Depolymerization**: a microwave-assisted process for recycling LDPE waste into value-added chemicals such as dicarboxylic acids in the presence of nitric acid as both catalyst and oxidizing agent. LDPE was converted mainly to dicarboxylic acids in 71% yield with a carbon efficiency of 37% after just 3 h at 180 °C.

This report details these and other catalyst advances which are now bearing fruit and require further assessment.
Technology Advances in Plastics Recycling: Polyolefin Copolymers Compatibilization

PO copolymers can be random, block or graft copolymers and usually have at least some ethylene (Et) and/or propylene (Pr) content along with other olefinic monomers. Examples studied in this report include:

- **ExxonMobil** has produced Vistamaxx™ isotactic polypropylene with random ethylene content for decades for compatibilizing mixed PE and PP recycle streams.

- **Equistar** discloses in a recent patent application compatibilizer compositions useful in compounding polypropylenes and ethylene elastomeric copolymers for injection molding applications; also disclosed is a PP-rich blends for automotive parts requiring impact resistance.

- **Dow Chemical** has also been actively researching compatibilization of polyolefins.

- **Cornell University** have disclosed in a patent application and two publications the development of alternating block copolymers containing PE and PP blocks; has been demonstrated to compatibilized blends of PE and PP; PE can be HDPE or LDPE.

*PE/PP blend compatibilized with alternating PE/PP block copolymer has smaller discrete phases and improved tensile strength and elongation.*

Source: Eagan, 2017
Technology Advances in Plastics Recycling: Functionalized Polyolefins 
Compatibilization

Several companies have developed and sold functionalized polyolefins for decades. With the emphasis on using recycled resins, often with mixed composition, this research has resulted in new commercial products in the past two to three years:

• **Arkema’s Lotader®** ethylene/acrylic ester/maleic anhydride terpolymer blend ratios for PET/PE, PA/PE, PA,PP, PLA/PP and PLA/PE

• **Dow’s** functionalized polyolefins functionalized **Fusabond®** maleic anhydride functionalized polyolefins and **Elvaloy®** methyl acrylate are useful for compatibilizing PA/PE, PET/PE and PE/EVOH recycle waste streams

• **Braskem** disclosed using a functionalized polybutadiene (PBd) resin for compatibilizing a PA rich blend with PE. The PBd functionalizing agent is one of an acrylic ester such as butyl or ethyl acrylate, glycidyl methacrylate or maleic anhydride

• **Toyota Boshoku Kabushiki Kaisha** studied LLDPE/PA11 blends using a compatibilizer that is an acid-, epoxy-, or oxazoline-modified elastomer.

• **Sabic** utilizes ethylene copolymerized with acrylic acid, methacrylic acid, maleic acid, maleic anhydride and esters to compatibilize blends with greater than 75% polyester and also containing 5-22.5% polyolefin

Reactive and non-reactive compatibilizer technologies have advanced to the point where they can be the most economic solution for recycling plastics. New compatibilizer technologies from Lushan, Ken-Rich, and others for recycling are covered in this report.
Conclusions and Recommendations

As with every TCGR Multi-client study, readers will benefit from our analysis of the latest technology advances. Some highlights from our conclusions and recommendations include:

- Pyrolysis or gasification is capable of treating most plastics without segregation, but at the expense of a high cost of energy.
- Depolymerization of PET and PS are at the early stages of commercialization; the next few years will determine the success of these techniques and subsequently the ability of those plastics to be a part of a circular economy.
- Catalytic depolymerization to recover the constituent monomers, purification, and repolymerization could be the basis for a circular polymer economy.
- For blends of polyolefins with non-polyolefins such as polyesters, polyamides and EVOH, polyolefins and polyolefin copolymers are functionalized, most often using maleic anhydride (or maleic acid), acrylic ester or glycidyl methacrylate.
- Challenges common in compatibilization is overcoming the strong immiscibility of different plastic types found in waste material and most recyclers are not able to understand the chemistry to adjust to these moving targets within the field.

In addition to being a critical environmental problem, the lack of recycling represents a tremendous amount of value that local economies fail to capture, which is globally estimated to be $100 billion.
TCGR Experience and Qualifications

- TCGR has leveraged its access to experts that have a mix of technical and commercial experience in the plastics industry via its Dialog Group® in completing this study.
- TCGR has utilized publicly available and in-house information to complete the deliverables as well as patent searches, technical literature reviews, and in-field interviews.
- TCGR Dialog Group® experts have deep experience in the required technology from a process technology, catalyst technology and market size & growth application perspective.

The Catalyst Group Resources has covered related technical process advancements in similar reports; those can be seen here on our website. Other advancements are also tracked as part of our Catalytic Advances Program and CO₂ Capture and Conversion Program.

The Dialog Group® is a renowned group of industry-leading experts that provide key intelligence and analysis of the plastic resins and plastics recycling industries.
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