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Fibre reinforced glasses

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A new method of preparing fibre reinforced glasses is put forward, which is based on further developments of the known slurry method and the sol–gel technique. This method combines the advantages of the two procedures. The prepregs are hot-pressed and the influence of preparation parameters on the bending strength are investigated. The pressure, temperature, time of pressing, granulation of the glass powder, the type of sol–gel solution and the gas atmosphere during the hot-pressing were all studied.

1. Introduction

In the literature two fundamentally different procedures for preparing fibre reinforced glasses are described, the slurry technique and the application of sol–gel technique.

In the case of the simple slurry technique the material of the matrix, as a glass powder, is mixed together with a binder (alcohols and/or organic binders such as wax and/or surface acting agents) within a whirl-pool [1]. The fibre is drawn through this slurry and covered with the matrix material [2, 3]. After drying of the binder or after burning out of the organic components, the prepregs are hot-pressed. The disadvantage of this method is that the composite can be contaminated with organic relicts of the binder and an additional working process, the burning out process, is necessary. If alcohol is applied as a binder, the adherence of the matrix powder at the fibres is unsatisfactory and leads to material losses during preparation of the prepregs (taking off the drum and cutting or sawing) [4]. The necessary densification of the prepregs is made by hot-pressing.

In the case of the sol–gel technique the fibres are either drawn through the sol–gel solution and spooled up on a drum or they are spooled up in dry condition and subsequently impregnated with the solution once or several times [5–8].

The disadvantage of these procedures is the long and complicated drying process of the prepregs (hydrolysis and poly-condensation), if the prepregs should form poreless and crack-free composites by pressureless sintering. The large volume shrinking of the solution and of the gel are the main problems associated with this technique, along with the evaporization and hydrolyzation of the alcohols. If the fibres are spooled up in the wet condition, the problem may arise where the solution hydrolyzes too early thus causing viscosity to increase during the continuous process of preparing the prepregs. If the gel condition is reached, the conversion to glass by sintering at elevated temperatures is again connected with shrinkage, a long lasting process during which SiC- or C-fibres are endangered by oxidation. Therefore, the sol–gel technique is dependent on densification by hot-pressing as is the slurry method [9–12]. Further disadvantages of the sol–gel method include its high cost, its restriction to simple oxide systems and the very complicated chemistry of the solutions.

In the present paper a method is described for preparing fibre reinforced glasses, which takes up the fundamental ideas of the two techniques mentioned and develops them further. The fibres are drawn through a whirl-pool filled with a slurry which consists of the glass powder and a sol–gel solution as a binder. Thus, the alien binder is eliminated if, for example, a SiO_2 solution is chosen, which is converted to glass after hydrolysis, polycondensation and pyrolisis. SiO_2 has the highest glass transition temperature, but other solutions with other compositions can also be used. In this way the chemical composition of solution and glass powder can be varied and directed. The addition of the solid powder to the sol–gel solution acts as a filler and the prepregs can be dried quickly without cracks because volume shrinkage by vapourization of the alcohols is low in the presence of the solid powder. With the help of catalysts a stabilized SiO_2 solution is obtained which shows a constant viscosity of 2.0 to 2.4 cSt during a time over several months. Because the matrix is formed not only by sol–gel, the method is less expensive than the pure sol–gel technique and the possibility exists for formation of more complicated matrices by variation of the solid materials composition.

2. Experimental procedure

2.1. Materials and equipment

The composites are formed from the following materials: a borosilicate glass (DURAN) from Schott Glaswerke, Maine, FRG, as matrix, SiC-fibres (NICALON) from Nippon Carbon, Tokyo, Japan, type 202, and a SiO_2 alkoxide solution from Schott Glaswerke as binder.

The prepregs were made with the help of a winding apparatus which is similar to that described in [13]. The finished prepregs were densified by means of an inductively heated hydraulic press in a graphite die. The temperature was measured with a pyrometer at a point which is situated in a hole of the graphite pressing bar about 5 mm above the samples. Before pressing the furnace volume was evacuated and then flooded with protection gas (N_2 at 99.9995% and Ar at 99.998% purity, respectively) during the whole procedure. The hot-pressed samples were cut into testing rods by a diamond saw and the bending strength was measured in a three-point device with a distance of the bearing support of 75 mm. It is important to use samples with a ratio of the bearing distance/thickness which is larger than 18 [14] in order to eliminate as far as possible the influence of shear component of the strength. Each strength value is the mean value of at least 5 single measurements at a deformation rate of 0.015 mm sec^{-1}.

The volume content of the fibres was determined automatically using an optoelectrical counter supported with a screen analyser (type 40-10, from AI Tektron) which is counting the fibre density in a cut perpendicular to the fibre axes.

2.2. Preparation of the prepregs

After burning off the resin on the fibres in an electric current furnace at 600° C the fibre bundles are drawn continuously through the slurry with the glass powder sol–gel binder mixture. From below air is blown into the slurry producing a whirl-pool effect. This is done in order to prevent sedimentation of the particles and to spread and open out the fibre bundle. In this way and together with the excellent wetting behaviour of the used sol–gel solution it is guaranteed that the fibres are coated with the glass matrix material also in the interior of the fibre bundle. As an example for the composition of the suspension in the whirl-pool a mixture of 100 g glass powder and 250 g sol–gel solution results in prepregs of about 50 to 70% of the final density after hot-pressing.

3. Results

Two limiting requirements have to be met when composites are prepared: the temperature during pressing should be high or the viscosity should be low enough that the fibres are not cut or sheared by the glass particles; on the other hand the temperature should be low enough so that the fibres are not damaged thermally by recrystallization or oxidation.

In order to perform the experiments within these limits and to find out the optimum temperature interval, a temperature–pressure run was chosen for which the pressure is applied not before the prepreg is heated up to a temperature within the working range of the glass; in the case of DURAN glass about 1270° C. Thus, a damage of the fibres is excluded. Also the rate of pressure increase of maximum 3 MPa min^{-1} is soft enough. Thermal damage will be prevented by as short as possible duration at the temperature of the pressing procedure. This time is usually in the range of 5 min. Apart from that the glass melt acts as a protection coating for the fibres from the beginning of pressing, because the fibres will be increasingly enclosed without pores by the glass melt. The pressure has to be kept constant during cooling at least until T_g, the glass transition temperature, is reached in order to prevent formation of bubbles.

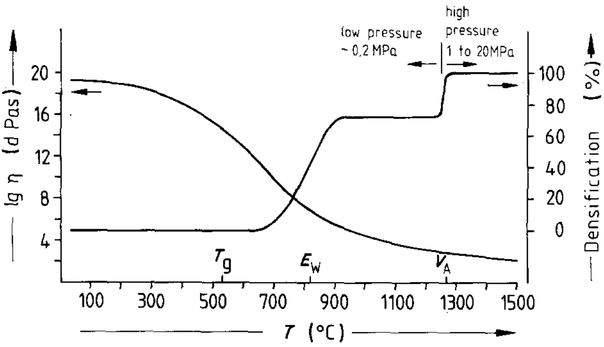

Figure 1 Process of densification of composites during heating up the samples in comparison with viscosity temperature curve of the borosilicate glass DURAN (schematically). T_g: glass transition temperature, E_W: softening point ($\log \eta = 7.6$, η in dPas), V_A: working point ($\log \eta = 4$, η in dPas).

Already during heating-up the prepregs a low pressure of 0.2 MPa is kept by the pressing bars. When the softening temperature of the glass is reached ($\log \eta = 7.6$ dPas) 70 to 80% of the densification is performed already without additional pressure. This corresponds in the case of DURAN to a temperature interval of 650° C (about 100° C above T_g) to about 800° C in which this nearly pressureless densification happens. The final densification is performed when pressure is applied in the working range V_A, the working point, of the glass ($\log \eta = 4$ dPas) as is shown in Fig. 1.

In order to prove the influence of the grain size of the glass powder in the slurry on bending strength of the composite, three different glass powder granulations were put into the slurry. The various distribution curves of these granulations are shown in Table I. In the literature [3, 15, 16] usually glass powder with granulation K4 was used. Table II implies that there is no influence by grain size on strength. The reason for this is the temperature–pressure program for heating up the samples to a temperature where the glass is melted and the pressure does not damage the fibre anymore. Additionally, the size distribution in Table I shows that the K4 powder has a 50% portion with fine grains smaller than 8 μm.

As mentioned above, the furnace is flooded with protection gases N_2 or Ar. No influence on strength could be detected (Table III) even in the case of N_2 which could have lead to formation of oxynitrides in the glass phase in the reducing atmosphere of graphite environment. But the time at higher temperatures might be too short for such a reaction. Only an amount of less than 0.14% was found by gas chromatographic method.

The pressing procedure was done according to the scheme of Fig. 1; the duration of pressure was 5 min. The fibre content for all samples was 40 ± 2 vol%. The bending strength is demonstrated in Fig. 2 and listed in Table IV as a function of temperature at

TABLE I Grain sizes of the glass powders used.

Designation	Grain size distribution
K3	99% < 60 μm, 50% < 10 μm
K4	99% < 40 μm, 50% < 8 μm
K5	95% < 25 μm, 50% < 6 μm

TABLE II Influence of the used grain sizes on the bending strength of DURAN glass-SiC-fibre composites. (SD in parentheses).

Grain size	Sample designation	Strength (MPa)	Fibre content (vol %)	Pressure (MPa)	Temperature (° C)
K3	SD3D	743(42)	41	10	1260
K4	SD6B	700(50)	41	5	1300
K4	SD7	693(112)	39	10	1255
K4	SD8A	784(77)	40	10	1250
K4	SD8B	740(121)	40	5	1250
K5	SD4C	136(37)	38	10	1360
K5	SD4A	647(100)	39	10	1255

TABLE III Influence of protection gases on bending strength of DURAN glass-SiC-fibre composites. (SD in parentheses).

Protection gas	Sample designation	Strength (MPa)	Fibre content (vol %)	Pressure (MPa)	Temperature (° C)
N_2	SD3D	743(42)	41	10	1260
Ar	SD8ABC	784(77)	41	10	1250

various pressures. For all three applied pressures of 1, 5 and 10 MPa the following conclusions may be drawn: at low temperatures no sufficient densification takes place and the fibres are damaged at too high pressures. At too high temperatures on the other hand the fibres are damaged thermally.

Investigations on the dependence of tensile strength of the fibres on thermal treatment for 1 h at pressing temperatures show that the strength decreases. This qualitative statement is confirmed meanwhile and quantified by [17]. A very steep decrease in strength was observed after a thermal treatment of 12 h duration in ref. [18]. In another paper [19] the fibres have been heated up within 45 min. and kept constant for 2 h. After this treatment at 1200° C similar strength values were obtained as in the case of the present paper. However, Mah and co-workers [19] have measured higher values which may be due to the much shorter fibre length in the tensile test (down to 1/5).

The maxima of bending strength of the composites are shifted to lower temperatures with increasing pressure. This means that a good densification at low pressure is obtained only with a relatively low viscosity glass melt. However, if the applied stress at too low temperatures is too high, the above mentioned damage of the fibres occurs (e.g. at 1050° C and 10 MPa). It seems that this is also the case at higher temperatures if the pressures are too high, e.g. the experiments with pressures of 15 and 20 MPa at temperatures of 1320 and 1350° C, in which the strength is clearly reduced (Fig. 3 and Table IV).

In all experiments described hitherto, the pressing time was 5 min. In the following experiments the duration of pressure at the temperature of pressing process will be varied in two ways: first, by keeping the samples at the temperature of pressing action for 15 and 30 min (Fig. 4, point A). Second, by an extremely slow rate of pressure increase after having reached the softening temperature (log η = 7.6 dPas) in a manner that maximum pressure is simultaneously obtained with maximum temperature within a time of 30 min (Fig. 4, point B). By means of the early action of pressure, but slow rate of pressure increase in order to prevent mechanical damage of the fibres, the glass melt should protect the fibres against oxidation by oxygen from the pores of the prepregs. This oxygen cannot be extracted totally by evacuation and flooding with protection gas. Fig. 4 shows that with increasing duration of pressure the strength of the composites decreases, which may be a consequence of a lack of thermal stability of the fibres. It is interesting that already after 15 min a value of strength is reached, which is also obtained after 30 min.

In order to find out the influence of the sol–gel solution on the properties of the composites, the hitherto applied SiO_2 alkoxide solution was exchanged

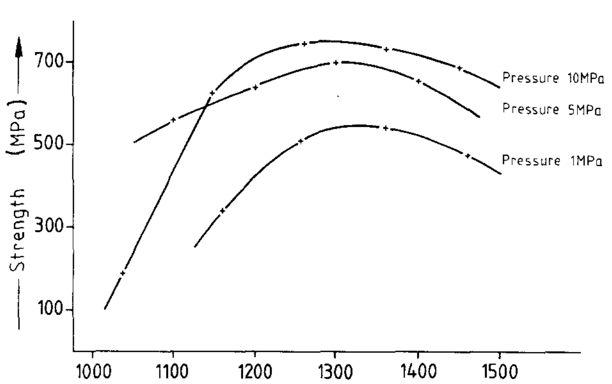

Figure 2 Bending strength of DURAN glass-SiC-fibre composites (fibre content 40 ± 2 vol %) as a function of pressing temperature at various pressures.

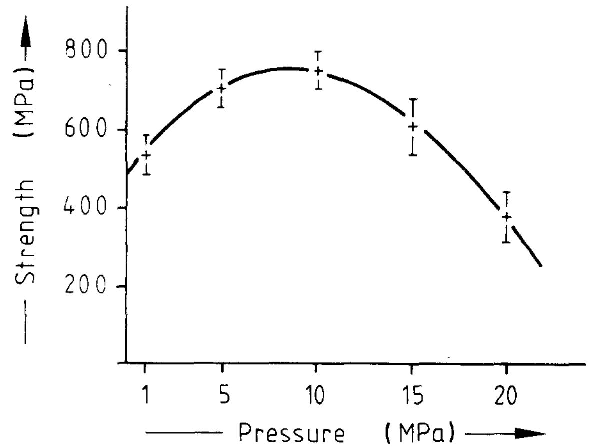

Figure 3 Bending strength of DURAN glass-SiC-fibre composites (fibre content 40 ± 2 vol %) as a function of pressure at constant temperature (1335 ± 15° C) and constant duration (5 min) of pressing process.

TABLE IV Bending strength as a function of pressing temperature and pressure (SD in parentheses).

Sample designation	Strength (MPa)	Fibre content (vol %)	Pressure (MPa)	Temperature (%)
SD3A	340(109)	41	1	1145
SD3B	506(130)	38	1	1265
SD3C	545(60)	41	1	1360
SD3E	478(92)	41	1	1455
SD6E	559(164)	42	5	1100
SD6C	646(166)	38	5	1200
SD6B	706(50)	41	5	1300
SD6D	654(57)	41	5	1400
SD5A	191(40)	38	10	1060
SD4B	625(75)	40	10	1165
SD3D	743(42)	38	10	1260
SD4C	736(37)	38	10	1360
SD4E	693(60)	39	10	1450
SD4F	615(77)	42	15	1320
SD4D	386(64)	40	20	1350

with a TiO_2 alkoxide solution. Taking into consideration the results of Brennan *et al.* with a TiO_2-containing glass ceramic, it was expected that the SiC-fibres would react with TiO_2 in the solution. Indeed, the strength of composite samples of this kind dropped drastically (by 86%) to a value of $104 (\pm 71)$ MPa for samples pressed for 5 min at 1270° C and 10 MPa. X-ray diffraction diagrams show peaks of several Si-Ti-C compounds. The fracture of these samples is brittle, similar to that of the pure glass and no pull-out fibres was observed. Similar reaction products are described in ref. [21].

4. Conclusions

The investigations have shown that fibre reinforced glasses can be produced very easily by a new method which is based on a further development of the original ideas of the slurry and the sol–gel techniques. It could also be shown that it is possible to influence the properties of the composites by using the sol–gel solution as a binder. The method retains some variations for purposes like this. The strength values obtained are comparable with those of other authors [22, 23], assuming these authors have eliminated shear forces in a similar manner.

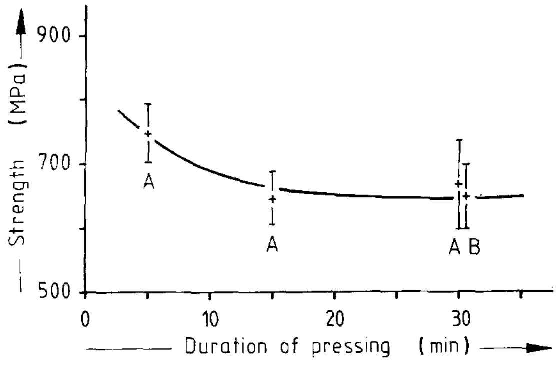

Figure 4 Bending strength of DURAN glass-SiC-fibre composites (fibre content 40 ± 2 vol %) as a function of duration of the pressing process at constant temperature (1250° C) and pressure (10 MPa). Point A indicates constant temperature and pressure duration at 1250°C. Point B characterizes a sample which was heated up from E_w (810° C) to V_A (1250° C) apart from the course in Fig. 1 with simultaneous increase of pressure from 0.2 to 10 MPa during a time interval of 30 mins.

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