# The characterization of recycled PMMA

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## ABSTRACT

The paper presents a study related to the possibility of obtaining polymers through the polymerization of liquid products, consisting mainly on methyl methacrylate (MMA), resulted from thermal degradation of poly(methyl methacrylate) (PMMA), at 450 °C in a laboratory scale installation. PMMA was obtained from MMA chemically recycled without any purification. The PMMA obtained from monomers resulted by thermal degradation of virgin PMMA is clear transparent; while PMMA polymerized from the liquid obtained by depolymerization of 20 years old PMMA (PMMA waste) is opaque due to the presence of impurities, which influence both the polymerization process and the properties of the obtained PMMA.

The compressive and flexural strength and Vickers hardness have been determined and closed values have been found for polymers obtained from MMA resulted through depolymerization of virgin PMMA and that from PMMA waste.

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## 1. Introduction

Poly(methyl methacrylate) (Plexiglass, Acrylic Glass), (PMMA), is widely used in many fields due to its excellent properties (transparency, lightness and safety) [1].

Recycling processes for waste plastics are classified into 3 categories: mechanical recycling; chemical (feedstock) recycling; incineration.

In Europe incineration with energy (thermal or electrical) recovery is the most largely used recycling method absorbing on average 23 wt% of the plastic waste [2–4]. Mechanical recycling covers a range of physical methods aimed at converting the polymeric residue into plastic pellets or directly into secondary plastic materials. Mechanical recycling, a generally accepted solutions cannot be applied without rigorously sorting the plastic materials [5]. Feedstock recycling, which currently absorbs only 1.6 wt% of the plastic waste, involves their transformation into chemical raw materials [6].

Laverty made a study related to mechanical recycling of mixtures of automotive thermoplastics containing polycarbonate (PC), PMMA and acrylonitrile–butadiene–styrene (ABS) showing that the presence of PMMA at a relatively high content determined inferior performance for the resulted polymers blends [7]. Later, Rybnicek et al. [8] made a study on rear lights parts containing recycled PMMA. They concluded that the transition from ductile elasto-plastic behaviour to brittle linear elastic fracture behavior takes places for the PC/ABS/PMMA blend at 10% PMMA.

A solvent technique for the recycling of PMMA decorative sheets [9] or PMMA molding compounds [10] was studied by Gouli et al. The process comprises the dissolution of the sheets in toluene, reprecipitation by n-hexane, washing and drying.

Breyer and co-workers [11–13] used a twin-screw-extruder to heat up PMMA beyond depolymerization temperature.

Feedstock recycling seems to be the best options, since by thermal degradation a large quantity (>90 wt%) of monomer (methyl methacrylate—MMA) is produced. PMMA is one of few cases in which feedstock recycling of plastics lead to products in an economic way [14], because of high yield of monomer recovered and because PMMA have a relatively high price, compared to other plastics [1].

Studies related to PMMA degradation were made using different type of installations [14]. Molten metal (lead [14] or tin) baths were used in order to assure a good heat transfer, but unwanted toxic organometallic compounds were found in the gaseous phase. Lead has been also found in the recovered monomer. Newborough et al. [15] and Smolder and Baeyens [16] presented another important

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disadvantage of using Pb as Melting bath for PMMA pyrolysis, such as the high consumption of energy.

The use of sand in fluidized bed installations overcomes this problem assuring also a good heat transfer and a uniform temperature in the reaction chamber [16–19].

In order to decrease the degradation temperature; Xi et al. [1] used various sulfates as catalysts and established that the order of their catalytic capability is: $Fe_2(SO_4)_3 > Al_2(SO_4)_3 > MgSO_4 > CuSO_4 > BaSO_4$.

The thermal degradation of PMMA and poly(2-methacrylamidopyridine) blends was investigated by Coskun et al. [20]. Thermal degradation of the 1:1 (w/w) blend has produced both monomer in lower percentages and 2-aminopyridine in higher percentages in comparison with those of the homopolymers.

Achilias [21] made a study related to the polymerization of recovered MMA obtained by chemical recycling in a laboratory fixed bed reactor filled with glass and concluded that the liquid fraction taken from the pyrolysis of PMMA, can be use directly as a raw material for the reproduction of the polymer [21]. Small amounts of other organic compounds included in this fraction act as potential non-ideal reaction retarders, lowering the reaction rate as well as the glass transition temperature and the average molecular weight of the obtained polymer. Literature [21] indicates that the MMA obtained by thermal degradation of PMMA must be purified by distillation in order to be used as raw material for new PMMA.

The aim of this paper is to establish if MMA obtained by depolymerization of PMMA waste can be used for the obtaining of new PMMA, without any purification before polymerization. As far as we know, in all the published paper the necessity of MMA purification after pyrolysis is presented. Investigations of some of the properties of recycled PMMA obtained from recovered MMA are also presented.

## 2. Experimental details

A bench laboratory scale installation for PMMA thermal degradation has been used for the recovery of MMA. The bench installation consists on a glass vessel electrically heated connected through an air condenser to an ice trap.

Twenty grams of PMMA were subjected to thermal degradation at 450 °C. Virgin PMMA samples with grains smaller than 0.5 mm and pieces of more than 20 years old used PMMA from a PMMA panel, with dimensions varying from 5 to 15 mm were used.

Thermal degradation of PMMA has been made with or without a Melting Sn bath. The vapours were condensed with an air condenser. Liquid phase was collected in previously weighted jar cooled in water—ice trap. Remained uncondensed phase was released to the vent.

FTIR analyses of the PMMA degradation products were performed on KBr pellets by using a PerkinElmer FTIR Spectrometer.

The composition of PMMA degradation products was analysed by GC–MSD (GC: Agilent 6890N; MSD: Agilent 5975 inert XL) on a HP5-MS column using a 100:1 split ratio, 1 ml/min He flow and the following temperature program: 35 °C (2 min); 10 °C/min > 300 (7 min). Quantitative analysis of the main MMA peak in PMMA degradation products was obtained from GC–FID analysis performed under similar conditions as GC–MSD.

A prepolymer was prepared from MMA by slow heating to 70 °C in water bath using 1% lauryl peroxide as initiator. After exothermal polymerization reaction begins the temperature was maintained at 92 °C in order to increase the viscosity. Then the reactor content was cooled in cold water and kept into the refrigerator in order to be used. For specimen preparation 1% benzyl dimethyl cetal was added to the prepolymer. The obtained viscous material was poured in Teflon moulds and polymerized using a Doctor Hölne Sol 2 ultraviolet lamp.

For mechanical tests an Instron Universal Testing Machine (LOYD) was used. For the determination of Vickers microhardness a Carl Zeiss Jena instrument equipped with a Neophot 21 Microscope was used.

Visible transmission and reflection spectra have been determined with a PerkinElmer Lambda 35 UV–VIS Spectrophotometer.

The morphology of the samples was studied using a Philips XL30 ESEM Scanning Electronic Microscope and the structures have been determined using a 6000 Shimadzu Diffractometer, with a monochromator of graphite for Cu Kα radiation ($\lambda = 1.54$ Å) at room temperature.
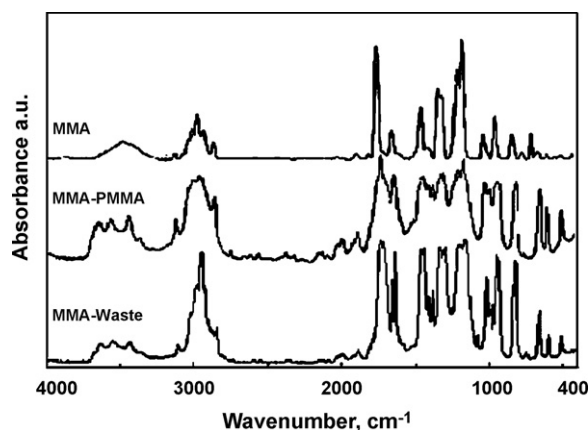


Fig. 1. FTIR spectra for MMA–COM, MMA–PMMA and MMA–waste.

## 3. Results and discussions

In the first stage the influence of using melted Sn bath was investigated for thermal degradation of PMMA waste. The yield of liquids formed decreased from 97% (without Sn bath) to 95% (using Sn bath). The quantity of heat accumulated in melted Sn was quickly released to PMMA waste. The amount of formed vapours was high and probable a part of vapours were not condensed. The quantity of carbonaceous mass remained in the reactor was higher when using melted Sn bath.

In the case of fine PMMA grains the yield in liquid degradation products was smaller (90–94%), than in the case of PMMA waste cutted in pieces. During heating PMMA tends to melt and then starts to decompose in vapour products. The evolution of vapours is faster for PMMA waste because the pieces do not form a compact melted PMMA mass, as in the case of PMMA grains.

After pyrolysis a small quantity of carbonaceous solid mass remains in the reactor. The amount of carbonaceous phase was higher in the case of PMMA powder neat than in the case of PMMA waste cutted in pieces.

The FTIR spectra for commercial MMA (MMA–COM), MMA obtained from virgin PMMA (MMA–PMMA) and MMA obtained from PMMA waste (MMA–waste) are presented in Fig. 1. The recording of MMA spectra was difficult because MMA tends to polymerize during analysis even if small amounts of inhibitors (hydroquinone) was added to the sample.

In Table 1 the assignment of some Absorption bands are presented.

One can remark that all samples have the same main adsorption peaks.

The shifting of some peaks towards higher wavelengths for MMA obtained through pyrolysis can be explained both by the formation of polymer during analysis and by the presence of some impurities.

**Table 1**
The assignment of some absorption bands for MMA–COM, MMA–PMMA, MMA–waste [22].

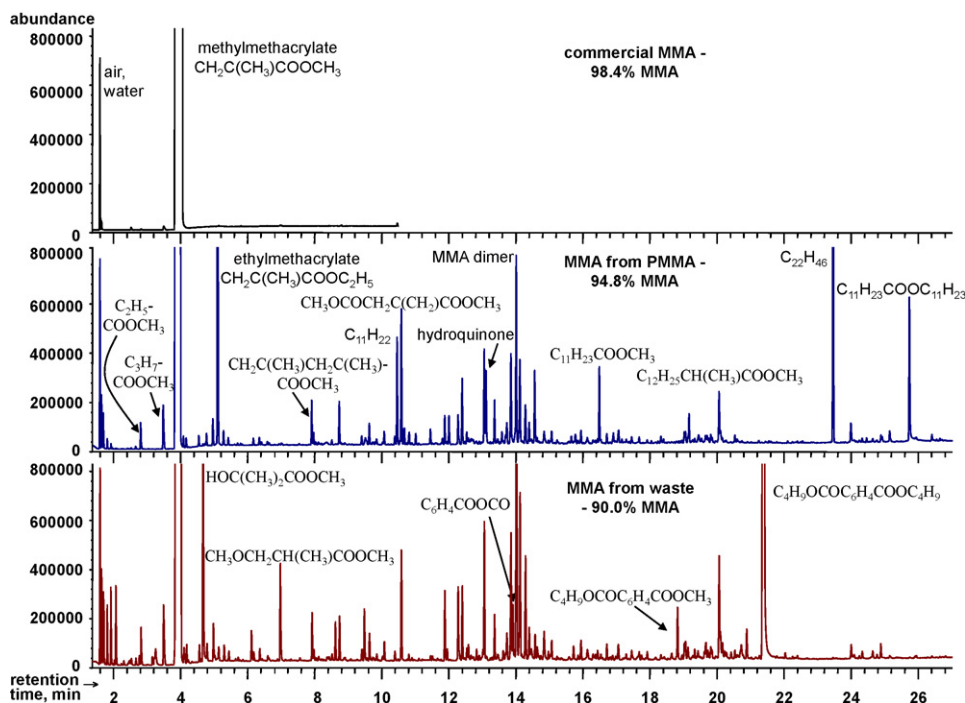| Group | Wavenumber [cm⁻¹] | | |
|---|---|---|---|
| | MMA–COM | MMA–PMMA | MMA–waste |
| Carbonyl stretch C=O | 1746 | 1724 | 1726 |
| Double bound C=C, C=O stretch | 1638 | 1638 | 1639.2 |
| C H bending | 940 | 941 | 942 |
| —C—O, C—H stretching, $OCH_3$ | 1444 | 1438 | 1437 |
| $CH_2$ stretching, C—H asymmetric | 2964 | 2955.4 | 2955.4 |
| Methyl $CH_3$ | 1329 | 1326 | 1326 |
| C—O—C, C—O ester | 1272–1147 | 1272–1147 | 1272–1147 |

**Fig. 2.** GC–MSD chromatograms for MMA obtained from virgin PMMA and for MMA obtained from waste (amounts of MMA calculated form GC–FID).

The peaks from 3250–3750 cm$^{-1}$ correspond to some impurities, as identified using GC–MSD.

GC–MSD chromatograms of PMMA degradation products are presented in Fig. 2.

Methyl methacrylate at retention time (Rt) of 4 min is the main product from thermal degradation of PMMA (more than 90 wt%), being obtained in smaller amounts from waste PMMA compared than from virgin one. Other significant compounds from thermal degradation of virgin PMMA were ethyl methacrylate (Rt of 5.1 min) and methyl methacrylate dimer (Rt of 14 min), accompanied by MMA and its dimer derivatives (Rt of 2.8, 3.5, 7.9 and 10.6 min). Undecene was found at Rt of 10.5 min, accompanied by its dimer at Rt of 23.5 min (found in high amount of 3% GC–MSD area) and by its ester derivatives at Rt of 16.5, 19.1 and 25.8 min.

Hydroquinone was found at Rt of 13.1 min in the chromatogram of degradation product from virgin PMMA but it was not found in the case of waste PMMA; probably hydroquinone leaved the PMMA material during its service use.

MMA dimer was also obtained in significant amounts beside MMA from thermal degradation of waste PMMA; however ethyl methacrylate was not observed and the main MMA ester derivatives (Rt of 4.7 and 7.0 min) have different structures than for virgin PMMA degradation oils. Phthalic anhydride was found at Rt of 13.9 min, dibutylphthalate at RT of 21.4 min being the second degradation product of waste PMMA (20% GC–MSD area), accompanied by methylbutylphthalate at Rt of 18.8 min.

In order to characterize the obtained PMMA cylindrical specimens (4 mm diameter, 8 mm length) were obtained in Teflon moulds by photopolymerization, for compressive strength (CS).

The time of polymerization was 5 min for MMA obtained from MMA grains, but increased to 10 min for MMA obtained from PMMA waste. The impurities of MMA recovered from PMMA waste acts as a polymerization inhibitors, as Achilias has shown in a recent paper [21].

In Table 2, the results for the strength and hardness tests are presented.

In the case of PMMA recovered by depolymerization of PMMA the CS is smaller than the CS of PMMA obtained by polymerization of liquid products of thermal degradation of PMMA waste. It seems that the impurities from recovered MMA (and their polymerization products) play the role of plasticizer in the obtained PMMA, leading to higher CS.
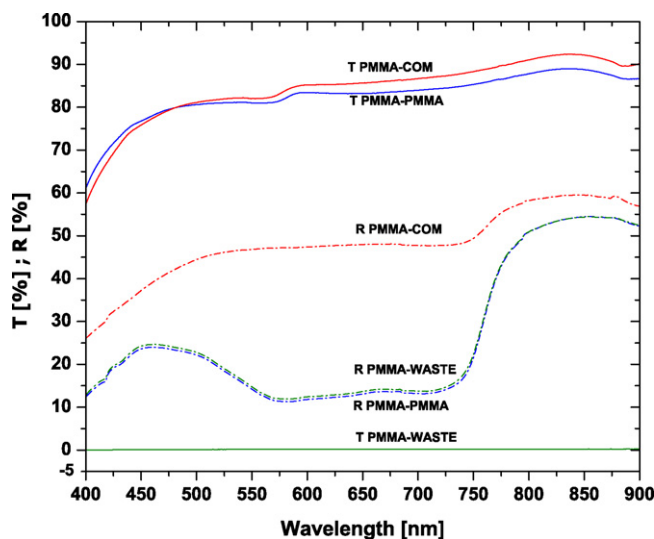
**Table 2**
The results for the strength test of recycled PMMA samples.

| Sample | PMMA from PMMA | PMMA from waste |
|---|---|---|
| Compressive strength [MPa] | 137.46 | 191.35 |
| Flexural strength [MPa] | 50.25 | 51.00 |
| Vickers hardness [MPa] | 425.6 | 365.4 |



**Fig. 3.** VIS transmission (*T*) and reflection (*R*) spectra of PMMA samples.
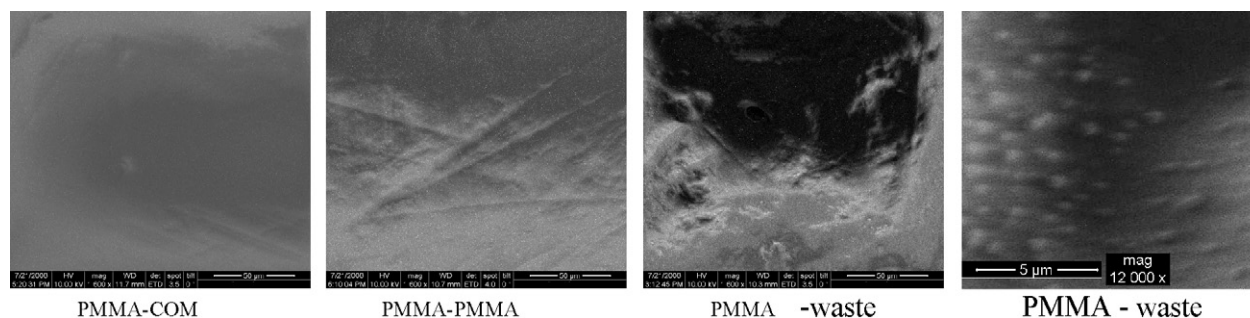
**Fig. 4.** SEM micrographs of PMMA samples.

The values obtained for the two samples for flexural strength are very close. We presume that the difference can be attributed to some experimental errors.

Even if the differences of concentration of MMA in the samples of MMA recovered by thermal treatment through depolymerization of commercial PMMA and PMMA waste is of about 4%, optical properties of the polymer obtained through polymerization is different. The sample obtained by the polymerization of MMA–PMMA is perfectly transparent and clear resembling to the PMMA obtained using virgin MMA. The samples have a slightly yellow shade due to the used initiators. The polymer obtained using MMA–waste is almost opaque, having a butter yellow colour. In order to record VIS transmission spectra (Fig. 3) for the samples presented in Table 2 specimens of 2 mm thick PMMA were prepared.

The sample obtained from new PMMA has a good transmission in visible while the sample obtained from degraded waste have no transmission.

SEM micrographs (Fig. 4) revealed that the impurities from the monomers have influenced the microstructure of the polymers. New PMMA have a uniform morphology. PMMA obtained from PMMA grains is almost uniform (MMA–PMMA), but the PMMA obtained from PMMA waste (MMA–waste) contain big aggregates than can cause light scattering. Increasing the magnification it can be seen that PMMA waste contains very fine (0.5 μm) bubbles, increasing the phenomena of light scattering.

XRD diffraction pattern (Fig. 5) revealed that all the samples have a highly disordered amorphous structure.

Reflection spectra (Fig. 3) showed that PMMA waste reflects for about 47% of the light for wavelengths of 560–780 nm contributing to the decrease of the transmitted light, while for the other samples the reflectance is of 15–25% for the same wavelengths.
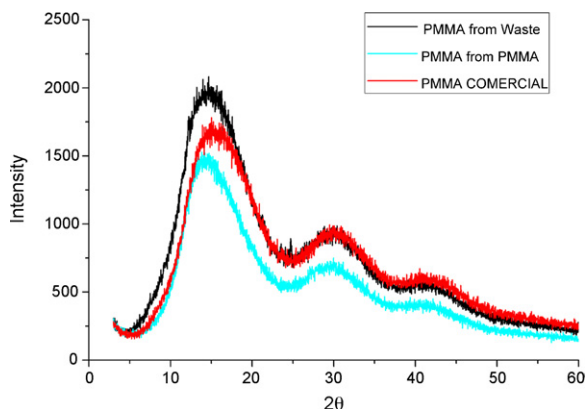
## 4. Conclusions

The possibility of chemical recycling of PMMA by thermal degradation of waste material followed by polymerization of the recovered MMA to obtain new PMMA resins has been studied. Optical and mechanical properties of the recycled PMMA have been determined.

Thermal degradation of PMMA leaded to about 97 wt% liquid products that contain about 98.4% MMA when virgin PMMA was used and 90% when waste PMMA was degraded. The other degradation products of PMMA consist of MMA esters and dimer derivatives. These impurities in recovered MMA retarded the polymerization compared with pure MMA.

The impurities from sample obtained from PMMA waste improve the compressive strength of the obtained PMMA, comparing to virgin PMMA.

MMA obtained by depolymerization from PMMA old waste is opaque due to the presence of impurities, while PMMA obtained trough the depolymerization of PMMA virgin grains is optically clear and transparent, having the same aspect as PMMA obtained from commercial MMA.

The MMA obtained by thermal degradation in air at 450 °C can be used for the production of PMMA parts for other applications than the usual one because the optical properties differ from the properties of virgin PMMA. The applications must be in concordance with their optical and mechanical properties.

### Acknowledgement

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**Fig. 5.** XRD patterns for PMMA samples.

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