

Low loss poly(methyl methacrylate) useful in polymer optical fibers technology

Pawel Mergo*, Malgorzata Gil, Krzysztof Skorupski, Jacek Klimek, Grzegorz Wójcik, Janusz Pędzisz, Jaroslaw Kopec, Krzysztof Poruraj, Lidia Czyzewska, Aleksander Walewski, Andrzej Gorgol

*Laboratory of Optical Fibre Technology, Maria Curie-Skłodowska University,
Pl. Skłodowskiej 3, 20-031 Lublin, Poland*

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Abstract — The paper presents comparison of thermal and optical properties of the typical commercial available and manufactured in our laboratory poly(methyl methacrylate) polymer useful in polymer optical fibers technology. The thermal studies were made by thermogravimeter connected on-line with FT-IR and QMS spectrometer, the optical properties were characterized by spectral attenuation measurements. It was found that polymer obtained in our laboratory is characterized by higher temperature (about 100°C) of beginning mass loss occurred and lower attenuation than commercial available polymer.

Microstructured optical fibers (MOFs) provide extra degrees of freedom in manipulating the optical properties of light, such as dispersion, nonlinearity, and birefringence [1-5]. Therefore they have attracted increased interest over the last two decades. Due to specific material properties, the technology of microstructured polymer optical fibers (mPOF) has been intensively developed in recent years. Polymer fibers may show better parameters than fibers made of silica glass in a variety of applications. One of the advantages is biological compatibility, which opens the possibility for medical applications. Moreover polymers have higher flexibility than silica glass, therefore can withstand much higher strains, which enables applications of polymer fibers as elongation sensors in a strain range unattainable for silica fibers [6]. In order to obtain a polymer optical fiber with the proper optical characteristics, it is necessary to prepare specific preform from which optical fibers are drawn or extruded. Now polymer optical fibers are mainly manufactured from poly(methyl methacrylate) PMMA (linear polymer), produced by the polymerization of methyl methacrylate. Unfortunately the main disadvantage of “PMMA optical fibers” is their very high losses, in comparison with “silica fibers”, mainly caused by C-H bonds and impurities. In this letter we present the low loss poly(methyl methacrylate) polymer manufactured in our Laboratory. The manufactured from our polymer mPOF was characterized by significant decrease of the losses.

* E-mail: pawel.mergo@poczta.umcs.lublin.pl

A sample of “our PMMA” was prepared from methyl methacrylate (ALDRICH). In polymer technology two methods of polymerization are used – thermal and photopolymerization. The chemical reaction, essentially, takes place in the same way, except the source of initiation. Due to the crosslinking of the polymer during photopolymerization, this technique is not used in the polymer optical fibers technology. A very important issue in the production of materials for optical applications is their purity. Even a small amount of impurities can significantly decrease the transmission properties of the final product such as an optical fiber. Therefore, MMA was purified before starting the process of polymerization. The purification is performed by distillation process in under pressure conditions getting rid of impurities as well as undesirable inhibitor, which is added to prevent the initial process of prepolymerization of methyl methacrylate. The initiator benzoyl peroxide (ALDRICH), which was also purified before the use, and chain transfer agent thioglycolic acid (98% ALDRICH) were used in thermal free radical polymerization of examined samples. Sample was prepared as described in [7].

In order to demonstrate the advantageous properties of the PMMA obtained in our Laboratory compared to the commercially available PMMA, a comparison of thermogravimetric (TG), spectroscopic (MS and FT-IR) and optical analysis both polymers was made. The chemical composition of the “our” sample consisted of: methyl methacrylate, benzoyl peroxide (0,4% w/w) and thioglycolic acid (0,8% w/w) which were used as an initiator and as a chain transfer agent respectively.

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Selb, Germany) under the following operational conditions: heating rate 10°C min⁻¹, a dynamic atmosphere of helium (40mL min⁻¹) in the temperature range of 40°C–600°C, sample weight of about 10 mg, sensor thermocouple type S TG-DSC. The identification of a gas composition coming out during depolymerization and decomposition process were detected and analyzed by quadrupole mass spectrometer QMS 403C Aëolos

(Germany) as well as FT-IR spectrometer Brucker Tensor 27 TGA 585 (Germany) coupling on-line to STA instrument. The QMS was operated with an electron impact ionizer with energy 70eV. The FT-IR spectrometer with IR cell maintained at 200°C was connected on-line to STA instrument by transfer line evolved gases from TGA to the FT-IR with diameter of 2mm heated to 200°C. The FT-IR spectra were recorded in the spectral range of 600–4000 cm⁻¹ with 16 scans per spectrum at a resolution of 4 cm⁻¹. The optical properties of both “our” and commercial polymers were characterized by spectral attenuation measurements.

Both samples were subjected to thermogravimetric analysis, based on which it was possible to analyze the initial weight loss temperature and decomposition temperatures. The analysis was performed in two ranges of weight loss: 0.01%w/w – 0.05%w/w (Table 1) and 1% w/w – 5% w/w (Table 2).

Table 1. Determination of weight loss temperature from 0,01w/w% to 0,05w/w%.

Sample	Weight loss [%w/w] and temperature at which it occurs [°C]				
	0.01	0.02	0.03	0.04	0.05
“Our” PMMA	284.5	284.9	285.3	285.7	286
Comm. PMMA	110	113.1	115.1	118.3	120

The data presented in Table 1, clearly show that “our” PMMA has a higher strength and thermal stability. It should be clearly pointed out that the temperature at which the first weight loss is observed (0.01%w/w) is 285°C for the sample obtained in our Laboratory, and only 110°C for commercial PMMA. It should also be noted that samples exhibited a significant difference in the decomposition temperature (Table 2).

Table 2. Determination of weight loss temperature from 1w/w% to 5w/w%.

Sample	Weight loss [%w/w] and temperature at which it occurs [°C]					
	1	2	3	4	5	T _i [*]
Our PMMA	310	324	332	338	342	0.01 - 285
Comm. PMMA	225	300	313	320	325	1.27 - 268

*Initial decomposition weight loss/temperature

Commercially available PMMA begins its proper decomposition at 268°C, it is not a low temperature, but it should be noted that at this temperature for this sample 1,27%w/w of weight loss has already been registered.

Whereas the “our polymer” in the decomposition temperature exhibits only a 0,01%w/w of weight loss (Figure 1).

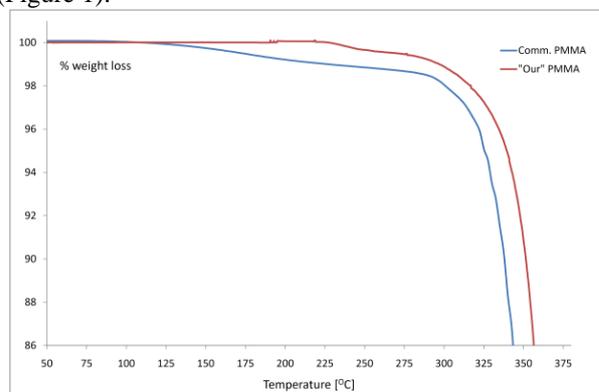


Figure 1. TG – thermogravimetric analysis samples: “Our” and commercially available PMMA

These temperature values are important parameters which determine the processing properties of the tested materials. The beginning of weight loss and its increase as the temperature rises will provide the thermal stability of the analyzed materials, whereas about the thermal resistance, the initial decomposition temperature. It is worth also take into account the temperature at which the polymer optical fibers are drawn (250°C - 270°C). On the basis of this information it can be concluded that sample “our PMMA” has a much better thermal properties and thus process ability as compared to the commercially available PMMA.

On the basis of MS and IR spectra, the analyses of gases evolved during the temperature increase of the samples were made. In the case of technical PMMA it was found that the weight loss, which was observed on TG curve (Figure 1), results from the insufficient polymerization degree. This observation was made on the basis of the presence (from 110°C) in evolved gases ions: 41 and 69 - resulting from the fragmentation of MMA molecules, containing in their structure double bonds. It should be added that the presence of ions: 27 and 29 - an aldehyde and vinyl group derived from MMA molecules (from 148°C) was also observed. IR spectra, in the analyzed temperature range, registered a small presence of water (the spectral range 3900cm⁻¹ - 3000cm⁻¹) and bands corresponding to the stretching vibrations of C–O methyl ester and the rotational vibration of the methyl ester –CH₃ (spectral range 1300cm⁻¹ - 1050cm⁻¹, from 150°C). The same analysis was performed for the sample obtained in our Laboratory. On the basis of MS spectra the presence of discussed ions were not observed. Only ion 41 appears in a small amount at a temperature of 127°C. While IR spectra registered in the spectral range 1300cm⁻¹ – 1050cm⁻¹ absorption increase in the temperature from 180°C to 300°C.

The rods about external diameter 1mm were drawn on the polymer optical fiber drawing tower from both (“our” and commercially available) PMMA. The spectral attenuations were measured by the standard cut-back method. For protection against penetration of external light rods were placed in special black box. Figure 2 presents spectral attenuation of the “our” PMMA. Figure 3 presents spectral attenuation of the commercially available PMMA.

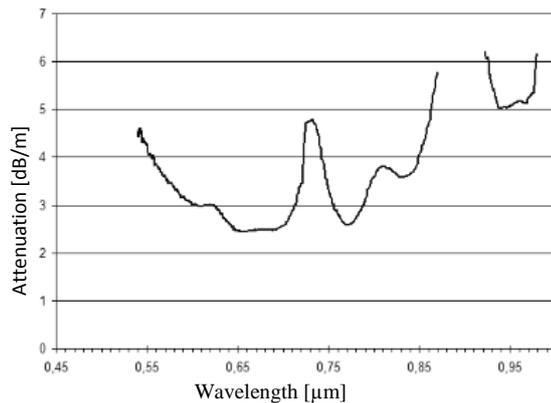


Figure 2. Spectral attenuation of “our” PMMA

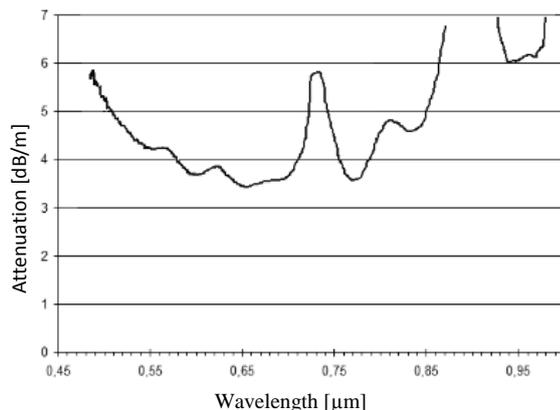


Figure 3. Spectral attenuation of commercially available PMMA

In this study, a comparison of two polymers used in optical fibers technology, was made. On the basis of presented studies it was concluded that PMMA obtained in our laboratory has a higher strength and thermal stability and that means better process ability as compared to the commercially available PMMA. Optical studies confirm presented conclusions. Attenuation of “our PMMA” is lower than that measured for the commercially available PMMA.

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