



POTENTIAL OF GLASS, BASALT OR CARBON FIBRES FOR REINFORCEMENT OF PARTIALLY PYROLYSED COMPOSITES WITH IMPROVED TEMPERATURE AND FIRE RESISTANCE

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The study considers the mechanical properties and temperature resistance of partially pyrolysed composites reinforced with various fibres. The composites were prepared by pyrolysis at 650 °C, where only partial conversion of the polymer to the inorganic SiOC structure takes place in the matrix. Such a hybrid matrix bears resemblance to polymeric materials in a density and Young's modulus, but oxidation resistance and creep behaviour are closer to silicate glasses. Pyrolysis also ensures that the whole composite material is non-flammable with very low potential for releasing toxic gases during a fire. Three types of glass fibres (E-glass, R-glass, E-CR-glass fibres), two types of basalt fibres, and two types of high-strength (HS) carbon fibres were used as reinforcements. The mechanical properties – Young's and shear moduli, flexural strength, and fracture toughness – were measured at room temperature. Thermogravimetric measurements and creep tests of these composites allowed estimation of their temperature resistance and fire resistance. The results obtained suggest that the materials under investigation can be applied as panels or shells in the building industry and in transportation facilities.

INTRODUCTION

Advanced fibre-reinforced composites are used in a wide range of applications. This versatility arises from the possibility of using different types of polymeric, silicate, ceramic, and carbon fibres, which can be combined with diverse matrix types to exploit the specific properties of these components. When low manufacturing price is a priority, as is often the case, silicate fibre is combined with a polymer matrix to yield composites. These compositions are widely employed but may have limited use in applications that call for thermal or fire resistance. The fire resistance of polymeric matrix composites can be improved by flameretarding additives but this solution has only a limited effect.

Partial pyrolysis is one of the ways to obtain a composite material with improved temperature or fire resistance and satisfactory mechanical properties. Composites with silicate fibre reinforcement and polysiloxane precursors and processed by complete pyrolysis at or above 1000 °C contain fully ceramised Si–O–C matrices and exhibit very low strength at room temperature with a considerable tendency towards brittle fracture. However, in the case of pyrolysis terminated at temperatures between 600 °C and 750 °C, the materials exhibit flexural strengths exceeding those of their cured-only counterparts [1]. This level of pyrolysis also significantly enhances the creep resistance of the composites. In addition, this partial pyrolysis is sufficient to ensure that the composite material is non-flammable with very low potential for releasing toxic gases during a fire as shown at the end of this study.

The fire resistance assessment of a material helps determine whether its physical and chemical properties meet a given set of requirements when it is exposed to elevated temperatures [2-6]. The release of toxic or suffocating gaseous combustion products or, in the case of oxygen deficiency, gaseous pyrolysis products is one of the most serious problems. Another risk is that of the ignition of these gases at temperatures exceeding the flash point. It is also necessary to assume that the heat released during the combustion of gaseous thermolysis products contributes to the strength of the fire. An important criterion for fire resistance is the maintenance of mechanical properties at elevated temperatures for several minutes or tens of minutes.

The fire resistance of composites has often been discussed in the literature. The effects of heat flow of 50 kW·m⁻² were studied on E-glass fibre-reinforced polypropylene [7]. Similar studies were carried out on E-glass fibre-reinforced epoxy [8] and carbon fibre-reinforced epoxy [9] composites. The fire resistance of sandwich structures using E-glass fibre-reinforced

epoxy skins with different types of polymer cores was tested according to EN 13 501 in another work [10]. The thermomechanical properties of basalt fibre-reinforced composites have been published [11-12]. A detailed fire resistance study examined various types of protective coatings on a tubular composite beam made of E-glass fibre-reinforced polyester [13]. Particular attention was paid to the thermogravimetric measurements of each material taken both in air and under conditions of pyrolysis as the other extreme case occurring during a fire. At present, the effects of temperature on building materials are of great interest [14-15]. These investigations are often focused on the fire resistance of composite rebars in concrete that replace conventional steel reinforcements [16-17]. Similar to the present study, an article explores the possibilities of improving the fire resistance of phenol formaldehyde matrix composites through pyrolysis after moulding [18].

Partially pyrolysed composites, which differ in the technology used, have been investigated in several articles. The influence of pyrolysis temperature on mechanical properties has been investigated for composites reinforced with 1D basalt fibres [19] and 2D woven basalt [20-22]. Gadow and Weichand used the H62C resin, an advanced type of solvent-free polysiloxane thermoset from Wacker (Germany), with Kamenny Vek basalt fibres as reinforcement [23-24]. Mingazzini et al. used 2D basalt reinforcement from HG-GBF Basalt Fibre and polymethylsiloxane resin as the matrix precursor [25]. After initial pyrolysis at 700 °C, impregnation and repeated pyrolysis were carried out. The mechanical strength achieved at 400 °C was in the range 90 - 120 MPa. Cox used woven basalt fibres as reinforcement, while polysiloxane SPR-688 and polycarbosilane SMP-10, both from Starfire Systems, were used as matrix precursors [26]. The pyrolysis was terminated at 850 °C. The values of the flexural strength obtained were between 30 MPa and 44 MPa. It seems that the fairly high pyrolysis temperature caused considerable embrittlement of the matrix and thus led to the low strength values.

The main objective of this study is to evaluate the suitability of different types of glass, basalt, and carbon fibres for the partial pyrolysis of composites with expected increase in thermal resistance. The second objective of this study is to investigate the temperature resistance and fire resistance of these composites at their optimal designs and devise future fire resistance experiments according to the standards.

EXPERIMENTAL

Material

Components

As mentioned above, seven types of composite materials with different types of reinforcing fibres were prepared in this study. For all the composite materials studied, the same matrix precursor i.e., polymethylsiloxane resin Lukosil M130 (Lučební závody a.s., Czechia) was used. This resin was used for the production of pyrolysed composites or studied with this intent in previous works [27-30]. A great advantage of this resin is its low weight loss during pyrolysis. Another advantage is its excellent oxidation resistance in a pyrolysed state at high temperatures. The properties of the partially and fully pyrolysed states of this resin have been previously studied with respect to the evolution in time of its weight loss, density, volume shrinkage, elasticity, and hardness during pyrolysis [31]. The pyrolytic properties of the resin used are shown in Table 1.

Basalt fibres are suitable reinforcements for partially pyrolysed composites. In this study, Basfiber[®] (Kamenny Vek, Russia) and Basaltex (Basaltex NV, Belgium) fibres were used. The properties of these fibres are listed in Table 2 and described in detail in the literature [32-38].

Similar to basalt fibres, E-glass fibres (Saint-Gobain Vetrotex, Germany) are promising fire-resistant reinforcements. In earlier experiments, due to their low alkali content, E-glass fibres have shown a slightly better resistance to creep compared to basalt fibres.

The R-glass (Saint-Gobain Vetrotex, Germany) fibres are declared as high-strength (HS) reinforcement materials and exhibit better creep resistance due to their higher Al_2O_3 content and the absence of alkali species and boron. The disadvantage of this fibre is that it is the most expensive of all the types of glass and basalt fibres used.

Among all the reinforcement fibres tested in this study, the E-CR Advantex fibres (Owens Corning Composite Materials, LLC, USA) are the most recently introduced to the market. Advantex fibres have chemical compositions and properties similar to those of E-glass fibres but do not contain boron and therefore meet higher health safety requirements. According to the manufacturer, they are suitable for applications requiring materials with high corrosion resistance.

Table 1. Pyrolysis properties of the matrix precursor used [17].

Matrix precursor	• Chemical structure of the precursor	Process	Young's modulus (GPa)	Density (g·cm ⁻³)	
Lukosil M130	polymethylsiloxane thermoset	curing at 250 °C	1.2	1.22	
		pyrolysis at 650 °C	12	1.35	
		pyrolysis at 1000 °C	67	2.05	

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Fibre trade name	Specification	Tex (g·m ⁻¹)	Tensile strength (MPa)	Young's modulus (GPa)	Density (g·cm ⁻³)
E glass	EC 16	200	3400	73	2.60
E-CR Advantex	T30 SE 1200	300	3100	80	2.62
R glass	RC10	800	4400	86	2.53
Basaltex		380	1920	77	2.70
Kamennyj vek	KV13	340	2070	71	2.60
Tenax	HTA40	400	4100	240	1.77
Torray	FT300	600	3530	230	1.76

Table 2. Parameters of the fibres used [22, 27-30].

Two types of HS carbon fibres – Toray T300 (Toray Industries, Inc., Japan) and Tenax HTA40 (Teijin Limited, Japan) – were also included in this study. Compared to most silicate fibres, carbon fibres are considerably more expensive and have inferior oxidation resistance at temperatures over 600 °C. However, the application of HS carbon fibres is common in conventional commercial products and, with sufficient oxidation protection, these materials retain high strength and creep resistance at temperatures exceeding the range under investigation. The basic parameters of the fibres used are given in Table 2.

Fabrication of the composite materials investigated

The prepregs were prepared by the winding of rovings, which were pulled through a dilute resin bath. Subsequently, the prepregs were dried for 48 h at 20 $^{\circ}$ C, then cut into suitable shapes and embedded into a mould.

Moulding (pressing and curing) of the composite samples took place in an open mould at constant pressure with program-controlled increase in temperature. The range of pressures applied was chosen with the foreknowledge that polycondensation (curing of the matrix) releases water. Four pressure levels -0.1, 0.2, 0.3 and 0.5 MPa – were used to assess the effect of pressure during the curing of the matrix. The temperature profile of moulding and the pressure-induced change in the distance between the upper and lower mould parts are showed in Figure 1. During moulding, the end stops in the mould were not used and hence the final thickness of the cured sample was determined by the constant pressure applied. The nominal dimensions of the resulting samples were $150 \times 4 \times 2 \text{ mm}^3$.

Pyrolysis of the composite specimens was carried out in a protective nitrogen atmosphere. Pyrolysis was carried out at up to 650 °C with a dwell time of 10 h at this temperature. A furnace, specially designed for pyrolysis based on long-term experience, allowed for the removal of a majority of the gaseous pyrolysis products. A schematic form of the furnace's structure is



Figure 1. Moulding process of the composites investigated: the temperature profile of moulding and the pressure – induced change in distance between the upper and lower mould parts.

Designation of composites	Composite reinforcement	Matrix	Temperature treatment	Density (g·cm ⁻³)	V_f (1)	Porosity (1)
E1	E glass	polymethylsiloxane resin	pyrolysis conducted to 650 °C	2.21	0.79	0.09
E2	E-CR Advantex	polymethylsiloxane resin	pyrolysis conducted to 650 °C	2.18	0.78	0.09
R	R glass	polymethylsiloxane resin	pyrolysis conducted to 650 °C	2.6	0.79	0.08
B1	Basaltex	polymethylsiloxane resin	pyrolysis conducted to 650 °C	2.35	0.79	0.02
B2	Kamenny vek	polymethylsiloxane resin	pyrolysis conducted to 650 °C	2.27	0.75	0.02
C1	Tenax	polymethylsiloxane resin	pyrolysis conducted to 650 °C	1.55	0.76	0.09
C2	Torray	polymethylsiloxane resin	pyrolysis conducted to 650 °C	1.59	0.76	0.06
B2-cu	Kamenny vek	polymethylsiloxane resin	cured at 250 °C	2.15	0.69	0.02
B2-ep	Kamenny vek	Epoxy	cured at 120 °C	2.5	0.68	0.07

Table 3. Designation of the composites investigated and their characterisations.

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Figure 2. Construction of the pyrolysis furnace: 1 - furnace, 2 - pyrolysis cuvette, 3 - protective gas inlet, 4 - mould for composite specimens, 5 - heating elements, 6 - temperature baffle, 7 - outlet for protective gas and pyrolysis gases.





Figure 3. Optical micrographs of polished cross-sections of the pyrolysed composites according to Table 3

shown in Figure 2. The designation of the materials studied and the parameters of the resulting composites after pyrolysis produced at nominal process using a moulding pressure of 0.3 MPa are given in Table 3. The microstructure of these composites is shown in Figure 3.

Measurements

The Young's modulus was determined from the lowest longitudinal resonant frequency. The shear modulus was evaluated using the spectrum of transversal resonant oscillations. Both measurements were taken using a resonant frequency tester, Erudite (CNS Electronics Ltd., United Kingdom).

Flexural strength and creep resistance were investigated using a testing machine, Inspekt100 (Hegewald & Peschke, Germany). A PMA 06 (Maytec, Germany) high-temperature flexometer and a PMA 04 (Maytec, Germany) high-temperature four-point bending jig (inner span of 20 mm, outer span of 40 mm) were used at creep experiments. The measurements were taken under a constant bending stress of 50 MPa applied in the middle part of the sample with temperature increasing at the rate of 5 °C·min⁻¹. The measurements at elevated temperatures were carried out in a HTO 02 furnace (Maytec, Germany).

The Chevron notch technique was used to determine fracture toughness in the transversal direction as crack propagates perpendicular to the fibres. The values were calculated from the maximum force obtained from the three-point bending test (span of 16 mm), and sample dimensions. An Instron 8862 (Instron, United States) universal testing system was employed for loading with a cross-head speed of 0.1 mm·min⁻¹. All the mechanical tests were carried out on prismatic specimens with dimensions of approximately $50 \times 4 \times 2$ mm³.

The weight losses of the oxidised materials were investigated using a Derivatograph, Q-1500D equipped with high precision weigh modul SAG 204 (Mettler Toledo, Switzerland). All tests were carried out in flowing air.

Microstructural observations of polished crosssections were undertaken using a confocal laser microscope, LEXT (Olympus, Japan), and further processed by image analysis using ImageJ software.

RESULTS AND DISCUSSION

Mechanical properties of the composites investigated at room temperature

The elastic properties of the composites prepared are compared in Figures 4 and 5. The Young's modulus and shear modulus were obtained from the spectrum of resonant frequencies of mechanical vibration, which was excited by the harmonic oscillation of electrostatic force. The lowest resonant frequency of longitudinal vibration was used to evaluate Young's modulus (Figure 4). The Young's moduli of all the composites investigated agree well with the rule of mixture that incorporates the elastic constants of the matrix and fibres and their mutual share. The value of Young's modulus increases slightly with moulding pressure because of the higher outflow of the matrix during moulding and the consequent increase in the fibre volume fraction.

The shear modulus presented in Figure 5 was evaluated from the spectrum of transverse mechanical vibrations. The shear plane is perpendicular to the lamina plane i.e., if the fibres are in the X-direction, the laminas in the XY plane, and the compression force in the Z-direction, then the shear modulus can be expressed as G_{xy}. The shear moduli of silicate fibre-reinforced samples are significantly higher than those of carbon fibre-reinforced composites, which is an expected result due to the generally low shear modulus of carbon fibres. The influence of moulding pressure differs with the type of reinforcement. Theoretically, if the samples are ideally compact i.e., without microcracks, pores, and other defects, the value of G_{xv} should increase with moulding pressure. Based on the dependencies measured for the given types of reinforcement, it can be concluded that some of the pressure levels applied are already very high, leading to extremely high fibre content and hence



Figure 4. Young's modulus of the composites investigated – an indication of individual materials according to Table 3.





increased risk of cracking or formation of gaps between fibres without a matrix. However, cracking may also occur if very low pressure is applied during curing, and this can lead to a dominant role of the internal stresses and resultant microstructure defects caused by the escaping polycondensation products.

The mechanical strengths of the composites investigated were measured using a three-point bending test with a support span of 40 mm. The results are summarised in Figure 6. The highest value of strength was observed in the basalt-reinforced composites. The relatively high scatter of the values, which may indicate the presence of sparsely occurring interlaminar cracks, is an unfavourable phenomenon. The lowest strength was shown by the composites reinforced with E-glass fibres. Their strength reached only about 15 % of that of the basalt fibre-reinforced composites. The strength of the other silicate fibre-reinforced composites usually exceeded 200 MPa. The flexural strengths of the carbon fibre-reinforced composites were between 230 MPa and 330 MPa.

All the composites measured exhibited lower flexural strength than their corresponding fibres. However, from the point of view of efficient utilisation of fibre



Figure 6. Flexural strength of the composites investigated – an indication of individual materials according to Table 3.



Figure 7. Fracture toughness of the composites investigated – an indication of individual materials according to Table 3.

strength, basalt fibres exhibited much better results compared to the other types of fibres used. In the case of fibre composites, it is necessary to also consider the influence of sizing, which differs across fibre manufacturers. However, all the fibres used are provided with sizing suitable for a wide range of polar thermosets. Additionally, previously published results show that after the removal of the sizing of basalt fibres, the strength of the resultant composite is reduced yet significantly higher than those of the glass- and carbon fibre-reinforced composites reported in the present study [19].

The second reason for the reduction in the strength of the composite after partial pyrolysis is likely the partial thermal degradation of the fibres that can be chemically influenced by the surrounding matrix as well as the escaping pyrolysis products.

The third reason for the decrease in strength can be the internal stresses arising from the shrinkage of the pyrolysed matrix [31]. This reason appears to be the most likely because at 650 °C, the nominal temperature used for pyrolysis, only the basalt fibres exhibit tension relaxation, as shown in Figure 9. This fact can also be evidenced by the considerable deformations of the basalt fibres whose cross-section changes from circular to polygonal.

All the fibres and partially pyrolysed matrices used in this study exhibit rather brittle fracture behaviours. Therefore, strength measurement was supplemented with fracture toughness measurement, the results of which are shown in Figure 7. In order to ensure the propagation of crack across the fibres, a method using the Chevron notch was chosen to facilitate crack propagation directly in a predetermined plane. Nonetheless, delamination along the fibres or prepreg planes occasionally occurred during these tests, resulting in increased scatter of the fracture toughness values. A comparison of the composites prepared shows that the trends in fracture toughness are consistent with those in flexural strength; basalt-reinforced composites display the highest values in both cases due to their extensive fibre pull-out. In contrast, composites reinforced with other silicate fibres showed the lowest fracture toughness values, except for those reinforced with R-glass fibres, which displayed values very similar to those of carbon fibre composites. This can be ascribed to the activation of some toughening mechanisms as seen in the case of basalt fibre-reinforced composites.

Temperature resistance of the composites investigated

The temperature resistance of partially pyrolysed composites has already been investigated in several studies [1, 20, 23, 28]. Most of the experiments described were designed to verify properties important for applications at elevated temperatures. They mostly dealt with the influence of temperature on strength, modulus of elasticity, and creep measurement at rising temperatures. Important findings were obtained by measuring mechanical properties after exposure for 1000 h to elevated temperatures in air [45]. The study has shown that long-term use of these composites above 300 ° C leads to a decrease in bending strength. However, the experiments below show that greater application potential of partially pyrolysed composites can be expected in the field of materials with increased fire resistance.

The thermogravimetric measurements for the composites investigated are shown in Figure 8a and 8b. This diagram shows the mass losses that occur in the composites upon heating up to 1000 °C. For all measurements, two prisms of dimensions $2 \times 4 \times 4 \text{ mm}^3$ were used. For comparison, the measurements were conducted on two composite materials with polymeric matrices and without subsequent pyrolysis: a carbon fibre-reinforced polymer C1-ep (1D reinforcement of Tenax fibre, epoxy matrix, $V_f = 70$ %) and a 1D epoxy matrix composite reinforced with basalt fibre B2-ep (see Table 3). The results clearly show that the partially pyrolysed carbon fibre-reinforced composites exhibit significant weight loss above 400 °C, which is 220 °C higher than the corresponding value for standard, curedonly, epoxy matrix composites.

All composites reinforced with glass or basalt fibres exhibit very low weight loss over the entire temperature range observed. Figure 8b shows these results in greater detail. The measurements are supplemented with a thermogravimetric record of partially pyrolysed MS resins without reinforcement. The pyrolysed composites exhibit total weight loss of up to 1 wt. %, whereas curedonly composites reinforced with either basalt or R-glass fibres have weight loss of about 3 wt. %. The low weight loss of partially pyrolysed silicate fibre-reinforced composites is a good prerequisite for fire resistance primarily because of the low potential for the release of toxic gases.

The rheological behaviour of the materials investigated was studied in a four-point bending test with an inner span of 20 mm and outer span of 40 mm. The results obtained are shown in Figure 9. Partially pyrolysed basalt and glass fibre-reinforced composites exhibit very similar behaviour. The basalt fibre composites exhibit a deflection of 0.3 mm (corresponding to an extreme fibre deformation of 0.55 %) at 706 °C and 732 °C, while the corresponding temperatures for the composites reinforced with E-glass, Advantex, and R-glass are 750 °C, 795 °C, and 825 °C, respectively. This order of creep resistance roughly corresponds to the creep properties measured directly on the threads in a previous study [32]. It can be seen from Figure 10 that both basalt and glass fibre-reinforced composites exhibit good creep resistance even in the outer parts of the shear-stressed sample compared to the other materials examined. This effect can significantly enhance the thermal resistance of the structures in areas that are subject to shear, bending, and buckling.

Carbon fibre-reinforced composites exhibit high creep resistance in the central part of the sample. However, the outer parts of the sample, which were subjected to shear stress, suffered serious damage. Figure 10 shows the total loss of fibre-matrix compatibility in the outer parts. This effect occurred probably as a result of simultaneous cracking of the matrix and oxidation of carbon filaments, which corresponds to published data in [39].



Figure 8. Thermogravimetric measurements of materials investigated in flowing air: a) in whole range; and b) in detailed scale for composites with basalt and glass fibre reinforcement.



Figure 9. Thermogravimetric measurements of materials investigated in flowing air: a) in whole range; and b) in detailed scale for composites with basalt and glass fibre reinforcement.



Figure 10. Composite samples after four–point bending creep test – see experiments shown in the diagram in Figure 8.

In order to compare the properties of the composites investigated with those of standard materials, the diagram in Figure 9 was supplemented with the measurements of the polymer matrix composites. These are an epoxy matrix composite B2-ep and a methylsiloxane matrix composite in the cured state without subsequent pyrolysis B2-cu. Both composites were reinforced with basalt fibres. Figure 10 renders evident the failure in the outer parts of these composite samples because of the excessive shear stress in the polymer matrices. As mentioned above, partially pyrolysed composites with glass and basalt fibre reinforcement do not exhibit this deficiency.

CONCLUSIONS

The above results show that basalt fibres are the most promising reinforcement material for composites produced by partial pyrolysis mainly because of the highest flexural strength and fracture toughness exhibited by these fibres among all the materials studied. Although basalt fibre composites have the smallest creep resistance among the composites investigated, serious deformations are seen above 700 °C and weight loss is negligible up to 1000 °C. These parameters significantly exceed the temperature resistance of conventional polymer matrix composites. In future, it is necessary to test these developmental composites in accordance with fire resistance standards to compare their characteristics with those of the composite materials currently used.

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