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Catalytic and compatibilization solutions for plastics recycling

A study completed in 2020 by The Catalyst Group Resources analyzes catalytic and compatibilization solutions for plastics recycling and the circular economy.

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January 13, 2021



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Plastics

International Recycling News

The Catalyst Group Resources (TCGR), a global consultancy based in Spring House, Pennsylvania, released a study in the summer of 2020 that looks at catalytic and compatibilization solutions for plastics recycling and the circular economy. The study's scope and specific contents reflect inputs from a group of "charter" subscribers who indicated their priorities for coverage, areas to be expanded and focal points for emphasis in opportunity identification. These are leading industrial developers, suppliers and end-users of technologies and plastics resins addressing recycling and the circular economy. TCGR reports that its **multiclient study** was launched in December 2019 and completed in June 2020.

A research and development effort is being undertaken by plastics producers, industry consortia and academia globally to understand the hurdles to improve plastics recyclability, which has taken center stage in a global debate. It is hoped that this will transform the way plastic products are designed, used, produced and recycled in the EU and in other parts of the world. China, the U.S., western

Europe and other regions are pressing for sustainable solutions to plastic recycling and a drastic reduction of plastic waste in the environment. The study addresses technologies and commercial development, identifies and addresses progress toward viability in two promising approaches—catalytic and compatibilization approaches—and provides guidance on the competitive landscape and future investment.

According to TCGR, its report defines “the challenge” from a market statistical basis as well as the current plastics industry’s recycling status. It also addresses new pipeline technologies for different segments (e.g., polyethylene terephthalate, polyolefins, mixed plastics) that are likely to be the best directions for producers and industry to pursue economically. It also provides insights on what plastics producers currently think about these challenges and their plans to address these issues. TCGR adds that its report looks at what country, regional and global regulations will affect plastics recycling, as well.

Challenges

As the production and application of plastics accelerated at an astonishing cumulative annual rate of 8.5 percent, so did the accumulation of plastic waste, creating a universal pollution problem for mankind. The problem has reached critical proportions, and solutions must be undertaken immediately, TCGR says. It is estimated that 435 million metric tons of plastics were produced in 2020, with that figure reaching 1 billion metric tons by 2050. The problem with plastic lies not in how it is used, which is generally harmless, but in the end-of-life management of products made from it, the report notes.

It is projected that the rate of virgin polymer production may start declining by 2040, though this rate will be affected by population growth. Older methods of disposal, such as incineration or pyrolysis, are no longer acceptable in light of tightening emissions and CO2 regulations, as well as greater societal recognition of the environmental cost of these disposal methods, TCGR says.

There are four types of plastics recycling:

1. primary (reuse for the same purpose);
2. secondary (for use other than the original);
3. tertiary, chemical or thermal depolymerization (recovery of starting materials and monomers);
and
4. quaternary or energy recovery (pyrolysis, hydrocracking and gasification).

Primary and secondary (mostly mechanical) methods produce generally lower quality material than virgin plastic. The most attractive method is chemical depolymerization because it produces virgin material, but today it can only be applied to limited types of plastic, such as polyethylene terephthalate (PET) and polystyrene, according to the report.

Presently only a small fraction of plastics is recycled—below 5 percent in underdeveloped countries and up to 30 percent in some developed countries. 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. Catalytic pyrolysis, hydrocracking, alkane metathesis and oxidative strategies have been used for polyolefin depolymerization. The catalyst decreases the reaction temperature, enhances the depolymerization efficiency and increases selectivity, TCGR says.

Catalytic approaches to plastics recycling

Catalytic routes and compatibilization routes to plastic recycling also are possible.

Catalytic depolymerization is one way in which chemical recycling of polymers via depolymerization of polymers to monomers or other small molecules, such as BTX (mixtures of benzene, toluene and the three xylene isomers) aromatics, is being piloted using known catalysts and infrastructures. Chemical recycling can in principle be achieved by depolymerization of plastics to recover the constituent monomers, which can (after purification) be repolymerized. However, depolymerization is extremely

slow under moderate reaction conditions and energetically inaccessible for most polyolefins. Thermal depolymerization is highly endothermic, as indicated by the high ceiling temperatures. However, partial depolymerization is thermodynamically much more accessible, and the use of a catalyst to achieve selective depolymerization to value-added products is potentially a simple approach to recycle and upcycle waste polyolefins, the report notes.

Catalytic pyrolysis today is the most common approach to chemical recycling of polymers, with companies such as GreenMantra, Plastic Energy, SABIC and Nesté proposing solutions. These solutions range from relatively simple, one-stream processes, such as those proposed by GreenMantra, to complex, multistream and multiproduct processes, such as those proposed by SABIC. Catalytic pyrolysis of polyolefins occurs under an inert atmosphere such as nitrogen at temperatures between 400 and 600 C. Many types of heterogeneous catalysts (e.g., simple solid bases, acidic zeolites with or without transition metal components to impart redox activity, metal-doped carbon materials, etc.) have been investigated. The hydrocarbon products show broad molecular weight distributions and may include gases, liquids and (usually not desirable) solid residues. The liquid products could include alkanes and aromatics, which have potential use as fuel oils, waxes and chemical feedstocks. Many of the catalysts used in catalytic pyrolysis are microporous, and ready access of the polymer to the active sites is critical.

In most catalytic pyrolysis of polyolefins, temperatures are 500 C or higher, requiring a great deal of energy input. These conditions cause rapid and severe catalyst deactivation, usually through coking. Other major disadvantages are the broad range of products and the broad molecular weight ranges within product categories. A techno-economic analysis of plastic pyrolysis as a classical chemical recycling method showed that it is not currently cost-effective. 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 ongoing challenges.

Hydrocracking is another method. The Institute for Cooperative Upcycling of Polymers reported the conversion of polyethylene (PE) to liquid alkanes in high yield and a relatively narrow weight by molecular weight distribution by hydrocracking with 170 psi H₂ at 300 C under solvent-free conditions. Platinum (Pt) nanoparticles in the Pt/SrTiO₃ support was proposed to stabilize the dispersed Pt via nanoparticle-support interactions that minimize sintering under the reaction conditions. The support also promotes binding of PE to the catalyst surface. Depolymerization of a single-use, commercial-grade plastic bag afforded similar high-quality liquid products, suggesting the additives present in the plastic bag do not affect the catalyst. The liquid product is suitable for use directly as a lubricating oil or as a feedstock for further functionalization. However, the process is slow (reaction durations up to four days) and demonstrated on a small scale.

The alkane metathesis methods have been extensively investigated for depolymerization of polydienes. Jones et al. depolymerized cross-linked polybutadiene networks using alkene metathesis. Solid cross-linked materials were rapidly depolymerized to an oil at 100 C using a commercially available ruthenium (Ru) metathesis catalyst at a loading of 0.024 mole percent or less. Dez et al. explored the use of ionic liquids as a medium for olefin metathesis degradation of natural rubber to acetoxylated polyisoprene oligomers. The oligomers are key intermediates in the synthesis of block copolymer compatibilizers, thermoplastic elastomers, etc. To apply metathesis depolymerization to polyolefins, an alkane dehydrogenation catalyst is required. Low-value short alkanes (for example, petroleum ether) were used as cross metathesis partners to decrease the molecular weight of PE and to convert it into useful liquid fuels and waxes via tandem catalytic cross-alkane metathesis under mild conditions. The tandem process uses an Ir-pincer complex as the alkane dehydrogenation catalyst and Re₂O₇/Al₂O₃ as the olefin metathesis catalyst. Dehydrogenation of both PE and a light alkane (using n-hexane as an example) creates olefins. Subsequent cross-olefin metathesis followed by hydrogenation leads to breakdown of PE chain into shorter chains. Polyethylenes with various molecular weights underwent complete conversion into useful liquid alkanes after one day in n-hexane at 175 C. The strategy is compatible with various polyolefin additives. However, the mass balance is poor: 120 milligrams PE gives over 1 gram liquid, showing that most of the product arises from the cross-metathesis of n-hexane. Basset and co-workers reported alkane cross-metathesis between light

and heavy linear alkanes in the presence of a silica-supported single-site catalyst under H₂ at 150 C. The results provide mechanistic insight into cross-metathesis depolymerization of macromolecules such as PE.

There is a long history of oxidative depolymerization routes to deconstruct polyolefins. Challenges remain to decrease reaction times, reduce reaction temperatures and improve selectivity. Recently Hakkarainen et al. developed a microwave-assisted process for recycling low-density polyethylene (LDPE) 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 percent yield with a carbon efficiency of 37 percent after just three hours at 180 C. The same group reported a microwave-assisted approach to degrade high-density polyethylene (HDPE) to a few well-defined chemicals (namely succinic, glutaric and adipic acids), which were used to synthesize plasticizers for polylactide films.

Compatibilization approaches to plastics recycling

In contrast to catalytic technologies to recover monomers, compatibilizers aim to ease recycling by avoiding the need to separate different types of polymers before recycling. There are four main types of compatibilizers:

1. nonreactive in which a chemical that does not form a covalent bond with the polymers being blended but instead work through noncovalent bonding such as hydrogen bonding and Van der Waals forces;
2. reactive in which a chemical that does form a covalent bond with at least one of the polymers being blended;
3. deactivator in which a chemical prevents undesired reactions between the polymers being blended; and
4. initiator in which a chemical that causes a desired reaction between the polymers being blended and is typically consumed during the reaction.

For recycled polyolefins, all four types of compatibilizers can be used, depending on what polymers are being blended and the desired end properties. However, the most common compatibilizers are the nonreactive and reactive types.

More information on emerging technologies related to plastics recycling and the ways regulations are impacting plastics recycling related to this study [can be found here](#).

This report was compiled by Steve Deutsch and Valerie Stephens. The complete study is available, and TCGR subscribers are asked contact Deutsch at 215-628-4447 or sdeutsch@catalystgrp.com to obtain it.

[HDPE](#)[LDPE](#)[PET](#)[Chemical Recycling/Pyrolysis](#)

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