Successful depolymerization trials in June 2021: stable operation over 8h at high feed rate

Word by Chair of Executive Board, Jean-Luc Dubois

MMAtwo has started to deliver its first important results: several hundreds of kilograms of waste PMMA have been depolymerized with mass yields above 90 wt %, and MMA content above 90 wt % in most cases. Crude MMA was distilled to purities above 99 wt %, and up to 99.8 wt %. The regenerated MMA (rMMA) achieves a purity equivalent to virgin MMA with major impurities below 0.1 wt %.

During our pilot campaign in June 2021, the pilot unit has been operated at high feeding rate and for long periods without difficulties, demonstrating the stability of this continuous process.

Samples of rMMA are available under Material Transfer Agreements, as we now want to assess the market potential of the various qualities of rMMA.

2 new partners are going to join the project with in-kind contribution: Altuglas International, which was formerly Arkema's PMMA business unit and now part of Trinseo, and Procoat. They were both interested to have access to large amounts of rMMA which will be validated in several new applications.

Polymer to Polymer yields

Recycling means that the cycle should be closed in the best case (known as closed loop recycling). So, from a polymer (or plastic) one should make again the same polymer. A second good option is to recycle the polymer into another material that still keeps the carbons in the economy (known as open loop recycling). What is important in this sequence of operations is to keep a high mass yield, while keeping a high technical property and performance for the polymer.

In MMAtwo, regenerated MMA is used to make new Cast PMMA, Extrusion sheets and Injection grades, but also kitchen sinks and composite. In most cases, 80 wt % of the PMMA is recovered as regenerated MMA, well above what can be achieved with other polymers, including Polystyrene.

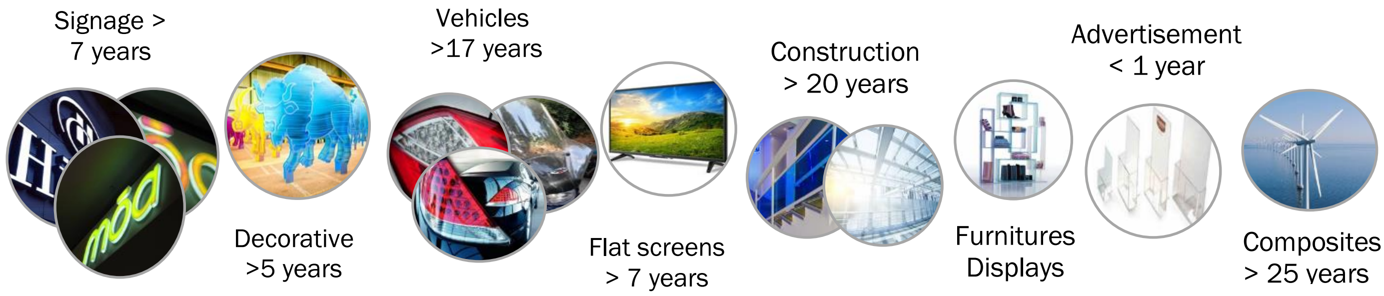
MMA regeneration technologies

Several technologies are currently used to regenerate MMA: Molten-metal reactor, Dry distillation, Rotating-drum process, Fluid-bed process, Stirred tank reactor, Auger-screw process, Micro-waves reactor, and finally the extruder reactor selected in the MMAtwo project. The Molten-metal process is still used in Europe and other countries, and was quite common in the past. The fluid bed process was a promising technology, with high heat transfer, and a plant had been built in Japan but is no longer in operation. The Dry distillation process was one of the first technologies for PMMA recycling and is still used in many countries. In this process, a pile of PMMA is placed in a tank, which is then heated until monomer generation stops. The rotating drum technology is a variation of the dry distillation in which the scraps are placed in a rotating cylinder. The Stirred-tank reactor is not common, but when used in semi-continuous mode, it avoids the accumulation of solid residues which tend to catalyze side reactions. Auger-screw process is gaining interest, and could be heated by Joule effect. Similarly, the microwave heating and the inductive heating processes are using alternative forms of energy and are still at lab scale. The rotating paddle technology in which heat transfer is done from the reactor walls to a heat transfer medium has been operated at pilot scale level. Finally, the technology selected by MMAtwo, which uses a twin-screw extruder, is a continuous process in which the PMMA scraps are heated to depolymerization temperature, and vapors condensed at the end of the extruder. The extrusion technology is common in mechanical recycling, and should be easily adopted by recyclers.

H2020
Grant Agreement N° 820687

Views on chain of custody. https://www.iso.org/obp/ui/fr/#iso:std:iso:22095:ed-1:v1:en:term:3.5.9

Post-Industrial PMMA scraps are easy to track with a clear *CHAIN OF CUSTODY*. It is possible to know the origin of each material. It is also essential to guarantee that the "Virgin" material, and its monomer, has been REACH registered. This is more challenging for post-consumer materials; in part because the PMMA parts can come for rather old materials (marketed before the implementation of the REACH regulation) – (for example tail-lights of cars (average age 17 years, construction materials >> 20 years) and, in part because the PMMA parts can have been included in finished products made outside of Europe (e.g. flat screens).



There are several possible chains of custody. PMMA depolymerization and purification is done in dedicated units, so it allows to use the ***Identity preserved*** model of the regenerated MMA. It means that the claim of 100 % "recycled content" is based on physical product. The user of the regenerated MMA could eventually use also virgin MMA, and in its plant have both productions with pure virgin or pure regenerated MMA, and use the ***Segregated*** model. The user can also decide to use a constant mix of virgin and regenerated MMA, and use the ***Controlled Blending*** model. But some customer might be ready to pay a premium to capture all the regenerated MMA in their claims even though the products are made with uncontrolled mix of virgin and regenerated MMA. In this case, the ***Mass Balance*** model can become appropriate. In this model, the amount of regenerated MMA is audited by approved stakeholders, and not more regenerated MMA claims can be sold than what has been effectively produced. The last possible model is the ***Book and Claim*** model. In this model, the regenerated MMA produced in one site is recorded, but the physical flow is disconnected from the supply chain, meaning that a consumer buys separately the "recycled credits" and the monomer.

The MMAtwo process allows all types of chain of custody, but has the major advantage to allow the "***Identity Preserved***" mode, and to ensure that the regenerated MMA returns in the economy in the very same application.

PMMA feedstock is not restricted to wastes

The PMMA feedstock that can be used in the MMAtwo recycling process is very diverse. Post Industrial scraps have been treated, such as Cast clear PMMA, extrusion and injection grades, colored, but also white and black products, mixed cast and extrusion coloured sheets… So far, no limits to the technology have been found.

Recycling Rate versus Recycled Content.

The recycling rate is important, and with MMAtwo technology we have already communicated in a previous newsletter that it can be between 65 and 85 wt % (regenerated MMA to PMMA waste) at a purity above 99 wt %. However, for customers what can be more important is the "Recycled Content", which mean the amount or regenerated MMA which is used in the product. With high purity regenerated MMA, such as the product achievable with MMAtwo's technology, it is not necessary to dilute the regenerated MMA with virgin MMA to achieve the highest technical properties. So, both a high Recycling rate and a high Recycled content are achievable.

Impact from substances of concern and additives, "Legacy additives"

The additives used in PMMA include: Pigments, Fillers, mold releasing agents, chain transfer agents, plasticizers,… For some other polymers, like PVC or Polystyrene, the additives that were used but no longer allowed on the market are restraining the use of mechanical recycling, since they would still be present in marketed products. When using a depolymerization process, like in MMAtwo, the monomer can be purified to virgin-like purity. However, it is important to guarantee that all the additives are properly sorted, decomposed and disposed in appropriate conditions. This is the next

H2020
Grant Agreement N° 820687

major challenge for MMAtwo, which aims to identify the additives that were used in the past, and to demonstrate where they end-up in the depolymerization process, and guarantee their fate, like the Pb, Cd, Se, pigments that were once used.

MMAtwo 3 major objectives:

- Construct a **new PMMA depolymerization value chain in Europe**, covering the whole value chain of the PMMA lifecycle with both production waste and end of life waste
- Avoid down-cycling through **reactive regeneration** (depolymerization)
- Develop an **innovative metal-free technology** enabling depolymerization of lower quality waste.

MMAtwo is divided into 7 Topics (so called Work Packages)

WP1: Collection of scraps and pretreatment,

WP2: Depolymerization,

WP3: Purification,

WP4: Exploitation, end-users tests, business analysis,

WP5: Techno-economic and environmental assessment,

WP6: Project management and

WP7: Communication, dissemination and academic outreach.

Main results achieved since January 2021

WP1 – Collection of scraps and pretreatment

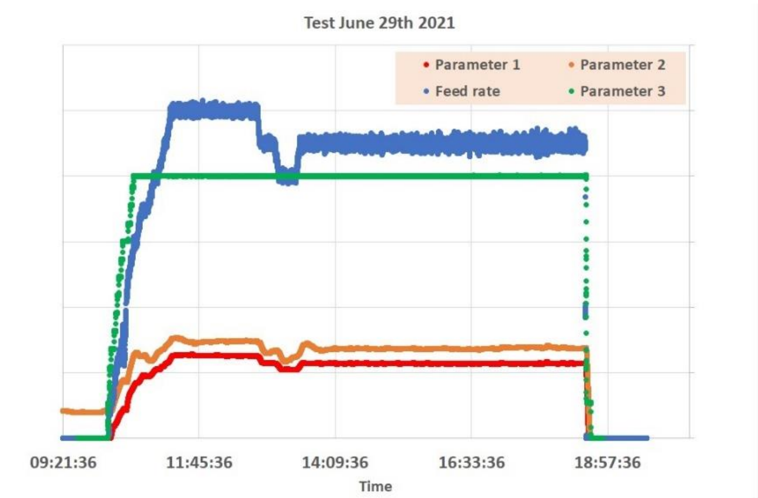
Heathland, in collaboration with **Comet Traitements, Ecologic, Arkema** and **Delta Glass,** collected PMMA waste for conversion into pre-treated materials ready to be depolymerized in the MMAtwo pilot installation. There were 5 campaigns in which different types of PMMA waste were tested and each type of waste required a specific type of treatment at **Heathland**. There was a specific focus on collection and treatment of post-consumer (End-of-Life) PMMA waste streams and certain heavily contaminated PMMA waste streams, which, despite the contaminants, were still converted into usable material. Particularly there were successes in separating PMMA from PVC waste. **Certech** and **Heathland** worked on new analysis techniques and guidelines aiding in the collection and subsequent processing of PMMA. **Ecologic** and **Heathland** made a model for predicting tonnages of PMMA waste until 2030 from WEEE and **Heathland** identified additional tonnage to serve as feedstock for depolymerization.

H2020
Grant Agreement N° 820687

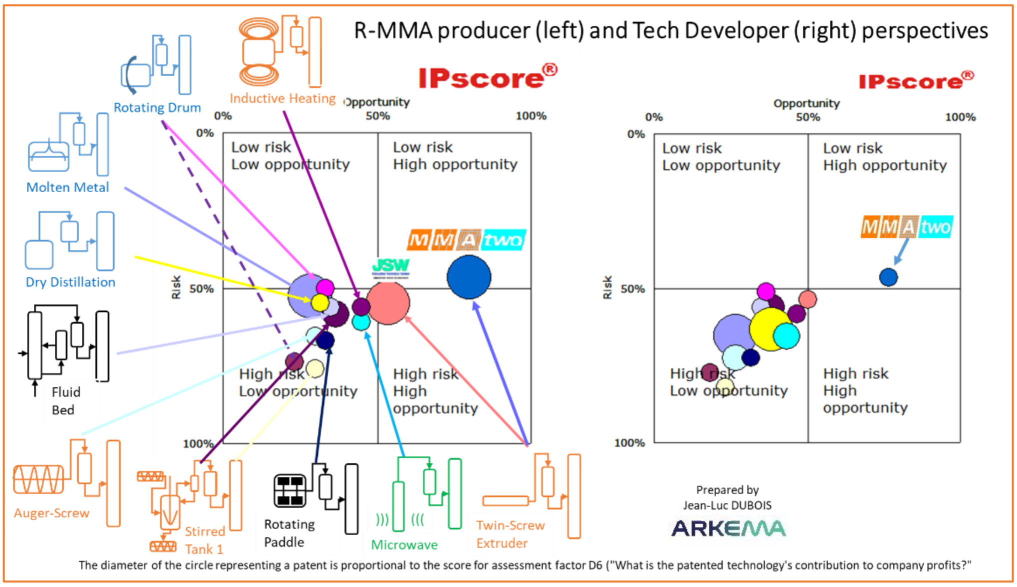
WP2 - Depolymerization

Heathland, **JSWE**, **PDC**, **Suster** and **Arkema** have conducted 4 pilot test campaigns, by June 2021. During the June 2021 campaign very long pilot tests have been made. The goal was to demonstrate that the pilot plant can operate stably over long periods. During that week, injection clear, extrusion clear, white cast (for bathroom applications), black cast PMMA have been tested successfully. Several 100 kgs of crude MMA were supplied to **Speichim** for purification.

© HEATHLAND



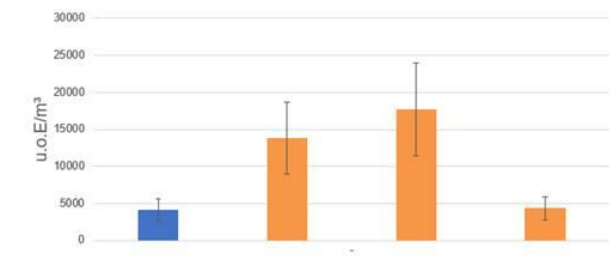
The IPScore ® tool developed by the European Patent Office to analyze the value of patents has been used to compare the IP portfolio of stakeholders. The value of IP was analyzed both from the perspective of the technology developers and from the regenerated MMA producer. Quite often the rMMA producer also produces PMMA sheets from it, but does not have multiple products on its portfolio. Concerning the technology developers, it can also be a large PMMA producer, as well as a start-up or small company, or like Japan Steel Works a company which has many other equipment which can be used in other fields. The impact for the respective companies is therefore different and is also reflected by the size of the balls, and the position in the Risk-Opportunity Matrix. The figure also illustrates the multiple technologies which have been patented for PMMA depolymerization, with some patents which are now in the public domain, and others which have been filed more recently.



The IPScore® tool is based on several sets of questions, with multiple choices, on the patent itself, policy of the owner, market size and potential… This part of the work is still on-going as data are being collected on other recent technologies which could be applied to recycle PMMA.

WP3 – Purification

Speichim supplied to **Certech** several samples of purified regenerated methyl methacrylate monomers (obtained from various PMMA streams) in order to determine odour concentration by dynamic olfactometry (see graph). It follows that while regenerated MMA 4 shows practically the same odour concentration as virgin MMA 4, the rMMA 2 and rMMA 3 were significantly higher by more than a two-fold values, which is significant. Correlating with GC-MS/FID data suggests that these high values are linked to ethyl acrylate (EA) concentration and not to methyl isobutyrate (MIB), two typical contaminants. The (odorous) detection threshold of EA was determined in a separate dynamic olfactometry experiment, together with that of MIB and MMA, and these values support the interpretation given above. Indeed, EA detection threshold is very low at 0.08 µg/m³ while other substances have higher values: 22.03 µg/m³ for MMA and 16.10 µg/m³ for MIB.



	Virgin MMA	rMMA 2	rMMA 3	rMMA 4
MIB (%)	0,00	0,00	0,02	0,02
EA (%)	0,00	0,05	0,04	0,00

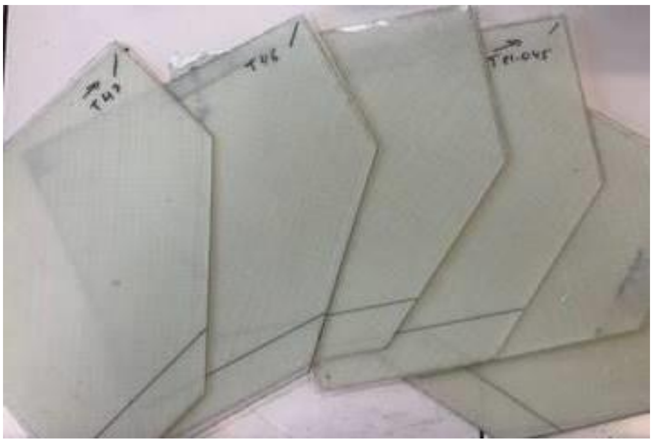
© Certech

WP4 – Exploitation, End-user tests, Business analysis

Delta Glass is sponsoring Solar Team, an initiative from the University of Technology Eindhoven. This project has designed Stella Vita (see pictures below), a sustainable mobile home powered by solar cells on roof top, for which **Delta Glass** is supplying PMMA side windows made from rMMA.

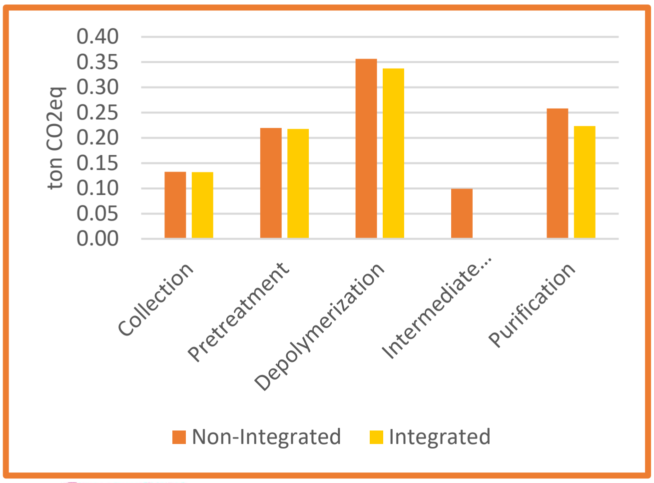
Stella Vita mobile home (University of Technology Eindhoven www.solarteameindhoven.nl)

Arkema evaluated several rMMAs samples from the latest pilot campaigns for windmill blade composite formulations (see picture below). All the composites prepared by infusion of glass fiber fabrics were shown to deliver mechanical properties identical to those based on virgin MMA.



Left: Composite specimens after polymerization **Right:** windmill blade end application ©Arkema, photograph Anthoine Fyot

WP5 – Techno-economic and environmental assessment,

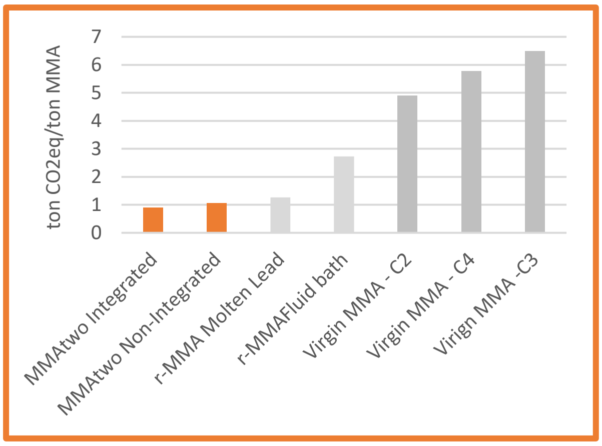


© Quantis

- The integrated process configuration (where the depolymerization and the purification are done on the same site) has 15% lower carbon footprint compared to the non-integrated configuration (where the crude MMA has to be transported)
- The difference in environmental performance is due to the avoidance of intermediate product transportation and to the heat optimization

- Compared to virgin production, there is a large impact reduction for MMAtwo (more than 75% carbon footprint) depending on the technology
- Compared to other recycling technologies, the impact reduction ranges between 20% to 60% carbon footprint

Other depolymerization technologies will be added in the future



© Quantis

MMAtwo Main events

Are you interested to contribute to the MMAtwo project or do you simply want to stay informed about all our news?

Please let us know by completing the following form

www.mmatwo.eu/contact/

MEET US THERE

- Plastic Recycling Technology, Vienna, October 19th and 20th 2021, Jean-Luc Dubois, presents the MMAtwo project.
- Next MMAtwo Workshop, May 2022
- Chemical Recycling, Cologne, June 2022

H2020
Grant Agreement N° 820687

A word from …

Helene Wiesinger, Researcher at ETHZ, Chair of Ecological Systems Design, new member of the advisory board

"To combat climate change and excessive resource use it is crucial that we learn how to make use of old materials. Be it by reusing (e.g. second-hand furniture and clothes) or by recycling (e.g. glass, metals, or some plastic products). To achieve this challenge new technologies are urgently needed, as full recyclability of many plastics remains difficult to achieve. MMAtwo is pushing for this for PMMA. I am very excited to newly be part of the process as a member of the advisory board. I am a researcher at ETH Zürich and myself involved in a project on recycling plastics (the Clean Cycle Project). In our team, we have been trying to better understand plastic additives and other impurities and their role in recycling. While there are still many open questions, I hope that we can contribute to a better understanding of how plastic additives may influence the depolymerization of PMMA and give some insights into where these substances might end up. A better understanding will hopefully help to (re)create clean starting material from waste without posing a risk

Sara Babo, Conservation scientist and Conservator-restorer of contemporary art

My recent research has been focusing on the preservation of artworks made with PMMA, which implied the characterization of acrylic sheets from the 1960s and 2000s, with different colorants, additives, and MMAs (virgin and recycled). In the conservation field, understanding the detailed material composition of an object is important to predict its long-term stability and develop preservation strategies. Surprisingly, this research could also provide interesting information for the MMAtwo project in what concerns the composition of historical PMMAs.

I have studied nacreous PMMA sheets used in the sculptures of the Portuguese artist Ângelo de Sousa (image at the right), that were produced originally for the button and cutlery industry. In all the samples from the 1960s, independent of its colour, synthetic plumbonacrite (a basic lead carbonate) was identified as the effect pigment responsible for the nacreous brilliance, while in more recent samples (2000s) the effect pigment identified was bismuth oxychloride. This alteration reflects the industry concerns regarding the toxicity of lead-based materials. For another case-study, red PMMA samples from the 1960s and 2000s were analysed; in both, cadmium sulfoselenide (cadmium red) was identified.

Awareness of the possible presence of lead and cadmium in the PMMA waste available as feedstock for depolymerisation has led the MMAtwo project to search for strategies to identify and safely eliminate these toxic heavy metals. I am looking forward to following the developments of the MMAtwo project!

Ângelo de Sousa, untitled sculpture, 1965-1967, artist collection, 29 x 47 x 25 cm. Photo by S. Babo.

H2020
Grant Agreement N° 820687