

Thermal properties of polymer-matrix composites reinforced with E-glass fibers

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Abstract: The influence of the fraction of the glass-fiber (EGF) reinforcement, from 0 to 15 wt%, on the thermal properties of the polymer-matrix composites with the CaCO₃ mineral filler is studied. The proper ratio of glass-fibers and mineral filler is important for obtaining good mechanical, and at the same time good thermal properties of the composites used in production of high-quality components in electro industry. For this purpose, the thermal stability and the thermal properties of the fiber-reinforced composites are determined from a set of different characterization techniques and linked with the microstructural changes induced by the different fiber content. The composites are stable upon heating to 260 °C, and undergo thermal oxidation between 280 and 560 °C, as found by thermogravimetric and differential thermal analysis. The specific heat capacity, C_p , of the composites slightly increases with increasing EGF content for 0 to 10 wt% EGF, with respective values 0.899 J/gK and 0.903 J/gK at 20 °C. Slightly lower C_p values of the composite with 15 wt% EGF could be related to a non-uniform distribution of EGF and presence of voids evidenced by scanning electron microscopy. Thermal conductivity of the composites decreases with increasing EGF content from 0.960(6) W/mK to 0.878(2) W/mK for 0 and 15 wt% EGF, respectively.

Keywords: glass-fiber composites; thermal stability; specific heat capacity; thermal conductivity

Toplotne lastnosti kompozitov na osnovi polimerov, ojačenih s steklenimi vlakni

Izvleček: V članku smo raziskovali toplotne lastnosti kompozitov na osnovi polimerov, ojačenih z različnimi deleži steklenih vlaken (od 0 do 15 utežnih %) in z dodanim mineralnim polnilom CaCO₃. Primerno razmerje steklenih vlaken in polnila omogoča doseganje dobrih mehanskih in istočasno tudi toplotnih lastnosti kompozitov, ki jih uporabljamo za proizvodnjo komponent v elektro-industriji. Toplotno stabilnost in toplotne lastnosti kompozitov smo analizirali z vrsto metod. S termično analizo smo zasledovali termično stabilnost in termični razpad kompozitov. Izkazalo se je, da so kompoziti termično stabilni do temperature ~ 260 °C, nato v temperaturnem območju od ~280 °C do 560 °C pride do oksidacije in termičnega razpada polimerne faze. Specifična toplotna kapaciteta, C_p , kompozitov narašča z naraščajočim deležem vlaken od 0 do 10 %. Nekoliko nižje vrednosti C_p kompozita s 15 % deležem vlaken povezujemo z nehomogeno razporeditvijo steklenih vlaken in prisotnostjo por v mikrostrukturi, ki smo jo analizirali z vrstičnim elektronskim mikroskopom. Toplotna prevodnost kompozitov se znižuje z naraščujočim deležem vlaken in je v območju od 0.960(6) W/mK do 0.878(2) W/mK za kompozita z 0 in 15 % vlaken.

Ključne besede: kompoziti s steklenimi vlakni; termična stabilnost; specifična toplotna kapaciteta; toplotna prevodnost

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1 Introduction

Glass-fiber reinforced polymer-matrix composites, including bulk molding compounds (BMCs) [1], are widely used in electro and automotive industry due to their easy processing, light weight, low cost and the possibility to tailor their properties. BMCs are available as pre-prepared mixtures of the polymer matrix, short glass

fibers and mineral fillers. Such composites are usually processed by injection or compression molding – the techniques commonly used for mass production of small complex shaped components.

Functional properties of the composites strongly depend on the weight fractions and properties of in-

dividual constituents, i.e. polymer matrix, fibers and mineral filler particles. In assembling parts for electrical motors, such as housings, yokes and shaft insulation, the composite material should effectively dissipate the heat generated during the operation of the device to avoid possible defects. For that reason, the composite materials should have high thermal conductivity. The latter can be enhanced by incorporating fibers, metal or ceramic filler particles with high thermal conductivity, such as carbon fibers, carbon black powder, silver and alumina, into the polymer matrix [2-6].

It was shown that the thermal conductivity of the fiber reinforced composites is strongly influenced by the microstructural parameters, such as the fiber volume content, fiber diameter and fiber orientation [7].

Kalapasrad et al. studied the effect of fiber composition and fiber orientation of low-density polyethylene composite laminates reinforced with glass fibers in the amounts of up to 20 % on the thermal conductivity and thermal diffusivity at cryogenic and high temperatures. They observed that the thermal conductivity of the composites increased with the fiber content and with temperature. They also reported that the difference between the thermal conductivity parallel and perpendicular to the fiber direction was marginal because of the isotropic nature of the glass fibers [8].

In our previous work we investigated the effect of E-glass fibers (EGF) weight content and distribution on mechanical properties of the polymer-matrix composites. We found that the highest flexural strength along with the highest degree of the EGF distribution homogeneity was achieved for the samples with 10 and 15 wt% of EGF, i.e., 109 ± 4 MPa and 121 ± 15 MPa, respectively. Note that the polymer content was 21 wt%. At an even higher EGF weight content the flexural strength decreased, which was attributed to increased fiber-fiber interactions and consequent poorer stress transfer between the fibers, while at the EGF content below 10 wt% there were not enough fibers to give a sufficient mechanical strength to the composites [9].

The aim of this work was to study the effect of the EGF weight content and their microstructure on the thermal properties of the composites as this is important for their application in electro industry. The thermal stability of the composites was studied by thermal analysis, and the materials were analysed by differential scanning calorimetry, in the expected temperature interval of operation, i.e. between room temperature and 180 °C, so that the values of the specific heat capacity could be extracted. Furthermore, the thermal conductivity of the composites was measured at room temperature depending on the weight fraction of EGF.

2 Experimental

Four sets of BMC test samples were commercially prepared from compounds containing 21 wt% of polymer-matrix (PM) based on thermosetting unsaturated polyester and with varying fractions of EGF and CaCO₃ mineral filler (MF). The sample with the mineral filler only was prepared as reference. The composition of the samples, denoted as BMC-0, BMC-5, BMC-10 and BMC-15 in further text, is presented in Table 1.

Table 1: Composition and density of the BMC composite samples.

Sample	PM (wt%)	EGF (wt%)	MF (wt%)	ρ (g/cm ³)
BMC-0	21	0	79	1.96
BMC-5	21	5	74	1.91
BMC-10	21	10	69	1.87
BMC-15	21	15	64	1.86

Compression molding technique was used to prepare the test specimens according to the standard ISO 3167 [10]. The dimensions of the specimens and the cutting position for obtaining the plan-view and cross-sectional samples for microstructural characterization are shown in Figure 1. The arrow indicates the flow of the compound during the molding process.

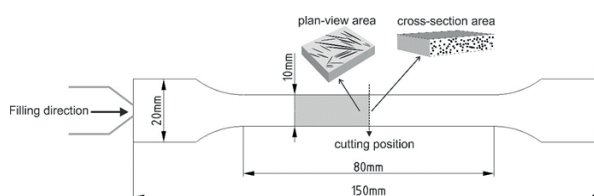


Figure 1: Dimensions of the test specimens and the cutting position for obtaining the plan-view and cross-sectional surfaces for microstructural characterization. According to [11].

The samples for microstructural analysis were prepared by standard metallographic techniques. Field emission scanning electron microscope JSM-7600F (FE SEM, JEOL Ltd., Tokyo, Japan) was used for microstructural characterization. The polished plan-view and cross-section surfaces of all samples were sputter-coated with a thin carbon layer to avoid charging in SEM. SEM images were taken in the backscattered-electron mode (composition contrast mode - COMPO) at an accelerating voltage of 15 kV.

The density of the samples was determined by the water immersion technique and calculated according to the equation,

$$\rho = \frac{m_s}{m_s - m_w} \cdot \rho_w \quad (1)$$

where the m_s is the mass of the sample in the air, m_w is the mass of the sample when immersed in the water and ρ_w is the water density at room temperature [12].

Thermal stability of the samples was studied by thermogravimetric and differential thermal analysis (TG-DTA) using a thermal analyzer Netzsch STA 409 PC. The samples of about 5 mm in diameter and the thickness of ~ 3 mm were placed into platinum-rhodium crucibles and heated from room temperature to 650°C at a heating rate of 5K/min in synthetic air atmosphere.

The differential scanning calorimetry (DSC) curves were measured by a differential scanning calorimeter DSC 204 F1 (Netzsch, Germany). The samples of about 5 mm in diameter and the thickness of ~ 1 mm were put in Pt crucibles with lids, and heated in a calorimeter with a heating rate of 2°C/min from room temperature to 180°C. To determine the specific heat capacity C_p of the BMC samples, sapphire (Netzsch, diameter of 5.2 mm, thickness of 1 mm) was used as the standard material. The C_p values at different temperatures (20°C, 100°C and 180°C) were extracted from the linear fit of the experimental curve.

Thermal transport properties of the composites were measured with the transient plane source technique [13] by using the HotDisk TPS 2500S equipment (Hot Disk AB, Gothenburg, Sweden) at room temperature. The samples for measuring the thermal conductivity were also prepared by compression molding, but they were of different dimensions, i.e. 340×80×4 mm. During the HotDisk measurement a thin disk sensor (kapton, 2 mm diameter), used both as the heat source and the temperature monitor, was sandwiched between two individual samples. The material was heated at 50 mW for 5s. The length of the current pulse was chosen short enough so that the sensor could be considered in contact with an infinite solid throughout the transient recording. In this way the thermal properties of the surrounding material could be determined by measuring the temperature increase of the disk sensor in a short period of time. [14, 15]

3 Results and discussion

3.1 Microstructure

SEM micrographs of plan-view and cross-sectional areas of all composite samples are collected in Figure 2. In the BMC-0 sample we can observe irregularly shaped

CaCO₃ filler particles with the sizes from a few μm up to a few 10 μm in the polymer matrix. Note that the plan-view and cross-sectional areas were very similar, meaning that the distribution of the filler particles does not depend on the compound filling direction (see Fig. 2a).

We observe that in the plan-view microstructures of the EGF-reinforced composites the fibers are mainly oriented in the direction of the compound filling flow during the molding process. This is also apparent from the intersections of the glass fibers in the cross-section micrographs (see Fig. 2b, d, f): namely, the cross-sections of the fibers that are perpendicular to the cutting position are circular and others, which are cut at an angle, are oval-shaped. At lower weight contents of EGF (≤ 10 wt%) the fibers are uniformly distributed in the PM. At the EGF content of 15 wt% we observe clustering of the fibers, meaning that their distribution is not homogeneous [9]. Presence of voids in the vicinity of the clusters may be related to a poor adhesion between the fibers and the PM in the latter sample (see Fig. 2f).

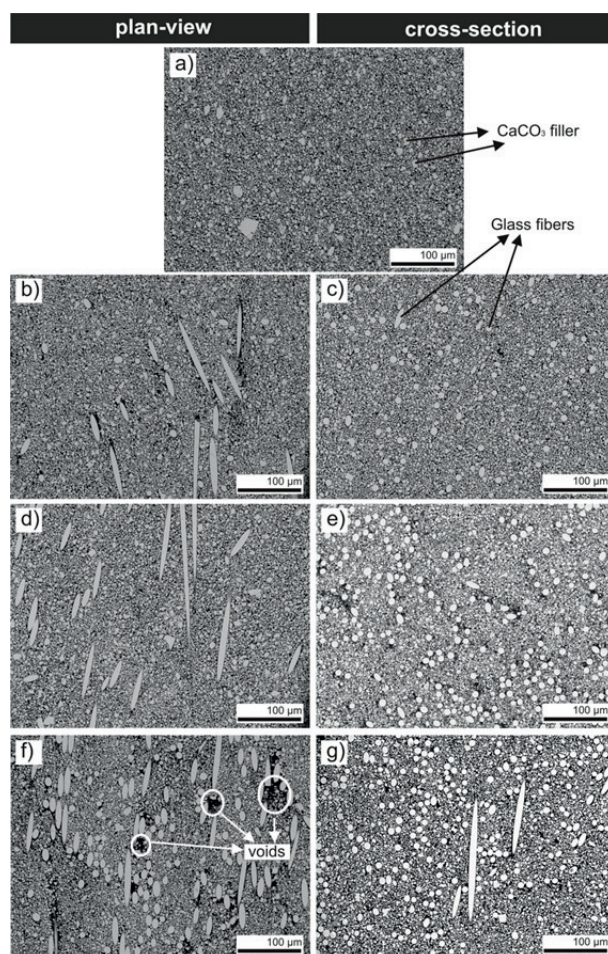


Figure 2: SEM micrographs of the plan-view and cross-sectional surfaces of the BMC samples: BMC-0: a, BMC-5: b, c, BMC-10: d, e, BMC-15: f, g.

The densities of the composite samples are slightly decreasing with increasing EGF weight fraction, from 1.96 g/cm³ to 1.86 g/cm³, for BMC-0 and BMC-15, respectively (cf. Table 1). Such small decrease could be tentatively connected to the porosity in the latter sample, but also to the increased weight fraction of the fibers. Note that the densities of the dispersed phases, EGF and CaCO₃ are quite similar, 2.54 g/cm³ and 2.65 g/cm³, respectively [16].

3.2 Thermal stability

The thermal analyses of the BMC-0 and BMC-10, which was selected as a representative EGF-reinforced composite, are collected in Figure 3. The TG-DTA curves reveal that the samples are thermally stable upon heating to 260°C. A slight inclination of the TG curves of both samples upon heating from room temperature to around 260°C, accompanied by a hardly discernible endothermic DTA signal, is attributed to evaporation of volatile species. The major weight loss occurs in the temperature range between 320°C and ~560°C and is accompanied by endothermic (383 °C) and exothermic (398 °C and 448 °C) events. It is attributed to the oxidation and thermal degradation of the PM [17]. Above the temperature of 560 °C only inorganic phase is still present, i.e. the glass fibers and CaCO₃ mineral filler, as confirmed by X-ray diffraction (pattern not shown here). The overall mass losses of 21.83 % and 20.85 % for the samples BMC-0 and BMC-10, respectively, correspond well to the initial content of the PM (21 wt%). This confirms the complete decomposition of the PM during the thermal treatment to 650°C.

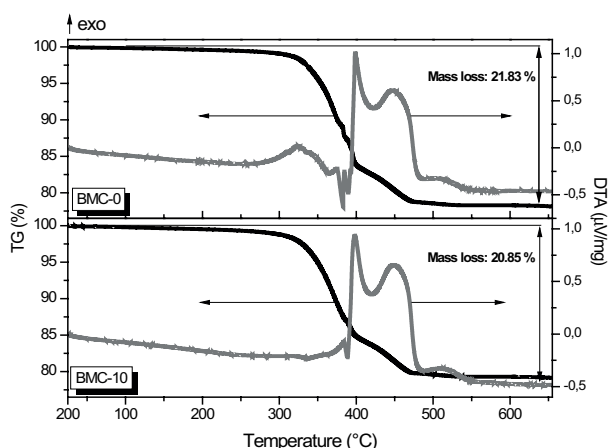


Figure 3: TG and DTA curves of the BMC-0 and BMC-10 composites.

The thermal stability of the composites confirmed by TG-DTA, i.e. the absence of any thermal effects between 25°C and 180°C, allowed us to measure the specific heat capacity, C_p , of the samples over the mentioned temperature interval by DSC. The C_p values at 20, 100 and 180°C were extracted from the linear fits of the C_p curves, calculated from the values of the heat flow measured during the heating of the sample.

The C_p of the sample with the mineral filler only, is 0.899 J/gK at 20 °C and it increases with temperature to 1.154 J/gK at 180 °C, see Table 2. The values of C_p of the samples with 5 and 10 wt% EGF are almost the same, and also very similar to the sample without EGF, and they show a similar, slight increase of C_p with temperature. Only the sample BMC-15 steps out from the observed trend, since the C_p values at all temperatures are lower than the values obtained for the samples without EGF or with lower EGF contents. This difference could be tentatively related to a non-uniform microstructure of the BMC-15 sample and/or to the presence of the voids between the clustered fibers, see Fig. 2f.

Table 2: Specific heat capacity (C_p) of the composites, obtained from the linear fit of the C_p experimental curves.

	C_p [J/gK]			
	BMC-0	BMC-5	BMC-10	BMC-15
20°C	0.899(1)	0.903(1)	0.903(1)	0.861(1)
100°C	1.027(1)	1.039(1)	1.038(1)	0.991(1)
180°C	1.154(1)	1.175(1)	1.174(1)	1.122(1)

3.3 Thermal conductivity

The thermal conductivity, λ , of the composites with different weight portions of EGF is shown in Figure 4. The values of λ for the composite BMC-0 is 0.960(6) W/mK and it decreases with increasing EGF content to 0.878(2) W/mK for the composite BMC-15.

The reported values of thermal conductivity for the polymer matrix, EGF and CaCO₃ mineral filler are respectively, a few 0.1 W/mK, ~1-1.3 W/mK and ~4.6-5.6 W/mK, see Table 3.

A slight decrease of the thermal conductivity of the polyamide-matrix composites with increasing glass fiber content (0 -5 wt%) was also observed by Li et al.

Table 3: Thermal conductivity, λ , of the polymer, glass fibers and CaCO₃ mineral filler obtained from literature.

	PM	EGF	CaCO ₃
λ (W/mK)	0.12 – 0.50 ^[16] ; 0.1 – 0.3 ^[18]	1.04 ^[20] ; 1 ^[21] ; 1.1 ^[22] ; 1.3 ^[19]	5.6 ^[20] ; 4.6-5.5 ^[23]

[22]. The composites contained alumina or magnesium hydroxide fillers with respective λ values of 30 and 80 W/mK. The authors explained that the decreased thermal conductivity of the composites was related to the formation of the thermally-resistive network of the glass fibers (cf. Table 3) which limited the heat transfer between the filler-particles. We propose a similar trend in our case, namely the increasing fraction of the heat-resistive glass fibers contributes to a gradual slight decrease of the thermal conductivity of the composites. In addition, the thermal conductivity of the composite with 15 wt% EGF could be affected also by the presence of voids, see Fig. 2f.

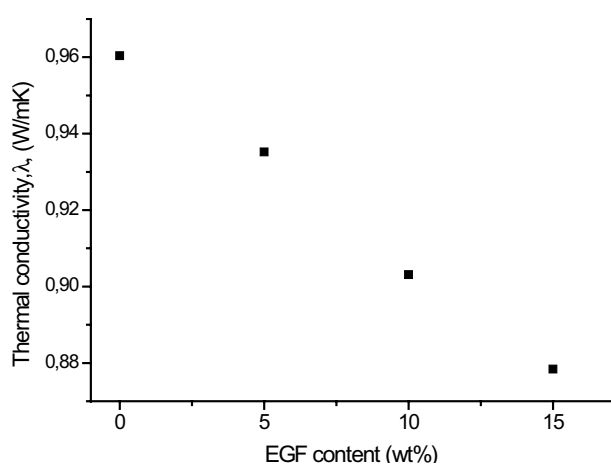


Figure 4: Thermal conductivity of the BMC samples versus the EGF content.

4 Conclusions

In the present study, we examined the thermal stability, specific heat capacity and thermal conductivity of the composites with glass-fibers in the amounts from 0 to 15 wt%. We found that the thermal stability of the composites is not influenced by the glass-fiber content, the composites proved to be stable to ~ 260 °C. The specific heat capacity of the composites slightly increases with the increasing glass-fiber content (0 to 10 wt%) and with temperature. However, the composite with the highest fiber content, 15 wt%, exhibited slightly lower values which could be tentatively related to its non-uniform microstructure. The thermal conductivity of the composites was found to slightly decrease with increasing fiber fraction, with the value of 0.878 W/mK for the composite with 15 wt% of fibers. Such decrease could be explained by the formation of the network of thermally resistive glass-fibers which effectively hinder the heat transfer through the material.

The right balance of the thermal properties, and fiber distribution homogeneity, necessary for a suitable

mechanical performance can be achieved by tailoring the EGF and CaCO_3 mineral filler content. Based on the results presented in this and our previous work [9] the composites with 10 wt% showed optimal mechanical and thermal properties.

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