

Information service offered to plastics & rubber technological companies by Maris SpA

N.07



JOURNAL

MARIS

NEWS FROM THE COMPOUNDING WORLD



60th ANNIVERSARY!

2022: IT IS TIME TO CELEBRATE OUR MOMENTOUS 60th ANNIVERSARY!

It has been 60 years of goals to achieve, choices to make and sometimes daring changes to face, 60 years of constant commitment and many satisfactions. However, we want to see this anniversary only as a single step of the long journey we have embarked on, persuaded that there will be many others to take, with the same passion and perseverance that have motivated us from the very

beginning and that have allowed us to get where we are. A special thanks to all the people who - over the years - have trusted us: our customers, our employees, our partners, and all those who have contributed to making these achievements possible. We look to the future with enthusiasm, certain that this anniversary is just a starting point for a continuously prosperous and successful tomorrow.



INNOVATIVE PROCESS FOR THE ODOR REDUCTION OF POST-CONSUMER POLYMERS

One of the most critical aspects of post-consumer plastic recycling is the presence of unpleasant odors. Maris has recently developed an innovative extrusion process specifically designed to solve this issue.

The odorous contamination of plastics is usually of organic origin, and the most common one comes from food residues and fuel tanks.



This study was divided into two parts:

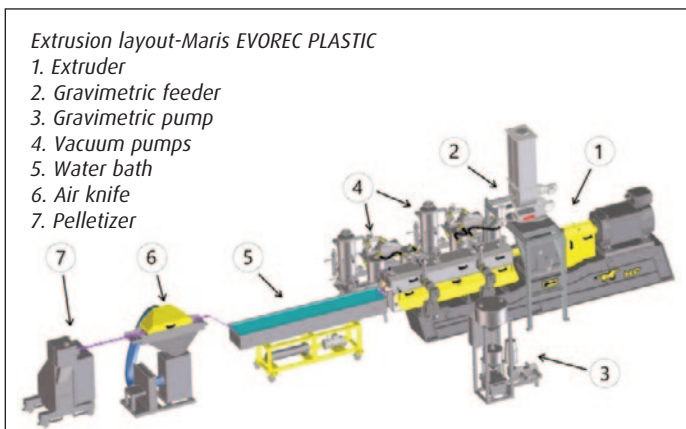
- the first concerns the development of an innovative extrusion process for the abatement of odors/contaminants from HDPE fuel tanks - a task carried out by F.Ili Maris;



- the second part concerns the characterization of the samples to identify the best process conditions - an activity which was carried out by the Università del Piemonte Orientale. Thanks to the work and synergy of these two different experiences, it was possible to break down **up to 98% of volatile and semi-volatile organic compounds.**

MARIS EXTRUSION PROCESS

Maris extruder developed for this specific recycling has the following technical characteristics: Do/Di = 1,55; extruder length 48 L/D, equipped with two different side degassing units, a water injector and a strand die. The downstream equipment is composed of a cooling water bath, a drying air knife and a strand granulating pelletizer. The contaminant reduction process has been divided into two phases. During the first one, the polymer was melted using a very high thermal profile and subsequent degassing of the material through the first side degassing unit. During the second phase, water was injected into the extruder with a gravimetric pump and subsequent degassing of the material through the second side degassing unit. The water injected at room temperature, instantly switched to the gaseous state. Thanks to the proper combination of the mixing screw elements, it was homogenized with the molten polymer. After mixing, the material was degassed together with water vapor, which acts as a stripping carrier for the organic contaminants.



In order to evaluate the best process conditions in terms of odor reduction / VOC removal, thirteen samples have been performed. Below is the summary table with the process parameters:

Test code	Screw speed (rpm)	Thermal profile (°C)	Water	Degassing
RAW material	-	-	-	-
EXP 1	300	Low	-	-
EXP 2	450	Low	-	-
EXP 3	450	Low	-	yes
EXP 4	300	Low	-	yes
EXP 5	300	Low	yes	yes
EXP 6	450	Low	yes	yes
EXP 7	300	High	-	-
EXP 8	450	High	-	-
EXP 9	300	High	-	yes
EXP 10	300	High	yes	yes
EXP 11	450	High	yes	yes
EXP 12	600	High	yes	yes
EXP 13	600	High	-	yes

*All tests were performed at the same output.

ANALYSIS OF RESIDUAL VOLATILE ORGANIC COMPOUNDS

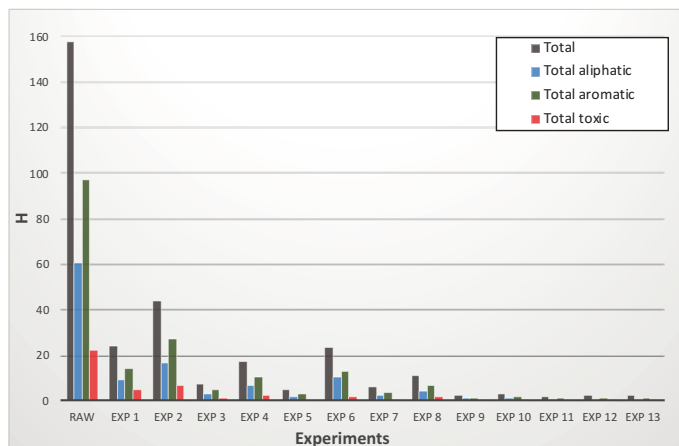
The characterization of the samples - useful to detect which are the best process conditions - took place in two phases:

- Headspace Sampling: sampling of the gases developed in the glass vials of the samples;
- GC-MS analysis: quantitative and qualitative analysis of the gases emitted by the samples.

Laboratory analyzes identified 58 peaks, each of them corresponding to a specific organic molecule.

To highlight the results more easily, data have been grouped into four categories: the sum of all contaminants, of aliphatics, of aromatics and of toxic contaminants.

Figure 2 shows the peak height values obtained from the chromatograms and scaled as reported in the experimental part for each experiment.



Histogram of the four categories: the sum of all contaminants, of aliphatics, of aromatics and of toxic contaminants.

As it can be seen from the histogram, the Maris process drastically reduces the presence of these organic substances and its efficiency varies with different processing parameters. More specifically, the high temperature profile, the presence of vacuum degassing and the injection of water increase the efficiency of the process, while the screw speed has an effect related to the filling degree of the screws which affects the vacuum degassing performance.

To verify that the HDPE has not been degraded because of the process, mechanical, chemical and physical characterization analyzes (dynamometer, DSC and TGA) have been performed. All these analyzes pointed out that all the samples produced did not show appreciable degradation.

The study has proven that the innovative Maris extrusion process can be an excellent way to recycle polymers when the limit of application is the unpleasant odor.

LCA 'Life Cycle Assessment'

The aim of this study is to investigate the environmental impacts of the patented Maris devulcanization process by using a co-rotating twin-screw extruder (EVOREC RUBBER line). The investigated recycled materials are gaskets in ethylene-propylene diene monomer (EPDM), sulfur vulcanized, deriving from the automotive sector.

Maris devulcanization process is a thermo-mechanical process that does not involve the use of devulcanizing agents, supercritical CO2 or solvents. It is possible to devulcanize different rubber curing systems (for instance sulfur base or peroxide base). Although different thermo-mechanical devulcanization processes by co-rotating twin-screw extruders (CTSE) have been proposed, their practical implementation has not been completely satisfactory till now.

Devulcanization produces a second raw material from a free-flowing form feedstock which is produced by sorting and grinding operation, obtaining a re-usable material in a virgin blend without altering its characteristics. The inlet feedstock needs to be contaminants free - especially metal contamination.

The feedstock quality in terms of homogenization and selection is one of the main fundamental factors to get a good quality devulcanized material.

The methodology used to perform the analysis of environmental impacts is the LCA and data used to configure the system refer to a real plant - Maris EVOREC RUBBER line, with a 58 mm c-TSE - procesing the devulcanization of EPDM waste from automotive gaskets.



Materials and methods

Goal and scope definition

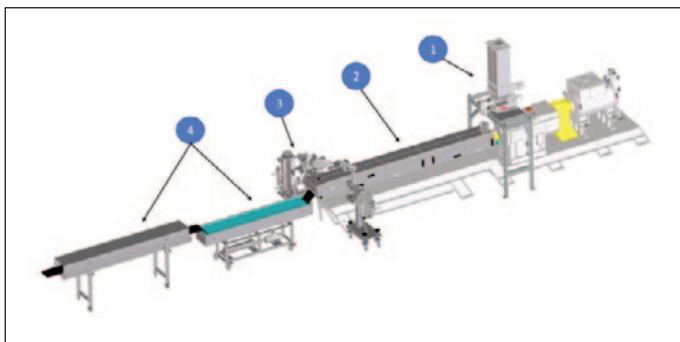
The analysis examined the production of the integrated system that allows the devulcanization process of 120 kg/h of EPDM. The goal was to demonstrate how the devulcanization process allows to reduce the environmental limit associated with the life cycle of rubber product. In those terms, through the quantification of resources, energy consumption, emission and waste it is possible to calculate a product or a process environmental impact.

LCA calculation

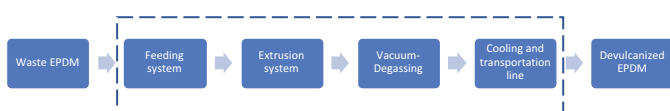
The first step of the study was the definition of the limit (Fig. 2) for the analysed system (Fig. 1).

The second step was the Inventory Analysis with the aim of identifying and quantifying the raw materials, resources, energy consumption, outputs and emission related to the functional unit considered.

Finally, the third step was the impact assessments where the set of resources and emissions from the previous step are converted into a series of environmental impact categories. To determine the relative contribution of the considered categories, the impact were also assessed on a global level by normalization.



Graphic representation of the devulcanization line EVOREC RUBBER (Maris S.P.A property). 1. Feeding system 2. Extrusion system 3. Vacuum-degassing 4. Cooling and transportation line.



Scheme of the thermo-mechanical EPDM devulcanization process; the dashed box indicates the system limit for the LCA.

Comparative analysis

The study was extended by including two comparative analyses.

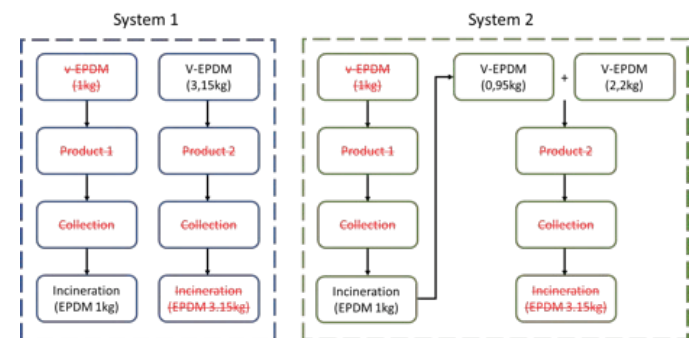
To highlight the impact generated by the production step, in the first comparison the production of 1 kg of virgin EPDM compound (v-EPDM) with 1 kg of EPDM obtained from EVOREC RUBBER (r-EPDM) process has been envisaged. A "cut-off" system was considered which involve the exclusion from the system limits of all the impacts attributable to the previous life of the material.

The second comparison (Fig.3) takes into account the different physico-chemical properties of the devulcanized material and the virgin one, comparing two different system models, each of which allows to obtain two rubber products. For System 2 the product 2 is the combination of 30% of r-EPDM and 70% of v-EPDM which shows the same physico-chemical properties of a product generated using 100% of virgin rubber (System 1).

It can be observed that in System 1 the end-of-life phase occurs by incineration, while in System 2 the first product undergoes a devulcanization process that allows its recycling and there is a 5% loss of material during the devulcanization process due to loss of material.

As shown, the analysis of the two systems is greatly simplified if the equivalent processes are neglected (boxes crossed out in red).

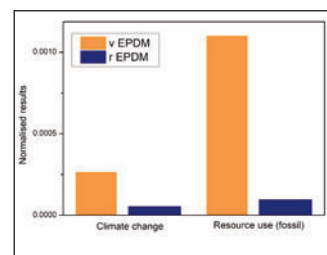
For System 1, only impacts associated with the incineration process of 1 kg of rubber and the production of 3.15 kg of virgin EPDM compound need to be considered. Instead, for System 2, it's enough to consider the impacts for the devulcanization process, which allows to obtain 0.95 kg of r-EPDM, and the impacts to produce 2.2 kg of v-EPDM compound.



Comparison of two systems to produce EPDM rubber product. EPDM amount for each product is indicated. The boxes crossed out in red represent the equivalent unit process between the considered systems.

Comparative analysis - first comparison

The devulcanization process allows to obtain EPDM with considerably lower impacts compared to the virgin one. In fact, the value for the r-EPDM is on average one order of magnitude smaller than those calculated for v-EPDM. Fig. 4 shows the comparison between the normalized environmental impacts of 1 kg of v-EPDM and r-EPDM.

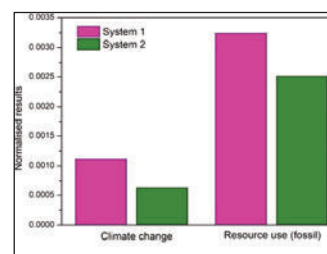


Normalized environmental impacts of 1kg of v-EPDM and r-EPDM.

The normalized results were reported to show the relative contributions of the impacts among the considered categories, when switching from v-EPDM to r-EPDM. As regards to the v-EPDM, the most relevant impact is related to the category Resource use (fossil) that is mainly caused by the energy consumption, from the Italian national mix, during the phases of the devulcanization process.

Comparative analysis - second comparison

Fig. 5 shows that impacts generated in System 2, configured assuming one recycling phase of the EPDM, are lower than impacts in System 1 (modelled using always virgin EPDM); this trend is common for all impact categories.



Normalized results for the comparison between the two systems.

For both compared systems, the main impacts are obtained for the category Resource use (fossil). In conclusion, both comparisons made in this study underline how recycled EPDM, obtained through a thermo-mechanical devulcanization process, allows to limit the environmental impacts compared to the production of virgin material.



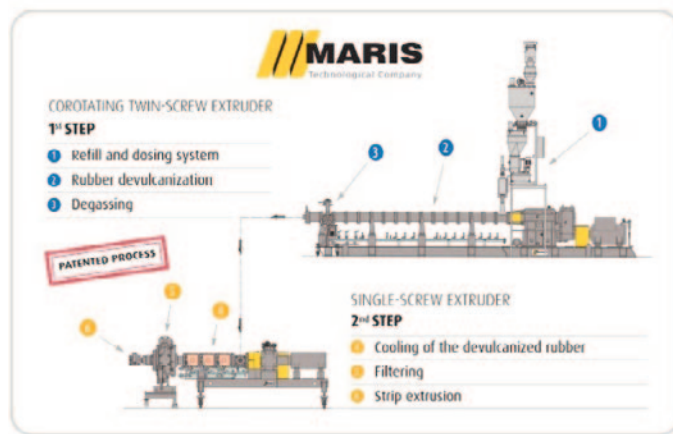
<https://doi.org/10.1016/j.jdepro.2022.131352>

EVOREC RUBBER Plus: a two-steps performance devulcanization process



To produce devulcanized rubber with very high-quality standards, we have designed and patented a new two-step devulcanization process.

- **The first stage** involves the devulcanization of the rubber by means of a corotating twin-screw extruder with characteristics equivalent to Evorec Rubber.
- The rubber thus devulcanized will feed, by direct connection, the second extruder.
- **The second stage**, given by the combination of a single-screw extruder and a screen-changer, offers the possibility to reach significant advantages:
 - Sudden cooling of the devulcanized rubber: this operation makes it possible to contain the temperature of the extruded strip while minimizing rubber degradation. The effects are observable both in terms of mechanical properties of the recycled material and in terms of reduced odor gas emissions;
 - Rubber filtration: this operation - made possible by the high thrust capacity of the single-screw extruder - allows the devulcanized rubber to be filtered before extrusion, again increasing the mechanical properties and, more generally, the qualities of the recycled material.



WELCOME TO K 2022

An exhibition is a place for emotions, a showcase of opportunities, a place for business. The economy needs trade fairs, especially in the light of its recovery after the pandemic, which has affected the world over the last few years. We are therefore eager to say that after a shutdown of almost two years, the World's No. 1 Trade Fair for Plastics and Rubber 'K 2022' is ready to re-open its doors in Düsseldorf from 19th to 26th October 2022.

For this event - and in occasion of our 60th Anniversary - Maris has been assigned a booth of 170 sq. in the Hall 16, stand number 16B59.

Our commercial and technical staff is looking forward to welcoming you at our booth,



where we will display a modern and versatile TM58HT/48D extruder, the result of the most recent technical innovations, along with our old TM70 extruder build in 1962 - our foundation year - belonging to one of our historical customers and still able to run!

A 60-year history told by the solidity of both our company and the machinery we manufacture.

Do not miss the opportunity to meet us in that occasion and to discuss new projects together!

