From the Sea to Electronics

Flame Retardant for Compounds Based on Recycled Ocean-Bound Plastics

Plastic waste in the sea has been shaping the negative image of the industry for several years. Various initiatives and mergers of companies have therefore launched projects to tackle this Ocean-bound Plastics (OBP). Components made of OBP could become a symbol for a sustainable use of plastics. For many demanding applications, however, such recyclates must also have the necessary flame retardant properties. A recycling project in Haiti shows how these properties can be achieved.

Community collection for bottles in Haiti © HP

According to current estimates, 86 million t of plastic already circulate in our oceans. There are many initiatives ongoing to collect waste streams and recycle plastics, for example polyester fibers for apparel. In this work we describe the use of collected and recycled plastics for flame retarded engineering plastic to be used in electric and electronic equipment.

One of the best examples for circular economy today is polyethylene terephthalate (PET) from bottles. PET recycled grades from bottles can be compounded into flame retarded PET or polyester blends and such compounds with recyclates are now spreading into structural parts of electronic equipment. Flame retardants are added to plastics to prevent ignition or significantly delay the spread of fire. Experts from Lavergne, Montreal, Canada, and Clariant, Muttenz, Switzerland, developed flame retarded polyester compounds based on ocean-bound PET.

Ocean-bound plastics are those that are likely to end up in the oceans because they are not properly disposed of. They are collected in villages and on beaches or coastlines in specific regions – in Clariant's and Lavergne's case, these are mainly bottles of Caribbean country Haiti (**Title figure**).

The major portion of OBP is PET, which is the most common polyester and is used in fibers clothing, bottles and containers for liquids and foods, as well as in combination with glass fiber for engineering resins. Most of the world's PET production is for synthetic fibers (more than 60 %), with bottle production accounting for about 30 % of the global demand.

Flame Retarded Polyester Compounds for E&E Applications

PET and polybutylene terephthalate (PBT) are the most commonly used thermoplastics among polyesters. They are resistant to solvents, heat-resistant up to 150 °C and over 200 °C with glass fiber-reinforcement and show good color stability. Both, PBT and PET, need UV protection if used outdoors, and most grades of these polyesters are flammable, although additives can be used to improve both UV and flammability properties. Especially glass fiber grades can be effectively flame retarded with halogen-free products. Such compounds with and without glass fibers can meet the most important fire tests required for electrical and electronic (E&E) applications, like the Underwriters Laboratories (Northbrook, IL/USA,) UL 94 flammability tests as well as the Glow Wire Ignition Tests (GWIT) and the Glow Wire Flammability Test (GWFI).

Compared to PET, PBT has a lower strength, rigidity, and glass transition temperature. However, it exhibits better impact resistance, faster crystallization, and better aesthetic properties. Moreover, it processes at a lower temperature profile, which makes it more advantageous for injection molding applications than PET. Flame retarded PBT compounds with halogen-free flame retardants show also excellent electrical insulation properties, e.g. comparative tracking index (CTI) of up to 600 V. That is »

Fig. 1. Initial factory used at the start of the project to process Ocean-bound Plastics (OBP) © HP

why injection-molded flame retarded PBT parts have found numerous applications in E&E equipment, more recently also in e-mobility, e.g. for high voltage connectors in signal orange color (RAL 2003).

Flame Retarded OBP Compounds

For ocean-bound PET, experts from the Canadian company Lavergne were able to develop flame retarded formulations of their recycled polyester grades in close collaboration with Clariant's specialists. Clariant's Exolit OP halogen-free phosphinate flame retardants have a proven track record for a very good environmental and health profile, as documented by the GreenScreen Benchmark 3 assessment under the NGO Clean Production Action's assessment tool, which identifies it as a good option to use because of its low hazard, for the key phosphinate ingredient. In October 2019, Clariant announced that selected Exolit OP grades will become available as Terra types based on renewable carbon sources, which allows a reduction of the carbon footprint by ca. 20% compared to the use of conventional raw materials. By using OBP compounds the plastic carbon footprint can also be significantly reduced.

The Process

The project initially started in 2016, with the goal to create a positive environmental and social impact in Haiti. The aim was to improve the working conditions of Haitians collecting bottles and to provide a path out of poverty for the people who work in the landfill.

The collection process begins when bottles are recovered from canals, roadsides, and the ocean shores. A new opportunity for 6000 to 8000 individuals who are to gather and collect plastics containers and bottles and sell them to the collection centers. The approximately 100 collection centers scattered around the country are equipped with scales and proper equipment to handle the first step of separation. This operation is done manually (**Fig. 1**), in order to provide employment and economic opportunities for the citizens.

Once sorted and separated, the plastic waste is transported to a central Lavergne factory in the capital of Haiti Port-Au-Prince, where the material is shredded into small flakes. A series of extensive washing, rinsing and drying is performed to clean the material. The wash line allows Lavergne to divert three types of plastics from the ocean, PET, HDPE (high density polyethylene), polypropylene (PP), respectively. The clean flakes are then shipped to Lavergne facilities in North America. Lavergne's transforming facilities are equipped with various technology enabling the upcycle of plastic waste. They specialize in formulating, blending, and compounding. The operation begins with post-consumer recycled plastics which are transformed into new engineering high-end formulations. The process is carried out to further clean the OBP and make it ready for the compounding step, either alone or in a blend with PBT, with other engineering additives and specialty chemicals, Exolit OP from Clariant in this case, to develop engineering compounds that can be used in different high-end applications such as automotive (transportation), and electronic and electrical equipment.

Challenges in Developing and Using Compounds Based on Ocean Bound PET

Compared to virgin resins, recycled plastics are in-consistent in properties and contaminated with other plastics. Therefore, the key to produce engineering compounds using such sources is steady feedstock, high technology sorting, processing, quality control and the use of excellent additives. There were some special challenges in developing the polyester compound based on OBP. One was to find the right balance between the required level of flame retardancy together with good flowability and good mechanical properties. This was achieved by optimizing the flame-retardant package in the formulation and using further additives. The compound properties could be further improved by using additional halogen-free flame retardant as a synergist, a lubricant and a process stabilizer. PET is also more sensitive towards thermo-oxidative degradation and hydrolysis than PBT, thus, pre-drying was essential for the final compound quality.

Lavergne's new flame retarded compound VYPET OBP-FR contains 30% glass fiber and has obtained UL 94 V-0 flame rating at 0.8 mm thickness with flexural strength that exceeds 140 MPa, which makes it suitable for most E&E applications, such as structural and aesthetic parts. It benefits from high stiffness and strength and low mold shrinkage of PET and good flowability and fast crystallization of PBT. Such a polyester glass filled compound reflects a balance of high stiffness, impact resistance and

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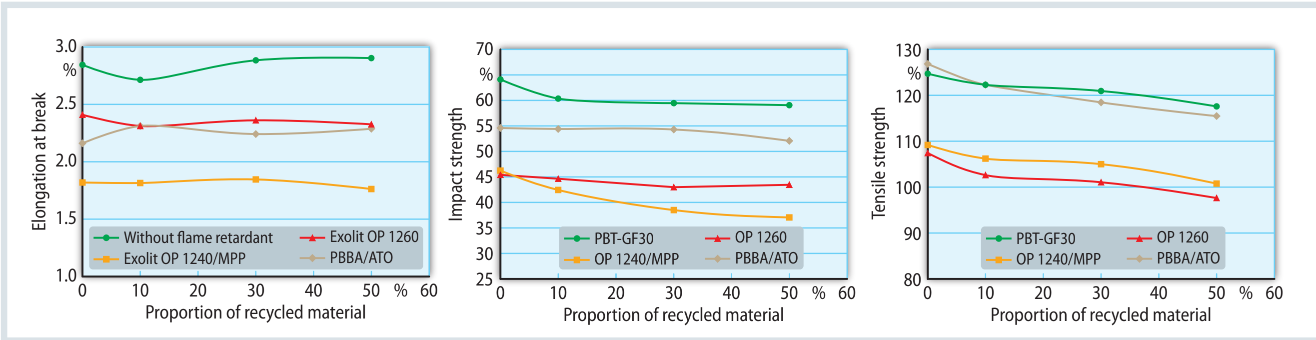

Fig. 2. Elongation at break of PBT-GF30 with and without flame retardant (FR) with different proportions of recycled material: with the flame retardant Exolit OP 1260, similar tensile and impact strength values can be achieved as with brominated flame retardants Source: Clariant, graphic © Hanser

good flowability, that also provides lower mold shrinkage compared to PBT 30% glass filled flame retarded resins. This fully recyclable OBP-based compound has passed molding trials at part manufacturers and is commercially available. VYPET OBP-FR has passed all the physical, mechanical, and hydrolytic tests and could outperform and replace virgin PBT 30% glass fiber-reinforced flame retarded grade. Among other things, the solution was tested for the following properties: density, ash content, tensile properties, flexural properties, impact strength, heat deflection temperature and mold shrinkage, flammability test.

Ecolabels and Regulatory Pressure

Some ecolabels, such as the US' Electronic Product Environmental Assessment Tool (Epeat), reward the use of post-consumer recyclates in electronics. Therefore, several original equipment manufacturers (OEMs) are looking to increase their use of resins based on recycled materials.

Use of halogenated flame retardants in electronics has come under increased regulatory pressure in the EU, with the European Commission recently adopting a ban on the group of chemicals in electronic displays under the Ecodesign Directive. Some halogenated flame retardants, such as HBCD and decaBDE, have been banned under international treaty the Stockholm Convention for their persistence in the environment and bioaccumulative/toxic effects. For most applications, alternatives with halogen-free flame retardants exist today, like Clariant's Exolit OP grades for polyamides (PA), polyesters and various elastomers, e. g. for cable insulations.

Post-Industry Recycling

Plastics can also be recycled before they reach the consumer market. When plastic scrap which was generated during production is recovered and reused, this is usually referred to as post-industrial recycling. For this process Clariant has also developed and tested its flame retardants. Important for the post-industrial recycling (PIR) process is the thermal stability of the flame retarded compounds. While in the post-consumer recycling (PCR) process properties can be improved with further additives, which normally cannot be done in PIR, where no compounding step is applied.

Flame retarded PA and polyesters with Exolit OP halogen-free flame retardants are widely used in all E&E applications like connectors, switches or circuit breakers. The recycling behavior of glass fiber-reinforced PA was investigated by Fraunhofer LBF (see "Secondary Raw Materials of the Future", ***Kunststoffe*** *international* 8/2018, pp. 39–42). The recycling study involved five extrusion cycles with granulation and intermediate drying of each material and injection molding of specimen. With the latest generation of Exolit, OP 1400, the PA keeps its flame retardancy even after five consecutive extrusion steps, simulating post industry recycling. The mechanical properties were reduced due to shortening of the glass fibers, but still sufficient for its use. The study demonstrates that shorter glass fibers have no negative impact on the fire behavior.

Clariant has made a similar investigation with flame retarded polyesters. In this study, PBT compounds with 30% glass fibers with and without flame retardants were molded to tensile and to UL bars with the addition of 10%, 30% and 50% of recycled material. The recycled material was simulated using molded parts made of fresh compound, grinded and added to the neat compound (the tests were carried out on a compounding system type ZSK 27 from Leistritz, Nuremberg, Germany, and an injection molding machine type Allrounder 320 from Arburg, Lossburg, Germany. It is common in injection molding to add sprues and other wastes after grinding and sieving in the molding process. Typically, up to 25% of grinded sprues can be added for glass fiber-reinforced plastics.

Halogen-Free Flame Retardants

The flame retardants being used were a combination of Exolit OP 1240 with a melamine polyphosphate, a widely used nitrogen-phosphorus synergist, and the latest Exolit OP grade for polyesters, Exolit OP 1260. For comparison, a typical polymeric brominated flame retardant with antimony trioxide synergist was tested as well. All flame retarded PBT formulations have kept the flame retardancy standard UL 94 V-0 at 0.8 mm thickness at all levels of recyclate being added. Even the afterburning times were not significantly increased. The mechanical properties remained unchanged as well, whereas glass fiber-reinforced PBT with Exolit OP 1260 showed very similar tensile and impact properties as the compound with brominated flame retardant and antimony trioxide (**Fig. 2**). The study shows that under the conditions used in the test, Exolit OP 1260 can be used even as a kind of drop-in replacement to brominated flame retardants. This allows the molders for flame retarded polyesters to add reground wastes from production when producing molded parts and therefore reduce waste in their process. ■