

# Research on the physical modification of PMMA-PO waste

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## Introduction

Because of a high production and wide use of polymer materials, currently the amount of waste and used constituent materials on rubbish dumps is increasing. The biggest amount of waste from polymer materials is supplied especially by the packaging industry, building industry, electrical engineering, automotive industry and agriculture [1, 2]. In accordance with the current environment protection requirements, the created waste should be useful for energy, material, chemical and organic recovery. The important notions related to environmental protection are regulated by the Directive of the European Parliament 94/62/EC on packaging and packaging waste. This directive has obligated all the EU countries to obtain proper levels of packaging waste recovery up to the year 2001. Recycling has been specified as the preferred recovery method. The level of packaging waste specified in the directive was 25%, and Poland was to reach it in 2007 – after the transitional period. In 2004 the European Parliament passed the 2004/12/EC Directive, amending the directive from 1994 on packaging and packaging materials. In 2005, a further amendment of the 94/62/EC Directive occurred – the passed 2005/20/EC Directive introduced the obligation to obtain (by Poland, among other countries) by the end of 2014 a level of packaging waste recovery at a level of min. 60%, and recycling – min. 55%, including 22.5% part by weight for plastics (taking into consideration only such material that is recycled again into a material re-used for obtaining plastic). The general aim of these rules is to aim at the limitation of the disadvantageous impact of packaging materials on the natural environment, i.e. the emission of harmful substances to the atmosphere and the pollution of waters and soils [3].

Requirements pertaining to packaging materials have been detailed in suitable norms issued by the European Normalization Committee in 2000. In 2002 they have been legislated as Polish norms. They specify the evaluation criteria and procedures related to the specification of usefulness for recycling [4].

The amount of recycled and re-used plastics is constantly rising in all European Union countries. The recycled polymer materials are used in the production of articles manufactured generally from original materials, as well as for substituting other materials in some applications. Very often, waste polymer materials constitute various mixes. It is important that the used up mixed polymer materials allow for the production of secondary materials with accepted properties, which in turn will eliminate long-standing and costly segregation processes. This process is currently based on an initial segregation performed by the customer, as well as on the manual or automatic processes which follow, performed by a recovery plant of polymer materials. The mechanical properties of such polymer materials are considerably lower than those of its specific components because the majority of polymers are incompatible and they create a multicomponent system in which the specific phases do not show a considerable adhesion. The obtaining of new compatible mixes provides the possibility of recovering polymers from waste mixes. Thanks to this, the cost of obtaining the product will be considerably lower than in the case of using “pure” materials, and will also allow for the obtaining of plastics with other, better mechanical or physical properties. With regard to a huge increase in post-consumption polymer material waste, this has a huge impact on environmental protection and industrial economy.

Out of the conducted literary studies it stands that obtaining new mixes is currently one of the more important fields of studies. Generally, polymers create immiscible systems composed of a dispersed and dispersoid phase (base). The way to improve the mutual miscibility and interfacial adhesion of polymer materials is to add a compatibilizer to the polymer mix. Adding a compatibilizer (homogenizing agent) to the system allows for controlling the mix's properties by steering the dimensions of the dispersed phase and adhesion at the interphase [5 ÷ 11]. In order to fulfill its role, the compatibilizer should be constructed from two blocks with different chemical properties. Each block should mix with another mix component and should be similar to it in terms of the chemical structure [8 ÷ 11].

The miscibility of polymer materials is improved also by adding a block or graft copolymer containing miscible blocks with specific constituents of the polymer mix [6 ÷ 8, 11].

## Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is a commonly used constructional plastic. It is characterized by very good optic properties, especially by a high permeability of visible light (approx. 92%) and ultraviolet radiation (approx. 50-70%). PMMA is often used as a material for cabin housings, windows (so-called organic glass) and fairings in airplanes, helicopters and gliders. It is widely used in the production of dashboards, navigation and measurement device housings, etc. [14]. PMMA does not have a harmful impact on the human body. This polymer is used in orthopedic cement, dental fillings and contact lenses [15].

PMMA is obtained as a result of mass, emulsion, suspension and solution polymerization in the presence of radical initiators. The industrial obtaining methods pertain solely to the production of an atactic PMMA [14].

From the point of view of construction applications, the most important thing is the obtaining of PMMA granulates via a suspension method, as well as shaping half-products of panels, panes and bars via mass polymerization. PMMA granulates are processed for ready-made products with the use of injection and extrusion molding. Half-products extruded in the form of panels are processed for readymade products via sub-atmospheric pressure heat forming and, more rarely, pressing, and also with the use of a mechanical, machining and bonding processing through gluing and welding [16].

The diversification of processing techniques and numerous application fields of PMMA is mirrored in the diversity of postproduction and after-utility waste.

Poly(methyl methacrylate) as a thermoplastic may be re-used through mechanical (material), chemical (raw material) and energy (thermal) recycling.

PMMA is one of the few polymers fulfilling the requirements of chemical recycling and it may be depolymerized with an efficiency close to 100%. As a result of temperature increase, PMMA is decomposed almost entirely to a monomer. The heat decomposition of polymer macromolecules is the reversal of the polymerization reaction [16 ÷ 18]

The material recycling of poly(methyl methacrylate) involves size reduction, melting and re- using the reduced PMMA. Postproduction waste such as the majority of thermoplastic waste may be mixed in

Table 1

Compounded composition of polymer mixes

Sample No.	PMMA %	PE I %	PE 2 %	PP %	EMA-GMA %	EBACO %	EMA %
I	9		89			I	I
II	9			89		I	I
III	8		88			2	2
IV	9	89				I	I
VI	24	74				I	I
VII	4			94		I	I
VIII	19			79		I	I
IX	9	89			2		
X	9			89	2		
XI	9		89		2		
XII	24		74		2		
XIII	19	79			2		
XIV	49	49			2		
XV	49			49	2		
XVI	49			49		I	I
XVII	49		49		2		
XVIII	49		49			I	I

small amounts with the original material and used, e.g. for the extrusion of panels [16]. During the processing of thermoplastic waste, the following phenomena occur: the reduction of molecular weight, oxidization, thermal mechanical fragmentation of macromolecules and other phenomena causing the deterioration of the processed polymer materials' properties. As a result of further processing, the mechanical and optical properties of poly(methyl methacrylate) deteriorate.

PMMA waste is used also in the removal of old paints from the painted surfaces. The size-reduced poly(methyl methacrylate) waste used in the air stream has turned out to be a soft abrasive that removes the paint layer without damaging the painted surface.

### Physical modification of PMMA/PO

For testing purposes, poly(methyl methacrylate) (PMMA), polyethylene (PE) and polypropylene (PP) waste was used. PMMA waste originated from the recovery of tail lights from cars. The collected PMMA waste was reduced in size. Polyethylene agglomerate waste, made from different types of packaging membrane waste, as well as polypropylene waste in the form of grinding was obtained from companies dealing with the recycling of after-utility polymer materials. The following compatibilizers were selected for testing mechanisms which favor the obtaining of ternary PMMA/PO systems:

- EMA-GMA – ethylene-methyl acrylate-glycidyl methacrylate (Lotader AX8900)
- EBACO – ethylene copolymer-butyl acrylate-carbon oxide (Elvaloy HP661)
- EMA – ethylene-methyl acrylate (Elvaloy I335EAC)

The compounded composition of polymer mixes has been presented in Table 1. Polymer mixes have been prepared at a station for modifying polymer materials in the process of concurrent extrusion BTKS 20/40D (temp. of the cylinder zones and extruder head 190-210°C, rotation speed of screws 250-300 rpm). From the granulates obtained at the extruder samples were prepared through an injection method at the Battenfeld Plus 35/75 injection molder (temp. of cylinder zones 210°C, temp. of head 215°C, injection pressure 110 Ba, holding down pressure 90 bars, temp. of the mould 25°C).

The examination of mechanical properties has been carried out on an INSTRON D 7418 TM-M testing machine, according to standard PN-EN ISO 527-1:1998 "Plastics. Determining the mechanical properties with a static stretching. General information" (working speed: 50 mm/min, sample length – 50 mm, sample width – 10 mm, thickness – 4 mm). The impact strength testing was carried out according to standard PN-EN ISO 179-1:2004 "Plastics. Determining the impact strength according to a Charpy impact test. Non-instrumental impact

Table 2

Results of mechanical properties' tests

Sample No.	esistance to tensioning	Unit elongation with a break	Notched impact strength
	MPa	%	kJ/m <sup>2</sup>
	Wartość średnia	Wartość średnia	Wartość średnia
I	21,7	13,8	1,1 (C)
II	33,5	17,4	1,5 (C)
III	21,5	15,9	1,3 (C)
IV	12,3	246,8	N
V	11,2	1,4	1,12 (C)
VI	35,3	12,8	3,14 (C)
VII	34,4	10,9	1,95 (C)
VIII	13,3	264,0	N
IX	33,9	12,4	2,47 (C)
X	23,3	70,0	1,37 (C)
XI	19,6	8,0	1,26 (C)
XII	14,9	70,5	0,53 (C)
XIII	27,8	5,2	1,78 (C)
XIV	35,2	4,2	1,52 (C)
XV	38,2	5,0	0,98 (C)
XVI	23,2	2,7	0,62 (C)
XVII	25,9	3,3	0,62 (C)

Notched impact strength has been marked additionally:

N- lack of break C- total break, H –hinge break

Table 3

Results of physical properties' tests

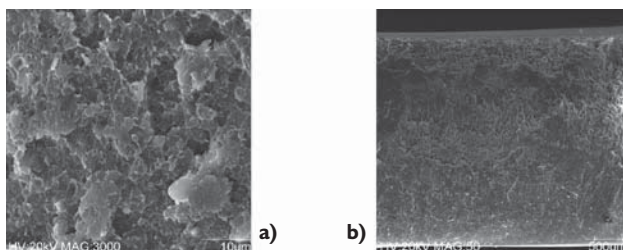
Sample No.	MFR g/10min	Density g/cm <sup>3</sup>
I	19,2	0,941
II	7,8	1,024
III	18,0	0,988
IV	2,8	0,987
V	0,2	1,100
VI	10,9	0,910
VII	11,0	0,920
VIII	1,9	0,970
IX	8,2	0,924
X	6,4	0,961
XI	3,4	0,979
XII	0,4	0,964
XIII	0,3	1,038
XIV	3,6	1,002
XV	5,5	1,002
XVI	0,8	1,033
XVII	1,3	1,031

strength testing" (sample length – 80 mm, sample width – 10 mm, profile type – I, notch type – A, impact direction – edgewise, hammer – 4J). The testing of thickness was carried out via the immersion method A, in accordance with norm PN-EN ISO 1183-1:2006 "Plastics. Methods of determining the thickness of non-cellular plastics. Part I. Immersion method, liquid pycnometer method and titration method". The determination of mass flow ratio has been performed in accordance with norm PN-EN ISO 1133:2006 "Plastics. Determining the mass flow ratio (MFR) and the mass volume ratio (MVR) of thermoplastics". The marking was performed on an AS Plastometer – 108, with a nozzle diameter of 2.095 mm.

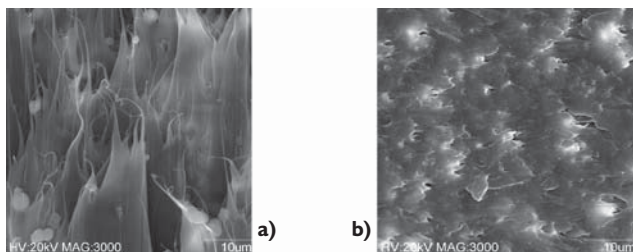
The obtained results of physical and mechanical properties of the obtained blends have been presented in Tables 2 and 3.

The structure of obtained mixes has been observed also through an SEM method. In a scanning electron microscope, the surface of the profile fracture of the created mix of plastics has been analyzed according to the following criteria: the samples were covered with a thin layer of technical gold in a vacuum evaporation machine, in case of differences resulting from macroscopic observations of various sample fractures, SEM microphotographs have been made for each sample from 2 fractures (A, B).

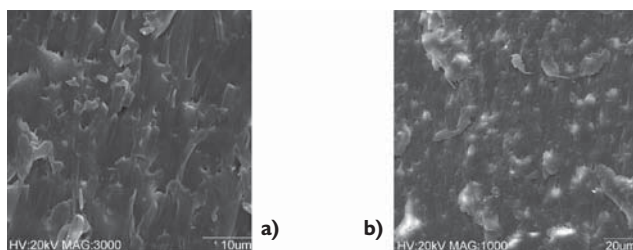
Figures 1 ÷ 3 illustrate exemplary microphotographs of the examined mixes.



**Fig. 1. SEM microphotographs of mix fractures:**  
 a) PMMA0/EMA-GMA(90/10) - sample XVII  
 b) PMMA1/PP/EMA-GMA(49/49/2) - sample XV



**Fig. 2. SEM microphotographs of mix fractures:**  
 a) PMMA1/PE/EMA-GMA(9/89/2) - sample XI  
 b) PMMA1/PE/EMA-GMA(49/49/2) - sample XIV



**Fig. 3. SEM microphotographs of mix fractures:**  
 a) PMMA1/PP/EMA-GMA(49/49/2) - sample XV,  
 b) PMMA1/PP/EBACO/EMA(49/49/1/1) - sample XVI

## Discussion of results

For testing poly(methyl methacrylate) PMMA and polyolefin (PO) mixes, PMMA was used in the form of waste from tail light housings obtained via the injection method. Also, polyolefin waste (marked as PE1, PE2 and PP) was used.

These materials differ considerably from each other with regard to their usefulness for further processing via an extrusion and injection method.

When evaluating the results of physical and mechanical properties' tests of injection profiles made from mixtures of PMMA waste with polyolefines and compatibilizers type EMA-GMA, EBACO and EMA, it was stated that the PMMA/PP mixtures have a higher tensioning resistance than PMMP/PE mixtures. This is a result of the higher resistance of polypropylene itself.

Furthermore, when comparing the resistance test results of mixtures with comparable PMMA portions with an EMA-GMA compatibilizer and mixtures with EBACO and EMA compatibilizers, it was stated that the injection profiles from mixtures with the presence of EMA-GMA have a slightly higher resistance to tensioning and notch impact resistance.

In the mixes, the size of interfacial connections is such that in the sample fractures increased 3,000 times the heterophase structure is not present. Dispersed polymers may create mutually permeating microphases.

## Conclusions

The testing program in this paper has been specified with regard to managing PMMA waste with polyolefin waste of various origins.

After examining the injection profiles in the tested mixes, no improvement of mechanical properties was stated with regard to the properties of specific initial polymers.

Tests of resistance properties during tensioning and bending constitute a source of information regarding the construction properties of plastics. It is known that because of the lack of miscibility of polymer mixture components, a deterioration occurs of the breaking tensioning and impact strength, while in conditions of favorable interfacial impacts an additivity or synergism of these properties occurs. The low impact strength considerably limits the scope of using the polymer material. One must also bear in mind that the processing of PMMA waste via an extrusion and injection method has a problem-free application only with regard to variations of PMMA synthesized especially for these techniques.

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