PEER REVIEWED

Certified ABS Plastics from Bio-Circular and Chemical Recycled Sources Instead of Fossil Ones

ABS (Acrylonitrile Butadiene Styrene co-polymer) is an engineering plastics material which is often used in medical devices applications. The reason resides in its relevant properties like processability, impact resistance, surface appearance or dimensional stability among others. For medical applications, specific ISO10993 biocompatible grades are also available, fulfilling with regulatory compliance while maintaining all advantages of ABS properties, like sterilisation and good chemical resistance.

Most plastics normally derive from petroleum as many other materials, like rubbers, synthetic fibers, resins, paints, coatings, adhesives, dyes, detergents, pesticides etc.. Petroleum is a non-renewable fossil resource that was formed over millions of years through the decomposition of prehistoric plants and animals under high temperature and pressure conditions. From the environmental sustainability perspective, the extraction and use of fossil oils is a relevant cause of global warming (due to the related CO_2 emissions) and depletion of fossil reserves.

The good news is that plastics do not need to be necessarily produced starting from petroleum, because nowadays bio-circular feedstocks and chemical recycled feedstocks are already proven alternatives. Most important, the recycling technologies that promote the use of such feedstocks are being progressively scaled up. This means, it is possible to continue relying on plastics properties advantages while moving away from fossil raw materials and heading towards sustainable alternatives. The mass balance approach enables this transition, preserving the already existing polymers supply chains while pushing the shift. In this article we will discuss how this is possible mentioning the specific case of ABS plastics. In fact, leading ABS manufacturers are already implementing the two types of sustainable feedstocks previously mentioned.

The petrochemical cracker is a pivotal point for many plastics supply chains. This is an effective stage where the substitutions from fossil-to-bio-circular and from fossil-to-chemical-recycled feedstocks can take place. Crackers are generally designed to process naphtha, which is normally obtained by refining and pretreating crude fossil oil. Nowadays, also bio-circular oils and pyrolisis oils (from chemical recycled waste) can be efficiently refined through methods like hydrotreating and fractional distillation. Once pre-treated, these sustainable oils can be used to feed the cracker, substituting fossil with sustainable naphtha (e.g. bio-naphtha). This input raw material for the cracker is a blend of saturated hydrocarbon chains, containing between 5 and 12 carbon atoms (C5–C12). Such chains need to be broken down by the cracker into smaller and often unsaturated hydrocarbons, producing primary basic molecules that are used in huge quantities in multiple supply chain industries. Approximately 90% of all worldwide plastics production is based on this reduced group of basic molecules. These are: olefins (e.g. ethylene, propylene, butadiene) and aromatics (benzene, toluene, xylene). As consequence, the choice of the cracker as input point of sustainable feedstocks offers huge economy of scales. Hundreds of millions of tons of volumes are produced, feeding different key polymers supply chains.

Let's consider the cracking process for the specific supply chain of ABS material. The primary basic output molecules of interest for ABS coming from the cracker are: ethylene, propylene, butadiene and benzene.[1]

The molecules ethylene and benzene are needed to produce ethylbenzene and in a second step styrene, which is one of the three ABS input monomers for the polymerisation process. Butadiene, second input monomer, is needed to polymerise into polybutadiene (the rubber phase contained in ABS, which provides impact resistance properties). Propylene reacts with ammonia (this one obtained from natural gas) to produce acrylonitrile, the third ABS input monomer, and to polymerise with styrene into SAN. SAN (Styrene-Acrylonitrile co-polymer) is the matrix phase of ABS, which provides chemical resistance and stiffness properties to the material. Polybutadiene, chemically grafted with Styrene and Acrylonitrile is already an ABS polymer, with high rubber content. This phase is dispersed in the SAN matrix, completing the ABS polymer formulation.

As can be noticed in the Plastics Europe flowchart,[1] all the previously mentioned molecules are traditionally obtained from fossil sources (including ammonia from natural gas). The important message is that, nowadays, they can be obtained also from sustainable sources like bio-circular feedstocks or chemical recycled ones. With the mass balance approach, the downstream supply chains do not need to physically segregate in their process the certified sustainable feedstocks from fossil feedstocks. In other words, the production process does not need to be doubled in two identical parallel processes, one for the sustainable certified product and one for the fossil-related product. If this would happen, huge additional investments in the chemical industries would be required, making the sustainable shift impossible from an economic perspective. On the other side, from a chemical point of view, ethylene, butadiene and benzene are identical to the ones obtained from naphtha oil (same chemical CAS number) and they come out from the same petrochemical plant: the cracker.

The second or third level chemical molecules (in terms of supply chain steps) mentioned before, such as ethylbenzene, or the ABS input monomers styrene or acrylonitrile, need specific chemical plant processes to be produced. Such processes can remain identical even if, upstream of the supply chain, the type of input feedstocks in the cracker are partially changed from fossil naphtha to bio-circular hydrogenated used cooking oil or to pyrolysis oil from chemical recycled waste. This represents the highest warranty in terms of product purity and quality for the outputs of each step of the industrial supply chain, as they become the input raw materials needed in the following step downstream. On the other hand, it is important to introduce a traceability system, like the ISCC+ certification with a mass balance approach. This ensures from one side the link with the new emerging advanced recycling supply chains and from the other side the progressive reduction of crude oil and natural gas extraction activities. Upstream in the supply chain, refined bio-circular feedstocks and/or chemical recycled pyrolisis oils will have been employed instead of fossil naphtha to

feed the cracker. Such a big switch cannot take place at once, and this is the reason why it must be progressive but growing. Legislators should take a clear position to promote such an important change to make it economically feasible from two perspectives: the existing chemical supply chain industry, which needs to be preserved, and the emerging recycling supply chain industry, which needs to be scaled up with huge investments.

Let's see an example of how bio-based feedstocks are already introduced in the ABS supply chain. There are existing grades like ELIX ABS E-LOOP M203FC CR100 (where M203FC means ABS medical grades for medical device applications requiring biocompatibility pretesting according to ISO 10993; E-LOOP means sustainable ABS grade; CR indicates the ISCC+ Certified Raw materials content, and 100 is the percentage of certified content, which is in this case 100%). The sustainable content is related to the input raw materials used to produce ABS (the ABS monomers). If all the three input ABS monomers are purchased by the ISCC+ certified ABS manufacturer with 100% bio-circular certified sustainable origin, the resulting ABS polymer can be 100% bio-circular ISCC+ certified with a mass balance approach. That's why in the case of E-LOOP CR100 bio-circular, the assigned input raw materials are Styrene and Butadiene monomers with 100% ISCC+ certified origin from Used Cooking Oil (bio-circular raw material certified category).

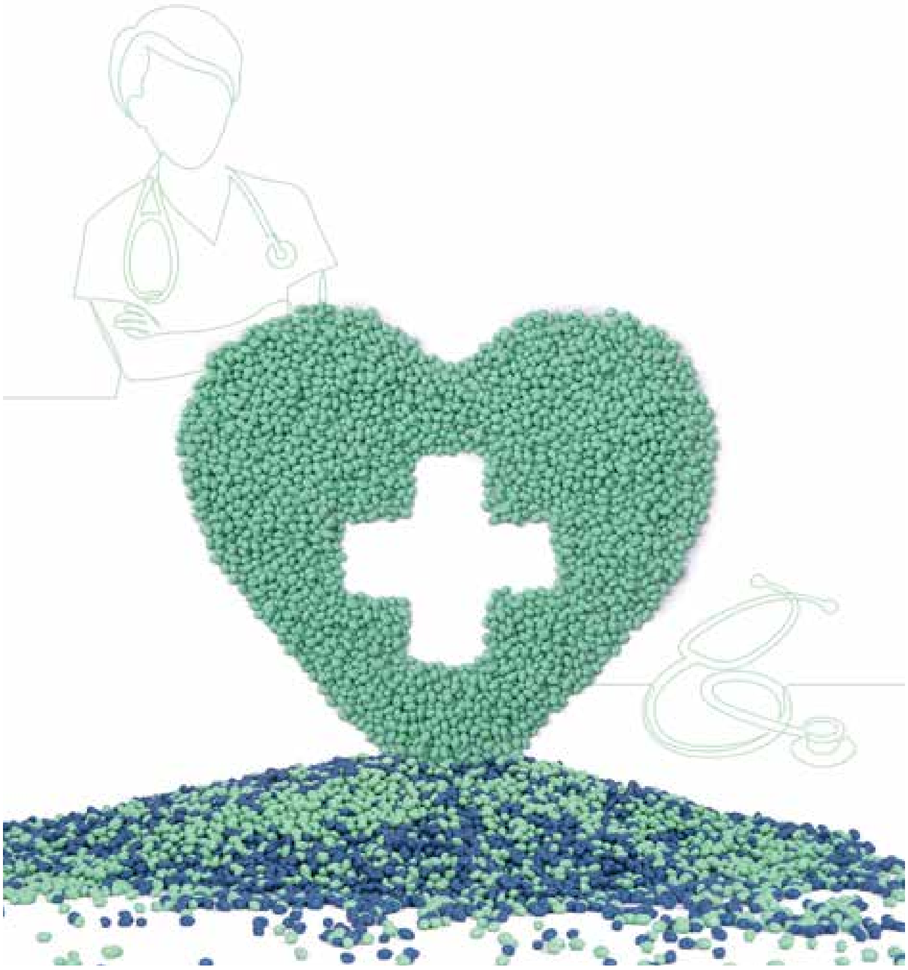
As first step, used cooking Oils (UCOs), generated for example in restaurants ("Point of Origin"), are collected by collecting points that can be ISCC certified to reintroduce it to the existing value chains. Also individual households can bring used cooking oils to authorized certified collecting points. Once collected, used cooking oils can be hydrotreated by a major petrochemical and refining technology company, converting them into a new type of oil (HVO or Hydrotreated Vegetable Oil). Such oil can be further processed to obtain bio-naphtha, that can substitute naphtha oil as input material of the petrochemical cracker. In this way, with a mass balance approach, it is possible to combine naphtha feedstocks, which is obtained from petroleum, with bio-naphtha feedstocks, that are obtained from used cooking oils, and from other bio-circular sources like vegetable oils or crude tall oils.

It is important here to make a distinction between first and second generation of HVOs. First generation refers to vegetable oils obtained from land cultivations and are in direct competition with food crops. On the other hand, the second generation of HVOs (also called 2G) are obtained from waste organic feedstocks like used cooking oil, without competing with food crops, saving land use. In addition, since they are a waste, they are removed from the environment as such (preventing potential negative impacts) and are converted into a sustainable feedstock alternative for the petrochemical cracker, substituting fossil naphtha.

As mentioned before, to produce ABS plastics, three input monomers are needed. We mentioned that Styrene and Butadiene have 100% ISCC+ certified bio-circular origin from Used Cooking Oil. A 100% bio-circular certified origin can be assured also for the third input monomer, Acrylonitrile. This monomer is produced starting from ammonia and propylene.[1]

Biogas can substitute natural gas to produce sustainable ammonia. Biogas is a renewable source obtained from bacteria when they break down organic waste, such as manure (animal feces), sewage and food scraps.

Forestal / agricultural waste (instead of fossil crude oil) can be used as input raw material for propylene production. This is the feedstock used to produce crude tall oil (CTO), a residue from the pulp and paper industry. It is obtained as by-product of the kraft paper production process, when pulping coniferous trees. Crude Tall Oil can be hydrotreated to produce second generation HVOs (similarly



to what we mentioned in the case of cooking oils). Again, the resulting HVO undergo a distillation process producing bio-naphtha among other products (e.g. bio-propane, HVO diesel, Bio-jet, heavy fractions). Bio-naphtha can be used as input raw material for the cracker, which will produce propylene as output (among the other basic primary molecules, as mentioned before).

Bio-based feedstocks, particularly those coming from waste (2G HVOs), are not enough to substitute the amount of fossil resources needed annually by the crackers as input materials. For this reason, chemically recycled waste is also needed, and pyrolysis oils production should be scaled up.

There are several types of plastics wastes that can be transformed into pyrolysis oils, like mixed plastic waste or used rubber tires. The more the waste flows are segregated, the more efficient the chemical recycling process is, providing more output in terms of tons of pyrolysis oils with less energy needed and less environmental emissions. From one side it is crucial to remove plastics wastes from the environment, but it is also important to find ways to avoid incineration processes, due to the high associated CO_2 emissions (even in the case where part of the energy produced can be recovered).

Nowadays the total amount of pre-treated pyrolysis oils (from chemical recycling) and bio-naphtha oils (from bio-circular feedstocks) used as input raw materials for the cracker is still very low and needs to be combined with fossil naphtha oils. This is a critical point, and reason of some misinterpretation of the mass balance concept, which should instead be adopted to make the sustainable transition feasible. In fact, it enables the use of the already existing product supply chains, which is what makes this approach so effective. It supports the progressive reduction of use of fossil feedstocks (something that is urgent but impossible to eliminate at once) and opens the door to the needed investments of the recycling supply chain, that can introduce bio-circular and chemical recycled feedstocks into the loop.

The key factor of success to reduce fossil oils and introduce sustainable oils is the joint cooperation work of the companies that are composing the entire supply chains, from final OEMs to part molder converters, polymer manufacturers, monomers, intermediate molecules chemical producers, petrochemical companies (the denomination referring to petroleum will hopefully need to be changed in a next future) and last but not least the advanced recyclers of bio and synthetic waste.

With time, the progressive demand increase for sustainable feedstocks alternatives will lead to no further need for fossil inputs. This will result in important support for the investments of advanced recyclers of bio and synthetic waste to reach synergic economy of scale. A long-term target for the mass balance approach: not just a coexistence of sustainable sources with fossil ones, but the exclusion of the latter and the exclusive use of sustainable alternatives for the existing polymers supply chains.

REFERENCES

1. (please check the Plastics Europe flow chart at this link, which helps to understand the actual supply chains of each type of plastics: https://plasticseurope.org/sustainability/circularity/life-cycle-thinking/eco-profiles-set/. By clicking on the "ABS" blue box, the conventional ABS supply chain is filtered from the other traditional plastics supply streams). The purpose of the Plastics Europe flow chart is the calculation of the eco-profiles for determining environmental impacts of plastics, in this article we refer more particularly to this chart as general map to understand the actual basic organisation of the plastic supply chains industries.

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Luca joined ELIX Polymers in February 2017 as Business Development Manager for Healthcare and Consumer sectors, focusing on identifying and developing new markets, products, and applications. He graduated in Management Engineering from Politecnico di Milano and has over 20 years' experience in thermoplastics, thermosets, composites, electrical insulation, and electronics. Since 2020 he has been actively involved in the development of ELIX E-LOOP sustainable solutions, including a new growing sustainable ABS blends portfolio, with chemically recycled, bio-circular and mechanically recycled content. Luca wrote several technical articles on behalf of ELIX about specialties and sustainable ABS for medical applications that were published on several renowned medical and pharmaceutical magazines.