MMAtwo in position to benchmark its results with state of the art virgin and regenerated MMA

Word by Chair of Executive Board, Jean-Luc Dubois

MMAtwo is now in its last year, and already generated plenty of results. 6 patent applications have been filed by project partners, and more are to come. Several hundred kilograms of crude and regenerated (purified) MMA have been generated, and purities as high as 99.8 wt % have been repeatedly obtained thanks to the combination of the depolymerization technology and of the purification processes.

A benchmark with virgin MMA and with rMMA already on the market is now possible. Data have been collected from several plants using different technologies. Based on those, the carbon footprint benchmark is now possible. In this newsletter, we present the results from the alternative PMMA depolymerization processes, and invite the recyclers who would like to share their data to contact us. All the regenerated MMA in our survey perform better than the virgin MMA processes, but there are variations linked with the processes used, the local scraps used and the purification level required by the local market.

Recyclable

The regular reader of our newsletters might have noticed that we are talking of regenerated MMA and try to avoid to call it recycled MMA. The main reason is that we are now able to reach "virgin-like" purity. It also means that the product is good enough to be able to use our rMMA in the most demanding PMMA applications, and what we called the optical grade. Indeed, the goal has been to close the cycle (closed-loop recycling) and to be able to return the rMMA in the very same application. So Recycled should also be understood that way, but there is confusion with the Open-Loop Recycling, in which the product is used in a less demanding application.

Lately, we have seen several companies communicating on their products, claiming that they are Recyclable. Being Recyclable does not mean that the product will be recycled, nor that it is made of recycled material. It is time to define a hierarchy in the communication levels, and to give a clear definition of "Recyclable" also. It is certainly much better to be able to communicate on a product that has a high level of Recycled Content, and with the appropriate chain of custody. To be able to make high recycled content, large amounts of wastes had to be collected and processed. Creating a market for the wastes, will increase the supply and should generate virtuous cycles.

So that means that a product can be called Recyclable, only when it is fully demonstrated that it is already recycled. What is important then is that a value chain that collects, sorts, pretreats, depolymerizes (like in our case) and purifies the material is physically demonstrated and readily available. Being made of PMMA is not sufficient to claim that a product is "Recyclable", especially if it does not contain Recycled/Regenerated MMA.

The benchmark of PMMA depolymerization plants that we have conducted with the information collected from various sources, including recyclers themselves, illustrates that it is possible to purchase MMA/PMMA from different recyclers but at different purity levels. Recyclable should also mean that the product followed an eco-design process, and does not contain additives that might compromise the possibility to reach the highest MMA purities.

MMA Specifications – role of each value

In rMMA specification each value provided should be important, and be an indicator of the quality. But some values can tell more… Let's revise the information that can be derived from them.

Density: if the product is pure enough the density does not give any additional value. That's easy to measure, and should always be the value of pure MMA, and so be the same than virgin MMA. One could say that at best it confirms that it is MMA and not water.. but it is affected by impurities, and by… time. An old MMA sample will have a higher density, because some oligomerization already started slowly.

Acidity: the acidity is expressed as the Methacrylic Acid content. It is measured by titration, and then converted into a single (most likely) molecule equivalent. But obviously includes also the other organic acids, and hopefully not the inorganic acids like Hydrogen Chloride. A high acidity reveals that the scraps that have been processed were not of the best quality, but also that the purification process has not been able to solve the

issue. Methacrylic acid itself has a high boiling point, so if it is still present in the distilled product, it means that many other impurities are still there also.

Color: PMMA is marketed in many colors, and valued for its optical applications. Many different pigments are used. The crude MMA generated from depolymerization processes can be from light yellowish (see our previous newsletters) to deep dark products. Besides the pigments, the color bodies are also degradation products generated during the depolymerization process itself. Many impurities are generated in small individual amounts, and come from PMMA itself but also from other polymers contaminating the scraps. So the color of the crude and regenerated MMA are important indicators of the quality of the products. But quite often the color of the PMMA product will change over time, even though the rMMA was transparent clear. So ageing tests on the rPMMA produced are a better indicator of the quality of the rMMA.

Acrylates content: acrylates are used as co-monomers with Methyl Methacrylate, especially in formulations for injection and extrusion grades PMMA. They are important to be able to process these materials (in extruders or injection press). In the depolymerization process, they are freed from the polymer structure along the MMA. But as they are chemically and physically close to the MMA, they are hardly removed in purification processes. However, they can be repolymerized, so they can be accepted in some applications.

C4 and C5 saturated Methyl esters: they are typical impurities in rMMA. They are produced by hydrogen transfer reactions. For example, Methyl Isobutyrate is the Hydrogenated form of MMA. It cannot repolymerize. So in PMMA it will contribute to odours and to Volatile Organic Compounds (VOCs). It is therefore important to minimize their contents in rMMA. The content is an indicator of the quality of the depolymerization process, but also of the purification process. High amount of those impurities is also the sign that other impurities are present in the rMMA.

Life cycle analysis… what do we want to demonstrate

All the rMMA plants in our survey have a lower carbon footprint than virgin MMA (and that will include MMAtwo's technology). But there are other benefits in the circularity: the water consumption is also much lower. In the recycling process, water might be consumed at a washing step, but also at cooling steps only. In the virgin MMA water is consumed also for the extraction of natural resources, in addition to the process itself. The circularity of MMA avoids the extraction of valuable natural resources and not only oil and gas. In the chemical processes to produce virgin MMA some critical raw materials are used, and in the current context of the Ukrainian crisis, we need to make a special focus on Nickel and Palladium. Nickel is used in the catalyst for selective oxidation of isobutene (so-called C4-route), and Palladium is used in the catalysts for the so-called-C2 route, and Russia is a major supplier of both strategic metals. Any recycling process is then contributing to the independence versus strategic materials. Human health impact is also important, and for that indicator we track all the side products from the depolymerization process and make sure they are handled properly. From our current results it means that we do not exclude waste streams, but that some wastes generated in the depolymerization process have to be handled properly.

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

WP7: Communication, dissemination and academic outreach.

ProCoat and **Trinseo** both joined the project in October 2021 as partners not receiving funding.

ProCoat Technologies is a company with more than 40 years of experience in the development of surface treatments for metal surfaces. The last generation in surface treatments developed by ProCoat are water based, VOC´s & Cr free solutions and they are all based on acrylic polymers well known around the world under the tradename BRUGAL®. ProCoat would like to develop more sustainable solutions inside the surface treatment market. Since ProCoat develops its own polymers, they will test different qualities of recycled MMA and check the minimum purity level that would be required for surface treatments market.

Ana María Navas Arias, Chemistry Engineer at ProCoat

ProCoat joined MMAtwo project with the aim of searching for new raw materials in order to get more sustainable surface treatments. After several lab trials, we expect to replace a large amount or our virgin MMA with rMMA maintaining the performances of our products.

Trinseo is a market leader providing a wide range of products in various applications/markets, including PMMA through its subsidiary Altuglas. Trinseo will develop resins (granules/beads) and sheets (cast and extruded) based on recycled MMA from MMAtwo to evaluate and validate them for market potential.

Pascal Lakeman, Global Director Plastics and Engineered Materials R&D at Trinseo

Trinseo is very grateful to the entire consortium to have been allowed to join in on the MMAtwo consortium in the last year of the project. Obviously through our acquisition of the PMMA business of Arkema we have now put our focus on establishing a PMMA business that will be fed by waste based feedstocks instead of oil based feedstocks. Undoubtably to get there this will take still a significant amount of time and resources however our resolve crossing the many hurdles related to process development, material development and supply chain will allow us to steadily ramp up the renewable content that feeds our acrylics businesses. Again, Trinseo is super exited to collaborate and is highly appreciative of the partnerships that have already been established through this project.

Main results achieved since September 2021

WP1 - Collection of scraps and pretreatment

Within MMAtwo there is mainly a focus on end-of-life PMMA scraps and one important waste type that was tested is PMMA from the recycling of vehicles. In collaboration, Heathland and Groupe Comet extracted waste of PMMA from this source, pretreated the material to increase purity and did the required analyses. The material was then supplied to WP2 for depolymerization. As can be seen, the purity of the waste was far from 100% and did contain several detectable impurities, such as other polymer types, but also substances that cannot easily be identified. Old carlights may contain heavy metals due to colorants that could have been used. Since the age of the PMMA from this source can be very old, substances can be inside the material that have been banned since. Depolymerization will result in such substances, that were previously locked into the material, to come out of the process and therefore special precautions must be taken when processing EoL or un-identified PMMA waste.

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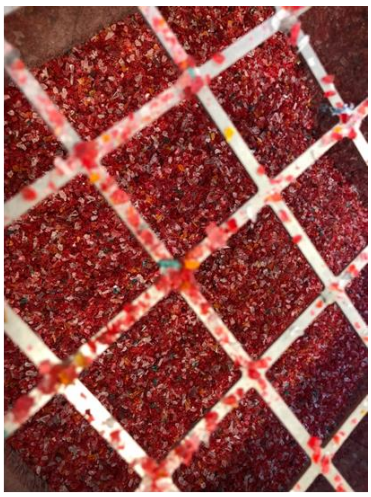
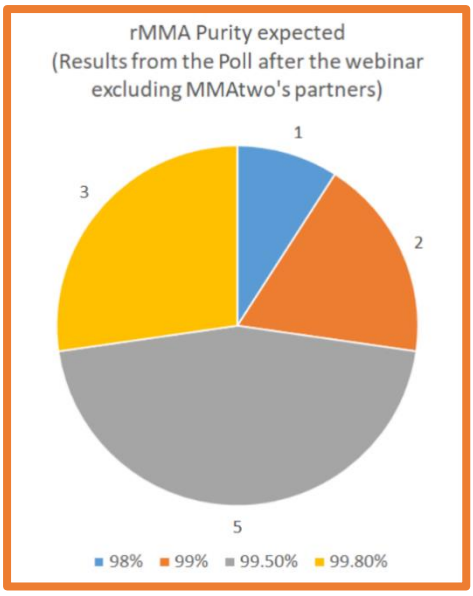
comet traitements



	Comet Traitements	
Quantity analyzed	2146 gr.	
NIR Analysis results		
Main components	%	ppm
PMMA	97,854%	978.543
PVC	0,001%	12
Trace components		
PP	0,003%	26
PS	0,019%	195
ABS	0,369%	3.694
PCABS	0,037%	371
PC	1,168%	11.684
EPDM		
Rubber		
POM	0,002%	23
PET		
Silicone	0,001%	12
PEINC	0,463%	4.626
Black (not readed)	0,083%	814
	100,000%	1.000.000

WP2 - Depolymerization

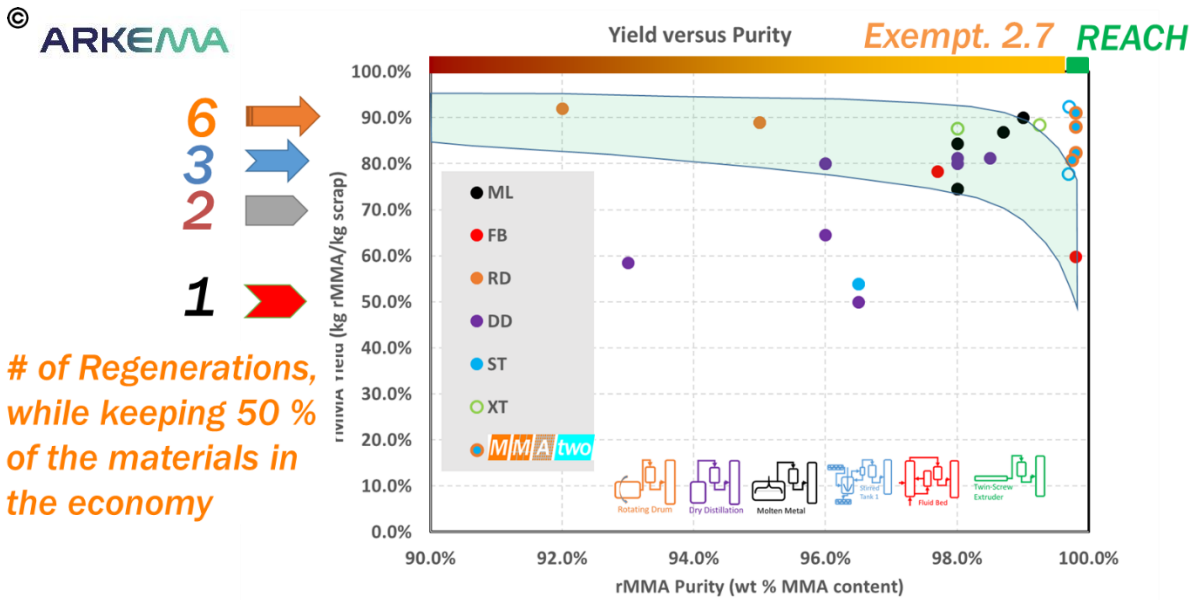
MMAtwo organized a webinar in February 2022. At the end of it, we asked the audience, which was mostly from the industry, which purity level in rMMA they would like to purchase, among 98.0, 99.0, 99.5 and 99.8 wt %. Three quarter of the replies were for 99.5 and 99.8 %. It illustrates that most of the demand is for a higher rMMA purity than what can be found on the market today. Proper scrap selection would then be needed to reach these high levels. The poll is available on LinkedIn.



An important task in the project has been to collect data from existing depolymerization plants and processes in order to feed our benchmark, and to feed the Life Cycle Analysis (see WP5). The figure below illustrate the purity and the yield achieved with different depolymerization technologies, but also processing different types of scraps. ML: Molten Lead, FB: Fluid Bed, RD: Rotating Dum, DD: Dry Distillation, ST: Stirred Tank, XT: TwinScrew Extrusion. The open symbols are from paper studies, and might not completely reflect the reality. The MMAtwo data points are from 4 different types of scraps, and illustrate the range of yields which are achievable at the best purity. At the best purity levels, the rMMA would be eligible to request a REACH registration number as the purity level is similar to the virgin ones. Below that level, the rMMA can request a REACH exemption (clause 2.7), which is in fact only an exemption of registration number. This is provided under a certain number of conditions but achievable for European plants. If the purity level is too low, it might be difficult to justify of this exemption in case of an Audit by authorities.

The figure also illustrates on the left side the impact of true circularity: at 90 % mass yield per cycle, it means that 50 % of the weight is retained in the economy after 6 regenerations (0.9^6), and so on for the lower yields. So with the best depolymerization process, more carbon can be retained in the economy and less natural resources need to be consumed.

People aware of existing facilities willing to provide data to add to the benchmark are encouraged to report to Jean-Luc Dubois (jean-luc.dubois@arkema.com) (**ARKEMA**) who is updating the mapping on regular basis.



WP3 – Purification

Due to the efficiency of the couple depolymerization/purification process and regardless of the PMMA origins, we always obtained an excellent and steady quality of rMMA.

		PMMA Scrap			
		Cast	Extrusion	Injection	Mixed Cast-Extrusion
Methyl + Ethyl Acrylates	(wt %)	<0.13	<0.02	0.06	<0.02
C4 and C5 saturated methyl esters	(wt %)	<0.03	0.06	0.10	0.087
MMA	(wt %)	99.80	99.80	99.75	99.80
Water	(ppm)	300	300	300	300
Acidity (as Methacrylic Acid equivalent)	(ppm)	<10	<10	<10	<10
Colour	(APHA)	<10	<10	<10	<10
Density at 20 °C		0.94	0.94	0.94	0.94
Stabilizer	(on demand)				

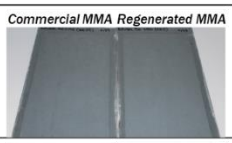
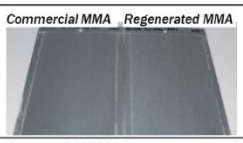
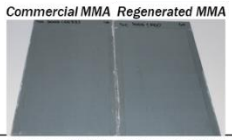
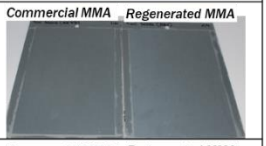
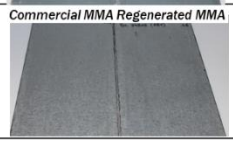
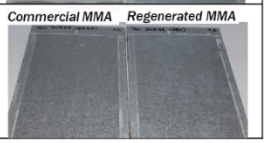
WP4 - Exploitation, End-user tests, Business analysis

Regenerated MMAs with varying purity (99,8%, 99,5% and 99%) were formulated as white and black acrylic composites for kitchen sink application by **Delta Plados** at laboratory scale. No significant difference was observed on the polymerization nor on the aspect of the end material, which shows that the manufacturing process is robust enough to accommodate moderate fluctuations in rMMA purity.

Left: white laboratory-scale applications **Right**: black laboratory-scale applications

© DELTA RESEARCH & DEVELOPMENT PLADOS TELMA THE SINK THAT BREATHES

Regenerated MMA was evaluated by **ProCoat** as replacement of commercial virgin MMA in various thin organic coating (TOC) formulations for corrosion protection. Salt spray test (SST, according to ISO 9227) and humidity test (HT, according to ISO 6270) carried out on various coated substrates evidenced no difference with rMMA after 100 hours of testing (see table with pictures).

Substrate + coating	100h SST	100h HT
Hot dip galvanised steel + BRUGAL ® TOC Cr free		
Hot dip galvanised steel + BRUGAL ® TOC Cr III		
Aluminum Zinc alloy +BRUGAL ® TOC low Cr III		

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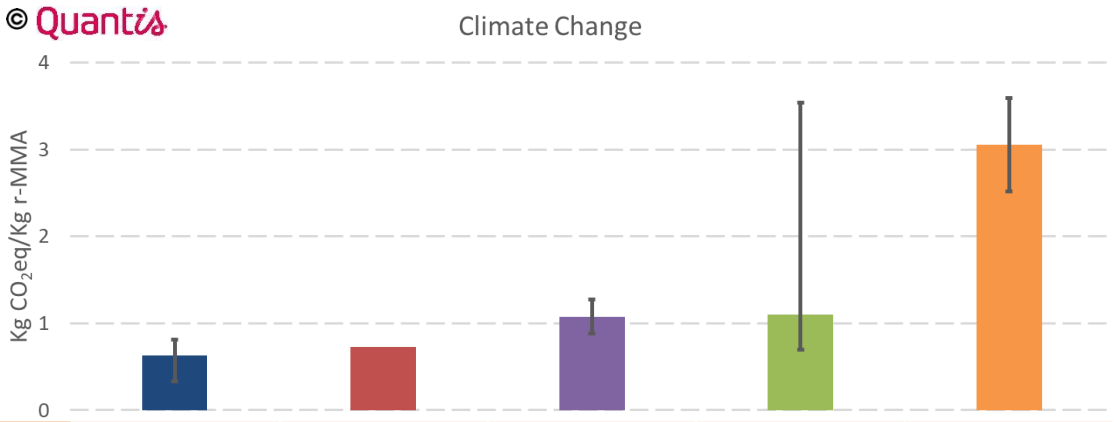
WP5 – Techno-economic and environmental assessment

Based on the benchmark data collected and processed by Arkema, **QUANTIS** has refined LCA results for benchmark technologies, grouped by depolymerization process families. The figure below illustrates the weighted average from several data sets, as well as the best and worst cases. Data are collected all over the world, with different energy mix and plant sizes.



Technology	Molten lead	Stirred tank	Rotating drum	Dry distillation	Twin fluid bed
Purity level	98%-99%	99.7%	95%	95%-98.5%	97.7%-99.8%

For the 5 recycling technologies, only 14 complete datasets out of 23 in total have been included in the LCA models. The depolymerization technologies have a carbon footprint ranging between 0.6 to 3.6 kg CO_2eq per kg of r-MMA, much lower than for virgin MMA. But not all the plants/processes deliver the same rMMA purity levels, which obviously also impact the yield and the energy consumption / carbon footprint.

Based on process design and simulation performed by **PDC**, MMAtwo partners will soon be able to test the sensitivity of rMMA environmental footprint depending on feedstock purity and operating conditions.

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

- Next MMAtwo Workshop, 12th July 2022
- Final project event, September 2022