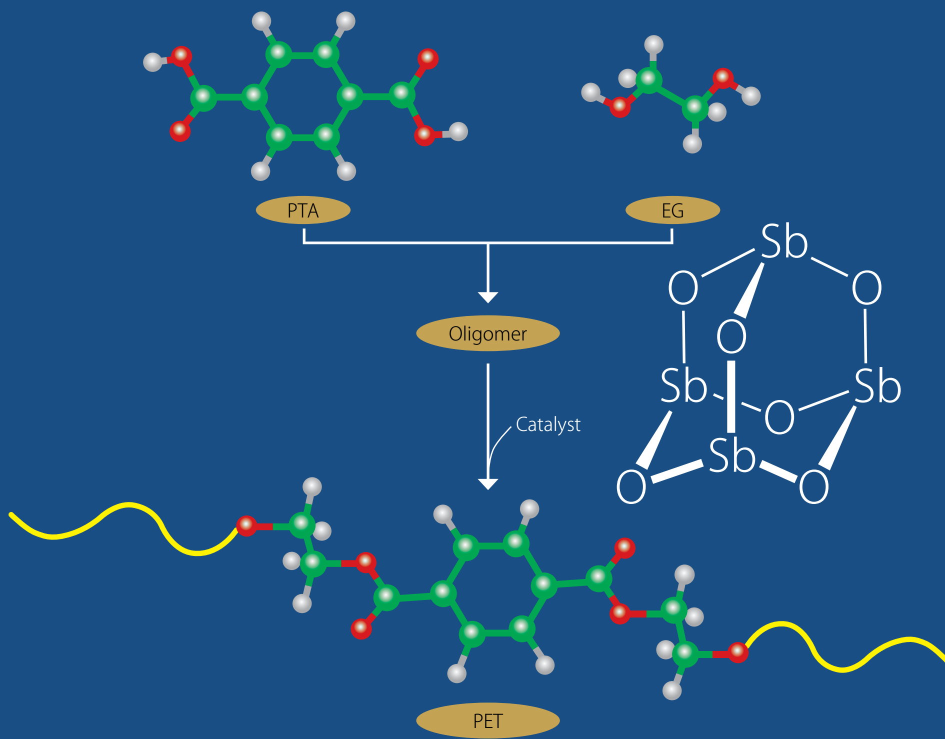

Antimony-free Polyesters

Is It Possible?

Over 95% of world's production of PET use antimony trioxide as the catalyst. Although there is yet no incontrovertible evidence that antimony present in polyesters leach out into the products at concentrations above permissible level, search is on to find out whether there is an alternative to the use of antimony, updates Dr. S. Sivaram.

Dr. S. Sivaram
Former Director, CSIR-NCL
Polymers and Advanced
Materials Laboratory
National Chemical Laboratory
Pune

Polyethylene terephthalate (PET) is a widely used commodity plastic for fibres, films and bottles. PET is produced by a two or three step process consisting of transesterification-polycondensation and optionally, a solid-state polymerisation process. The workhorse catalyst for the transesterification and polycondensation process is antimony trioxide, used at a concentration level of 250 - 300 ppm. Over 95% of world's production of PET use antimony trioxide as the catalyst. Antimony is a heavy metal and doubts have been raised about its safety; especially, when used in products that are in contact with water, beverages, pharmaceuticals and food products. Although there is yet no incontrovertible evidence that antimony present in polyesters leach out into the products at concentrations above permissible level (WHO: 20 μg/L, US: 6 μg/L, EU: 5 μg/L), search is on to find out whether there is an alternative to the use of antimony.

Any alternative catalyst must have the 'drop-in' capability since there is substantial manufacturing capacity already created worldwide. It will be uneconomical to retrofit these plants if substantial modifications are required. Additionally, any PET produced by an alternative catalyst must have similar processing windows for conversion to finished products since there is a close connection between the type of the catalyst used and the crystallisation behaviour of PET. These two challenges have proved to be daunting, resulting in high entrance barrier for any new technology.

Analysing Alternates

There has been substantial activity in the scientific and patent literature in this area. Germanium appears to be a good substitute, but is not an earth abundant metal; hence, expensive. Furthermore, we know less about the environmental and health related issues of residual germanium. Titanium based catalysts have been successfully used in the manufacture of polybutylene terephthalate (PBT) and polytrimethylene terephthalate (PTT). However, its use in the manufacture of PET causes the polymer to yellow, induces hydrolytic instability and undesirable formation of acetaldehyde as a volatile organic compound. Acetaldehyde has adverse effect on smell and taste of products stored in PET bottles. Also, alkoxides of titanium generally employed as catalysts, hydrolyse during the transesterification process leading to insoluble and less active titanium species. Improved versions of titanium alkoxides are now available for commercial use[1,2]. A few manufacturers (Teijin, Wellman) have shifted a small part of their capacity to titanium-based catalysts. Toyobo of Japan in 2003 developed an aluminum based catalyst for PET based on aluminum alkoxides and hindered phenols[3]. They were issued several Japanese patents and plans to commercially introduce the technology and license were announced. Yet, to this date, aluminum based catalysts have not been put to wide use. Little information is also available in published literature to assess the strength and weakness of this catalyst system.

Titanium based catalysts are much more active than antimony based catalysts. All commercial PET plants operate at a maximum temperature of 290°C. However, because of the propensity of the titanium catalyst to cause undesirable side reactions at this temperature, they must be operated at 265°C. The residence time of the reactors at lower temperatures is reduced by three times. This adversely affects productivity and plant capacity and, in turn, manufacturing cost.

There are other issues that confront titanium catalysts. They are hydrolytically unstable leading to insoluble titanium oxide derivatives in presence of water. Titanium oxides are not active catalysts. Consequently, a good titanium based catalyst should be ideally water-soluble and hydrolytically stable. Increasingly, solid-state polymerisation process after the polycondensation step is being done away with. Technology has emerged to increase the molecular weight of the polymer in the melt state itself. Titanium catalysts must be, therefore, capable of being operated at higher temperatures, without causing the polymer to degrade and form acetaldehyde.

Several patents have been recently issued to a start-up company established in 2010, Catalytic Technologies in UK[4], who claim superior titanium based technology for producing PET[5]. The patent claims a water-soluble and hydrolytically stable, well defined monomeric titanium citrate catalyst, formed by replacing two iso-propoxide groups in titanium tetra-iso-propoxide with citric acid. The catalyst is used in 10 ppm level and is claimed to produce PET with no discolouration and acceptable levels of acetaldehyde. The preforms can be converted to bottles at lower energy inputs and the resulting bottles are claimed to be brighter, clearer and have stronger sidewalls. The patents have been issued jointly to Catalytic Technologies and Uhde/Inventa-Fischer GmbH and have been evaluated in the continuous pilot facilities of Uhde/Inventa-Fischer.

However, it is not clear whether these catalysts are drop-in substitutes or will require changes in the manufacturing and processing processes. Additionally, the preforms produced with titanium catalysts have different processing windows on account of differing crystallisation behaviour of PET produced with titanium catalysts. Such PETs have lower crystallinity and have a higher crystallisation temperature. This will require lowering the processing temperature by as much as 10°C.

In Summary

In spite of many efforts, no viable alternative to antimony is within sight. It looks as though PET industry and users will have to live with antimony for many more years to come.

References

1. Catalysing PET. Plastics in Packaging, p.22, July 2014.
2. www.dorfketal.com
3. New aluminum based PET catalysts promises high activity at low cost, Japan Chemical News, Volume 44, January 30, 2003.
4. www.ctl8.com
5. Building better bottles, Chemistry World. p.23, December 2015; US Pat 2016/0108068 A1 dated 21 April 2016; EP 2, 765,149 A1 dated 6 February 2013; Indian Patent Application number 5573/DELNP/2015.