Thermal Analysis of a New Glass Fiber-Reinforced Bismaleimide Composite Material Used for Firefighter Helmets

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Abstract. Safety helmets represent essential Personal Protection Equipment (PPE) used in firefighter protection and emergency situations. They protect firefighter’s face and eyes against flames, heat and flying debris. When temperature levels are high, user’s thermal comfort is affected. A glass fibre-reinforced bismaleimide composite material has a number of improved properties in terms of mechanical and thermal characteristics, as compared to the materials that are currently used. The present paper aims to comparatively analyse the thermal behaviour of an injection moulded polypropylene helmet and the newly developed hot modelling material, under the form of a glass fibre-reinforced bismaleimide composite material. Thermal analysis was performed using Differential Scanning Calorimetry (DSC) and Dynamic-Mechanical Analysis (DMA). DSC and DMA thermograms were corroborated and discussed, from the point of view of the consecutive solid state transitions occurring during heating, mostly in the second heating-cooling cycle. The isothermal behaviour of glass fibre-reinforced bismaleimide composite material, during strain sweeps performed by DMA, enabled the determination of internal friction and storage modulus, under vibratory loads, at different temperatures. The advantages of the newly developed glass fibre-reinforced bismaleimide composite material were highlighted.

1. Introduction

Personal protective equipment (PPE) play an essential role in the work system of firefighters and are the tools that ensure the basic health protection and safety of user’s, from fire, chemicals or physical impact [1]. Fire protection helmets provide head protection against high temperatures [2] and are equipped with glass protection screens against smoke that can damage the eyes. Protective helmets must also provide head protection against impact and must be able to withstand penetration and absorb the impact force of a blow [3]. In some cases, the helmets should protect against electrical shocks as well. Protective helmets differ as a function of purpose and design but share the same component: the shell [4].

Currently, the most used materials for the production of shells are polyethylene, synthetic resin, ABS [4] and hybrid glass/jute reinforced epoxy composite [5]. The bismaleimide resins are recognized for high-temperature performance [6], outstanding thermomechanical and flammability behavior on the finally cured state [7] nonvolatility and low cost [8]. Firefighter helmet materials are essential for an effective intervention during rescue / accident operations. In order to have superior mechanical
properties, the deflective helmet shell surface can be produced from continuous fiber composites processed by long fiber thermoplastic processing techniques [9]. A long fiber thermoplastic structure can comprise a thermoplastic or thermoset polymer matrix (such as polyaryl amide, polyethylene terephthalate, bismaleimide) and a continuous reinforcing fiber (such as glass, aramid, carbon fiber) wherein the continuous reinforcing fiber is hot melt impregnated with the thermoplastic resin.

A glass fiber-reinforced bismaleimide composite material has a number of improved properties in terms of mechanical and thermal characteristics as compared to currently available materials [10]. The purpose of the present paper is to study the thermal behavior of a new composite material based on bismaleimide reinforced with fiberglass, using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) investigations and to compare the results with those obtained on commercial materials that are currently used for firefighter helmets.

2. Materials and methods

The new material was obtained, by hot molding process, as a composite of glass fiber reinforced bismaleimide. The bismaleimide resin precursor (PABMI) were prepared by reaction of 4,4-bismaleimidodiphenyl methane with 4,4-diaminodiphenyl methane according to the reported method [11]. Silica cloth was impregnated with a 50 wt. % solution of PABMI pre-polymer in N-methylpyrolidone (NMP) and allowed to dry at room temperature for 24 h and in a circulating air oven for 10 min at 140°C and 5 min at 170°C.

The pre-pregs dimension 10x10 cm were stacked over the female part of the mild steel mold coated with silicone release agent. The male counterpart of the mold was placed between the preheated plates (140°C). The first type of samples, (laminate samples) were obtained in sheets consisting of a single layer. Subsequently, by pressing several layers followed by heating according to the following scheme1h at 150°C, 2h at 180°C for, 4h at 200°C for and 4h at 230°C, after curing for 4h at 200°C, the samples were allowed to cool down to room temperature gradually under a pressure of 10 Kgf/cm² and the second type, of multilayer samples, were obtained.

2.1. DSC analysis

Up to 5-mm long sample fragments were cut from both sample types, weighing less than 50 mg, for DSC experiments. For this purpose, a NETZSCH differential scanning calorimeter type DSC 200 F3 Maya was used, with sensitivity: < 1 W, temperature accuracy of 0.1 K and enthalpy accuracy—generally <1%. The device was calibrated with Bi, In, Sn, and Zn standards.

Temperature scans were performed between 20 and 300 °C, in two cycles, with a heating rate 10 K/min, under Ar protective atmosphere. In order to compare the obtained DSC results with those characteristic to currently available material, a 12.4 mg sample was cut from a commercial firefighter protection helmet. The sample was heated from 20 to 130 °C, in single cycle, to avoid melting. The DSC thermograms recorded during heating were evaluated with Proteus software, provided by NETZSCH.

2.2. DMA analysis

For the DMA tests, one 20 mm-long fragment was cut from type 2 multilayer sample and another from a commercial firefighter protection helmet. The experiments were performed by means of an analyzer type DMA 242 Artemis NETZSCH, with force resolution of 0.0005 N, amplitude range: ± 0.1 up to 240 μm and amplitude resolution: 0.0005 μm. A three-point bending specimen holder was used and a maximum static pre-loading force of 12 N. The specimens were tested at a constant frequency of 1 Hz, and amplitude of 20 μm, under Ar protective atmosphere using a 5 K/min heating rate.

2.3. STA analysis

The thermal experiments dealing with degradation of polymers were carried out by means of an integrated TGA-FTIR NETZSCH STA 449F1 system in nitrogen atmosphere within 30-600°C range at 10°C/min heating rate.
3. Results and discussions

The pre-polymer PABMI, synthesized by powder mixture heating of the 4,4-bismaleimidodiphenyl methane (0.1 mol.) and 4,4-diaminodiphenyl methane (0.05 mol.) at 150°C for 20 min, having \( M_n = 8400 \) and polydispersity index of 1.4, was dissolved in NMP leading to a solution of 50 wt. % with which the glass fabric was impregnated.

The thermal behavior of pre-polymer was monitored by DSC measurements, in isothermal regime at 130°C (Figure 1) and in dynamic regime with 10°C/min (Figure 2). As it can be seen from the two figures, the exothermic curves are due to breaking of the unreacted double bonds.

During the first heating cycle, an endotherm minimum at the 110 °C was observed, a scribed to the melting point of the PABMI pre-polymer, and three exothermic peaks specific to the secondary amide group polyaddition reactions to the BMI group (at 178.3 °C), to the homo-polymerization of the molecular groups (at temperature of 222.7 °C) and to other crosslinking reactions (at 281.7 °C), respectively. During the second heating cycle, a retention of a minimum of endotherm is observed, and the crosslinking reaction is higher due to the increase of the viscosity of the material. During the
second heating cycle, a preservation of the endothermic minimum is observed and the crosslinking reaction tends to move to higher temperatures due to the increase in viscosity of the material.

The thermal stability of composite based on PABMI, compared with a sample collected from a helmet based on polyamide, are presented in the DGA thermograms from Figure 3. The two materials begin to decompose around 380°C but the material resulting from the helmet loses all the mass in a 50°C temperature range, while the PABMI-based composite has a residue of 84% even at 650°C. The decomposition products of PA_BMI-based material consist mainly of: benzene, aniline, toluidine, diethylamine, in varying proportions, and they can be seen at temperatures above 350°C.

![Figure 3. DTG thermogram of PABMI and PA.](image)

The DSC curves of the two materials are presented in Figure 4. The sample from helmet based on polyamide shows an exothermic peak at 110.8°C and is probably due to the softening or melting of the material. The composite based on PABMI presents an increase in heat flow, probably due to the continuation of crosslinking reactions and the breakdown of chemical bonds at higher temperatures.

The two materials are solid at room temperature and exhibit high elastic moduli, above 2 GPa for sample from helmet and around 10.7 GPa for PABMI-based composite. The sample from helmet begins to melt at 98.3°C and ends melting at 104.1°C, while the PABMI-based composite has a modulus loss of about 1.5 GPa in the temperature range of 167-190°C. A small drop in $E'$ of PA_BMI-based composite is noticed between 50 and 120°C that may be associated with a $\beta$ transition.

During the glass transition process the elastic modulus $E'$ abates till 1.5 GPa, that means that it decreases one order of magnitude. For an amorphous linear polymer the decline of $E'$ in the glass transition range amounts three orders of magnitude in a narrow temperature span. Consequently, we can infer that the compound contains crosslinking that obstruct the large movement of ample chain segments and it acts as a rigid material [12].
Figure 4. DSC thermogram of polyamide (a) and second type samples (b).

The viscoelastic behavior of the two materials was recorded by DMA (Figure 5).

Figure 5. DMA thermogram of polyamide (a) and second type samples (b).
4. Conclusions
The newly developed glass fiber-reinforced bismaleimide (PAMBI) composite material experienced a superior behavior as compared to commercially available fireman helmet based on polyamide (PA) with regards to the following aspects:

• after a first heating cycle, the material reticulated and became thermally inert and no solid state transitions are noticeable during subsequent heating;
• mass losses were only 16% at PAMBI, when heated to 650°C, while the PA base helmet totally decomposed, when heated to 380°C;
• PA based helmet totally softened above 110°C (storage modulus decreased to 0), while PAMBI maintained a value of 10.7 GPa, at the same temperature.

All these preliminary results recommend the newly developed glass fiber-reinforced bismaleimide composite material a promising candidate for a new generation of fireman helmets.

5. References
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