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Investigations of thermal degradation and electrical properties of polyamide materials versus polybismaleimide materials for fire-fighters helmets

P Ciubotariu-Ana¹, N-M Lohan^{1,*}, C A Micu¹, C Baci¹ and C Bejinariu¹

"Gheorghe Asachi" Technical University of Iasi, 63, Prof. dr. Dimitrie Mangeron Str., 700050, Iasi – Romania

E-mail: monica.lohan@yahoo.com

Abstract. In this paper, a study on thermal degradation of polybismaleimide materials for fire-fighters helmets compared to polyamide materials from commercial fire-fighters helmet was performed by applying simultaneous mass spectrometry and Fourier transform infrared spectroscopy of gas products from a thermogravimetric analyzer. The results of TG measurement indicate a difference in the mass loss behavior between the two polymers materials. The thermal decomposition of polyamide material takes place in the single stage in the temperature range of 400-460°C with a mass loss of 98% while that of polybismaleimide material takes place in two steps with a residue at 650°C of 85%. The electrical analyses consisted in the application of the electric breakdown test and the calculation of the breakdown parameters. Following the experiments, it has been found that the voltage breakdown has approximately 4 times higher values for polybismaleimide material than compared to polyamide materials.

1. Introduction

Personal protective equipment (PPE) is the equipment intended to be worn or held by the worker in order to protect him against the risks which might endanger his safety and health at work [1] and/or any additional accessory designed for this purpose, according to GD no. 1048/2006 [2]. PPE for firefighters is made up of protective helmets, masks, boots or other garments designed to protect firefighters from injuries [3]. PPE is necessary to protect against physical, electrical, thermal, chemical, biological hazards, and also to protect against various particles suspended in the air [4]. Firefighter helmets are made of various polymers such as polyethylene, synthetic resins, hybrid glass / jute reinforced epoxy composites [5] intended to be heat-resistant, mechanical-resistant, chemical and electrical shocks resistant. A fire helmet, according to SR EN 443/2008 [6] needs to provide head protection in various cases, such as: when a bulky object falls into the main areas of the head, a collision with a fixed or moving object, the propelling of solid or liquid materials, the fall or the movement of a part of the structure where the intervention takes place, the effect of a violent blow caused by an explosion, a strong and/or very strong combustion, contact with hot substances and contact with electricity or splashing with liquid chemical substances, respectively. Generally, a helmet consists of a cap and harness as well as other various accessories. Among the accessories we include: retaining strap, bracket and cable clip for the attachment of a lamp, eye shield, or face shield, neck flaps for protection against weather, molten metal splash, hot substances, lining for cold conditions or ear muffs [3]. In order to ensure the resistance to all listed, it is important that the material from which



the helmet is made to exhibit good thermal, mechanical and electrical properties. A good candidate for achieving the protective helmet cap that possesses a very good thermal and mechanical properties is bismaleimide. This material presents a number of advantages such as: high temperature stability, low volatility and low cost [7].

The purpose of this paper is to present the thermal and electrical properties of a new material made of polybismaleimide, in comparison with polyamide material from the commercial fire-fighter helmets.

2. Materials and methods

The material analysed in the present study (polybismaleimide), was obtained by a method described in a previous paper [8-11]. In order to explain the thermal degradation process of polyamide, the most used plastic material from commercial fire-fighters helmet and the new designed polybismaleimide material, TG/ MS/ FTIR technique was used. The results were obtained with a STA 449 F1 Jupiter (Netzsch, Germany) thermo-gravimeter device coupled with a 403C Aëolos QMS mass spectrometer (Netzsch, Germany) and a Vertex-70 FT-IR spectrophotometer (Bruker, Germany). Samples with 8 and 10 mg were analysed using a procedure that involves a heating rate of 10°C / min between 25°C and 680°C temperature range.

The electrical puncture test was carried out with the Megger® OTS60SX equipment, which is a semi-automatic dielectric resistance in oil test with a maximum power of 60 kV. For the electrical puncture test, four oil bath tests were carried out on samples of polyamide materials from commercial fire-fighters helmet and the polybismaleimide based material.

3. Experimental results

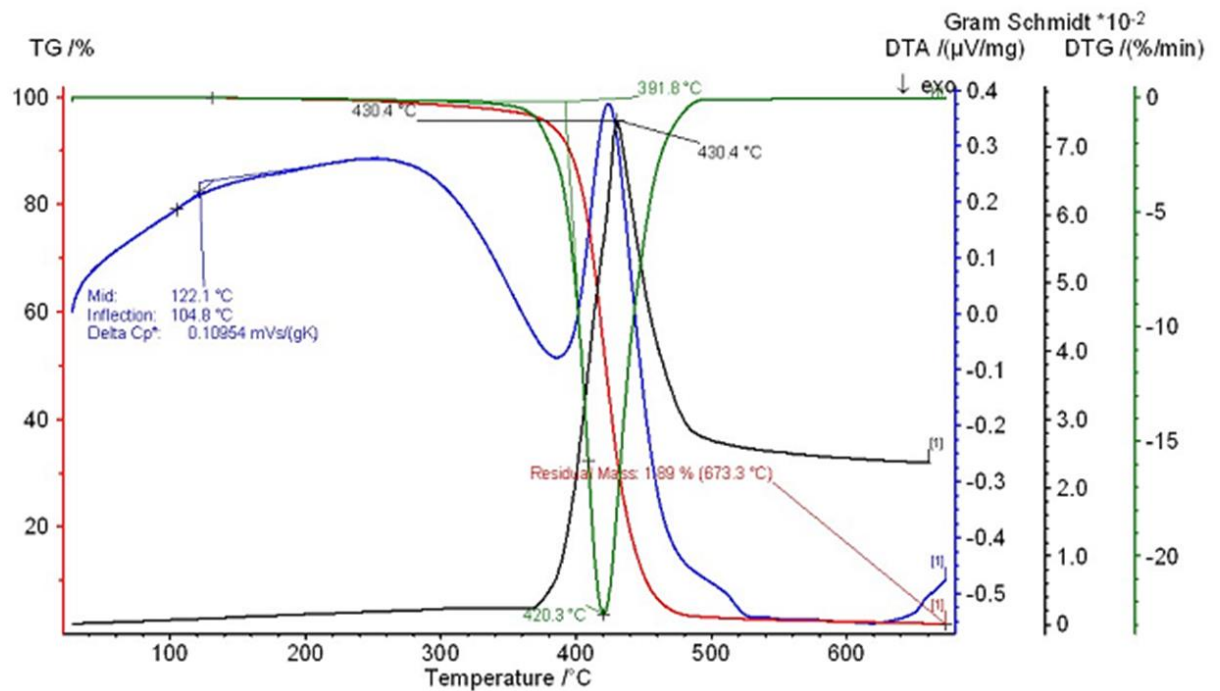
Figure 1 shows the TG / DTG / Gram Schmidt curves for polyamide material samples from commercial fire-fighters helmet (a) and polybismaleimide material (b).

Gram Schmidt curve (black line) indicates that the maximum concentration of the gas mixtures resulting from decomposition process is at 430.4°C for the old firefighters helmet sample and in range of 200-600°C for polybismaleimides material. In case of polybismaleimide, the removed gases are mainly formed by solvent traces and water. The loss of mass for the sample of polyamide materials taken from commercial firefighter helmet in temperature range of 400-460°C is 98%, while for polybismaleimide is 14% between 25-680°C (Figure 1, red line).

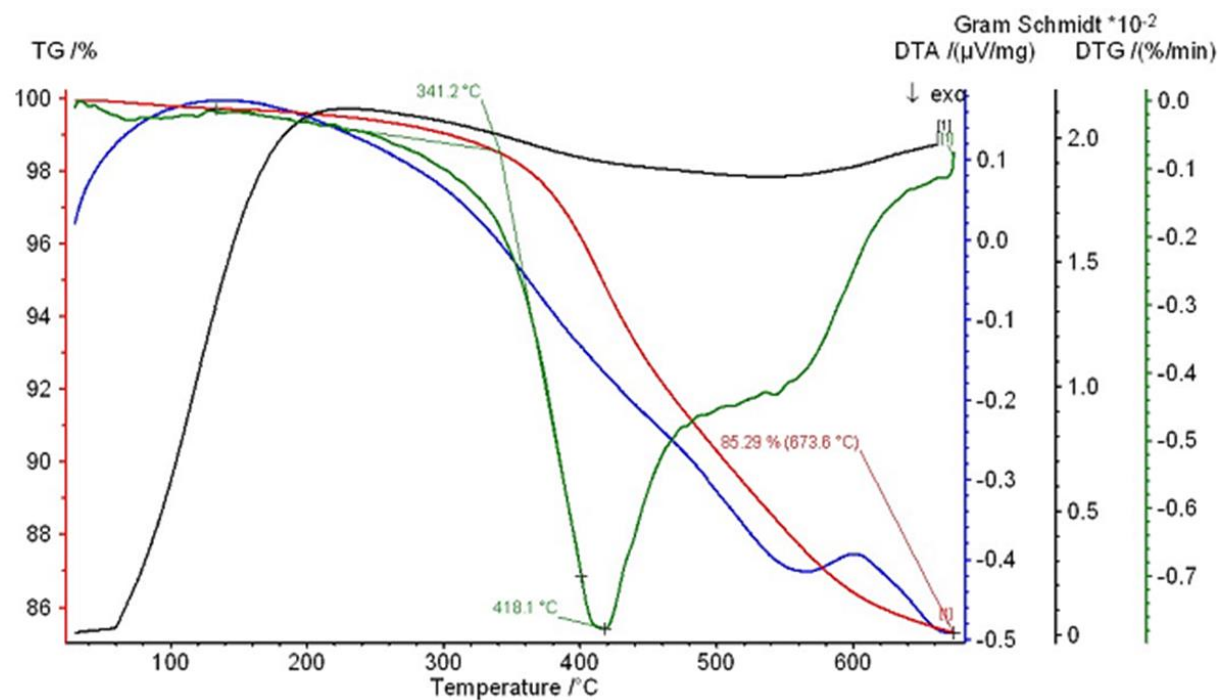
The two-dimensional FT-IR spectra of the gasses resulted at different temperatures from thermal decomposition of polyamide material are shown in Figure 2 (a) and for polybismaleimide material sample in Figure 2 (b).

From the FT-IR charts of the fire-fighter's polyamide samples at 430, 500, 550, and 630°C, it is noted that the absorption band peak decreases with growth of the temperature above 450°C. The FT-IR spectra at 430°C of the polyamide samples from the commercial fire-fighters helmet (temperature at which the resulting gas concentration is the maximum - see Figure 1 a, black line) shows the absorption bands at 3073-2872 cm⁻¹ (specific to amine and aliphatic groups), 2350 (CO₂), 1498, 1493, 905, 762 and 695 cm⁻¹, Figure 2 (b) red line.

The electric puncture is the destruction phenomena of an electrical insulation, which leads to the direct passage of electric current through the dielectric mass, between two electrodes at a certain potential difference. The phenomena may or may not be accompanied by an electric arc, depending on the power of the power supply, and is characterized by the puncture voltage (U_{str}). Dielectric rigidity (E_{str}) is the minimum value of the electrical field strength, when the material becomes inefficient. For the electrical breakdown test, four oil bath tests were carried out on samples of polyamide materials from commercial fire-fighters helmet and polybismaleimide material. The test results are shown in Table 1.



a)



b)

Figure 1. DTA/Gram Schmidt/DTG charts of samples of polyamide materials from: a) commercial fire-fighters helmet and b) polybismaleimide material.

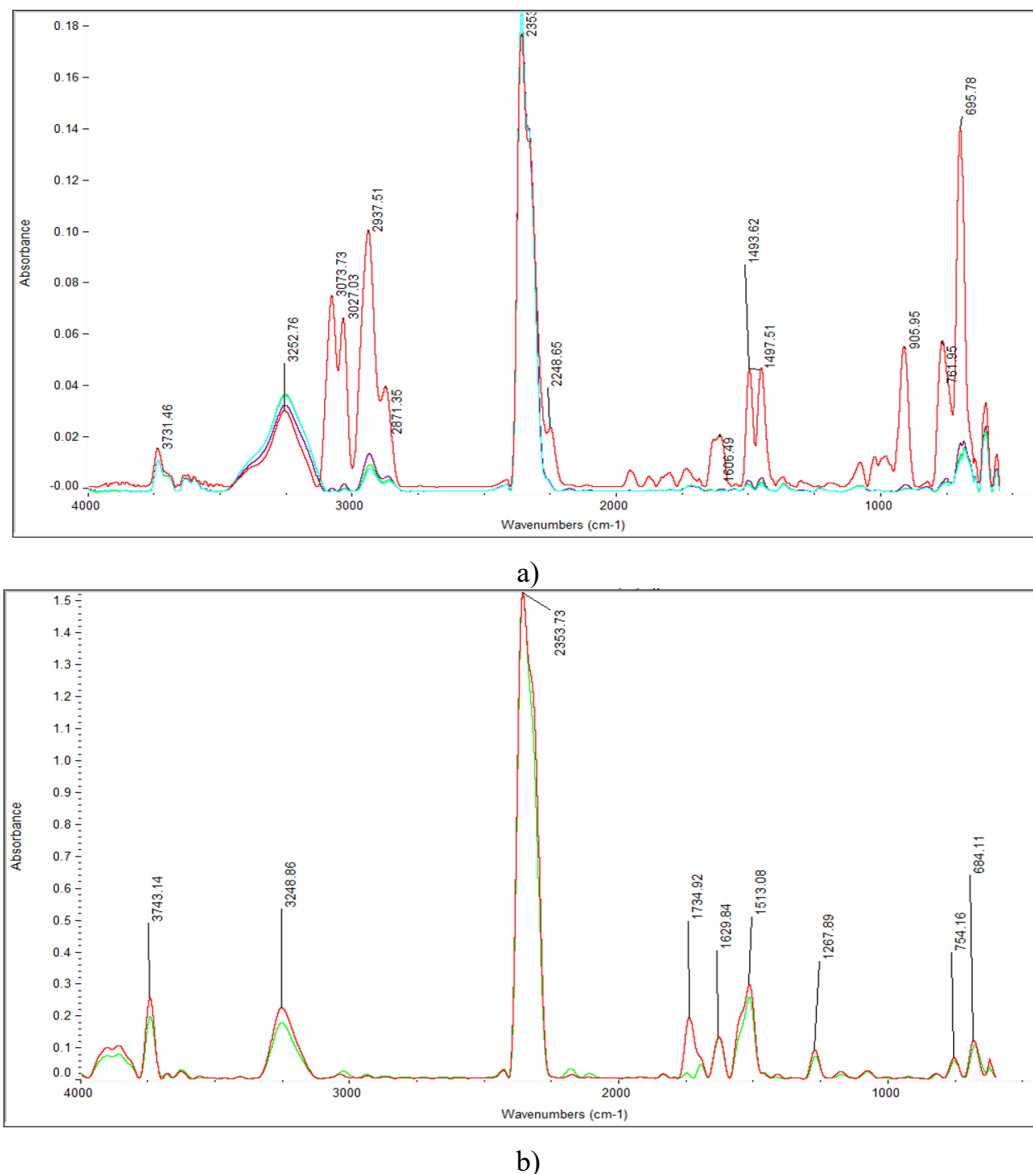


Figure 2. FT-IR spectra at 430 °C (red line), 500 °C (green line), 550 °C (purple line) and 600 °C (blue line) of a) polyamide samples from commercial fire-fighters helmet and 350 °C (red line), 530 °C (green line) of b) the sample of polybismaleimide material.

Table 1. The values recorded following the electrical puncture test for samples of polyamide materials from commercial fire-fighters and polybismaleimide material.

Material:	Sample	U_{str} [kV]	E_{str} [kV/mm]	E_{str} medium [kV/mm]
polyamide material	1	3.2	1.28	1.16
	2	2.7	1.08	
	3	2.9	1.16	
	4	2.8	1.12	
polybismaleimide material	1	11.5	4.6	4.96
	2	12.6	5.04	
	3	11.7	4.68	
	4	13.8	5.52	

From the above data, it can be seen that the puncture voltage, U_{str} , is approximately 4 times higher for the sample of polybismaleimide material compared to the sample of polyamide materials from commercial fire-fighters helmet. Also, the same behaviour is observed for dielectric rigidity values (E_{str}).

The experiments were carried out in compliance with the legal provisions on occupational safety [12-13], eliminating the risks which human resource may be exposed.

4. Summary and conclusions

The paper aimed at studying the thermal degradation and electrical properties from polybismaleimide materials for fire-fighters helmets compared to polyamide materials from commercial fire-fighters helmet.

Given the results of experimental measurements, the following conclusions may be formulated:

a) The polyamide material from commercial fire-fighter helmets have a mass loss of 98% for a temperature range of 400-460°C while the polybismaleimide material have a mass loss of 14% between 25-680°C. Furthermore, the quantities of volatile compounds generated in the degradation process are much smaller for polybismaleimide compared with the polyamide material. Taking all into consideration, the material containing polybismaleimide is more suitable for manufacturing fire-fighter helmets due to its heat-resistant properties and lack of volatile compound generated during temperature decomposition.

b) Puncture voltage, U_{str} and dielectric rigidity E_{str} is approximately 4 times higher for polybismaleimide material compared to polyamide materials from commercial fire-fighters helmet, making it a more efficient electrical insulator. This indicates that protection helmets made of polybismaleimide material can behave better to an electric shock during fire-fighters intervention, limiting the risk of accidental electrocution.

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