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Flame Retardent Coatings on Glass

The objective of the investigations was to develop a sol-gel coating to increase the thermal stability of glass substrates like plate glass, weavings or glass wool. An organically modified mixed polymer/colloidal SiO_2 basic sol has been synthesised, which allows the crackfree densification of coatings with thicknesses up to 8 µm after densification by 500 °C with a one step dipcoating process. The basic system has been adapted to plate glass and glass weavings. It has been shown, that the heat resistance of the substrate materials could be improved substantially by the coating.

1. Introduction

Coatings are one of the main fields of application of sol-gel processing. It has been shown by many authors, that the thickness of the coatings is limited since during drying and densification cracking or peeling off occurs with thicker coatings. The crack formation of thick sol-gel coatings results from various reasons. During drying and densification by heat, a uniaxial densification process has to be employed requiring either sufficient strength of the coating or sufficient relaxation of the coating both combined with a sufficient adhesion to the surface. However, in general gels are very brittle (pure relaxation behaviour) low-strength materials. The high brittleness is a result of the strong particle-to-particle interaction in e.g. colloidal gels and the low strength of the high porosity. The particle-to-particle interaction is based on van-der-Waals forces as well as chemical bonds. Since the particle-to-particle interaction is strong and the overall strength, due to the high porosity (low solid content)

is low, cracks appear as known from general experience if the coating thickness exceeds 0.5 to 1 µm. F. Lange [1] used these considerations to postulate a relationship between a critical thickness t_c and the modulus of elasticity E, the Gibbs free energy of crack formation G_c and the tensile stress σ.

$$t_c = E*G_c/A*\sigma^2 \qquad (1)$$

A is a proportionality factor which includes the relaxation behaviour of the system.
Quantitative calculations of tc from eq. (1) are quite difficult, since the value of A is usually not known, but qualitatively one can conclude, that if it is possible to decrease the tensile stress σ during drying and densification, then thicker coatings than the discussed "limit" of 1 µm should be obtainable. Another approach can be increasing the tensile strength of the gel, because then higher mechanical forces are needed to produce cracks. However, increase of the tensile strength of the gels may result in a reduction of relaxation too and by

this the effect can be compensated. The objective of this paper is to summarise the work carried out in order to control particle-to-particle interaction in sol-gel systems with respect to obtaining an improved relaxation behaviour and thicker coatings.

2. Experimental Procedure

The details of the synthesis of SiO_2 sols modified by methyl groups and SiO_2 have been described elsewhere [2,3]. For coating glass surfaces precleaned microscopy slides and 4 mm thick float glass pieces were dipped into the sols and withdrawn with 2-25 mm/s. After 15 minutes drying at 80 °C the samples were heated up to 500 °C with a heating rate of 0.3 K/min and held 1 hour at this temperature. The samples were cooled down to room temperature for 8 h in the furnace after switching off the power.
E-glass fibre weavings (1.1 00 g/m^2, fibre thickness approx. 9 µm) were dipped into the sol and withdrawn. The excess sol was removed by squeezing the weaving. The coated weavings were heat treated at 100 °C for 1 h.

Coating thicknesses were determined by profilometry and electron microscopy. Adhesion and scratch resistance of the coatings were determined by the Taber Abrader test with 500 g load and 100 abrasion cycles. The surface damage was measured by light scattering using a He/Ne 4mW laser in combination with an 12 cm Ulbricht sphere device (according to DIN 52347).
The coatings were tested by heat treatment either in furnaces with a well defined temperature program or by burner tests where the weavings and plates were fired by gas burners with a temperature of about 1500 - 1700 °C. Elongation of coated weavings under both thermal and mechan-

ical load was measured via LVDT (Linear Variable Differential Transducer) with a self-developed device where the hanging weavings were heated from both sides and loaded with a 40 g weight.

3. Results and Discussion

3.1. General considerations

The heat resistance of glass substrates is related to the T_g of the glass and the thermal shock resistance, which is a function of the thermal coefficient of expansion and strength. T_g describes the temperature range at which the glass becomes soft. Coatings with higher T_g values should be able to increase the overall value of the systems (substrate plus coating). If external forces are applied (e.g. gravity), the T_g of the coating and the volume ratio between substrate and coating are the controlling parameters for the stability of the shape with increasing temperature.
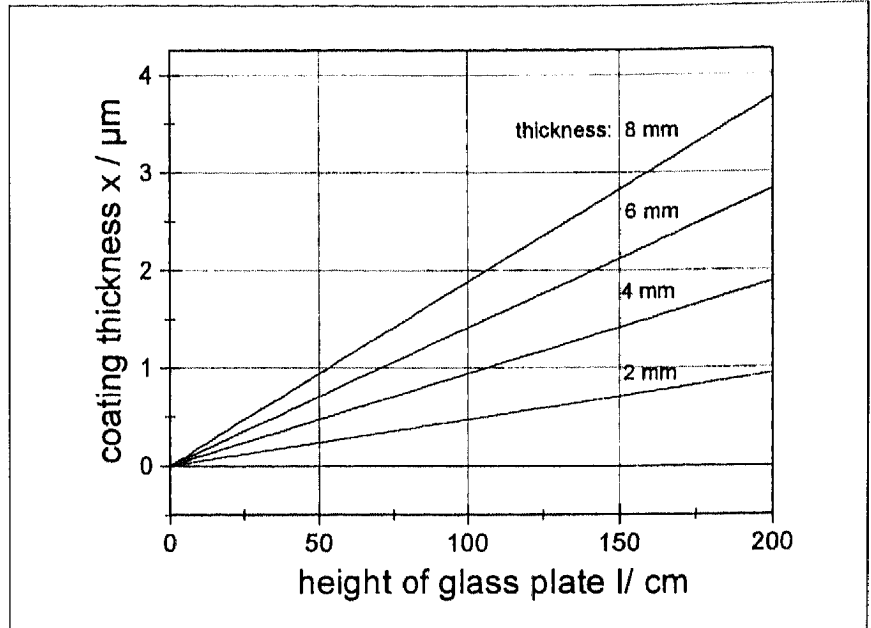
Fig. 2: Required coating thicknesses x as a function of the glass height and thickness, calculated from equation (4).

For the stabilisation of a plate glass under gravity conditions, the coating has to carry the weight of the plate, as indicated in figure 1. In this case, the mechanical strength of the coating has to be high enough in order to keep the plate in shape. The overall performance in this case should depend on coating thickness, coating strength and size of the plate. In order to estimate the requirements for a coating on a plate glass under gravity conditions, an estimation has been carried out to determine the range of the coating thickness to be applied. Fig. 1 illustrates the considerations.
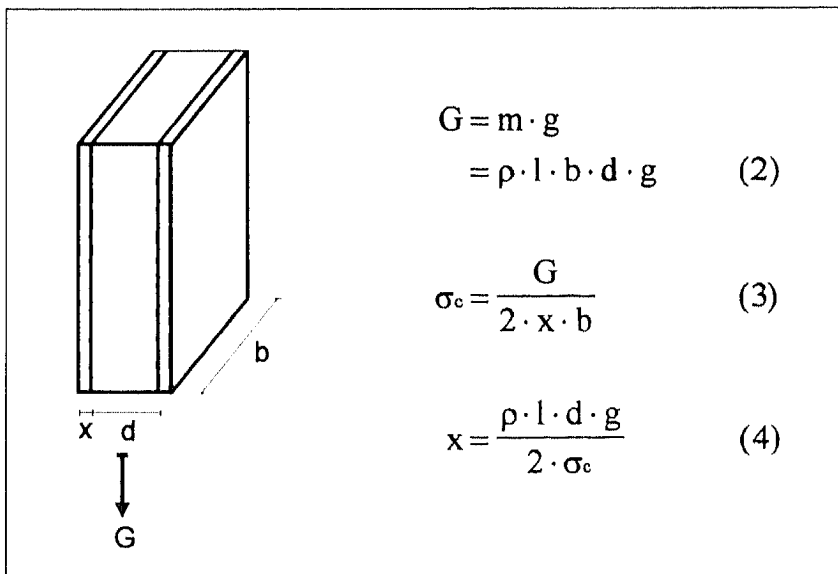
As one can see from equation (4), the required thickness of the coating only depends on the height and the thickness of the glass plate. In fig.2, the required thicknesses as calculated from equation (4) for different lass thicknesses and heights of the glass late is shown.

The estimations show that coating thicknesses in the micrometer range are sufficient to support even glass plates with considerable heights at temperatures above the T_g value of the glass plate. The support, of course, is limited in temperature by the T_g value of the coating which is not considered in these calculations.

$$G = m \cdot g$$
$$= \rho \cdot l \cdot b \cdot d \cdot g \qquad (2)$$

$$\sigma_c = \frac{G}{2 \cdot x \cdot b} \qquad (3)$$

$$x = \frac{\rho \cdot l \cdot d \cdot g}{2 \cdot \sigma_c} \qquad (4)$$

Fig. 1: Illustration of eq. (4). The weight G of the melting glass plate is carried by the cross section of the coating. l, b, d are the height, length and width of the glass plate with a density p (2,4 g/cm³). x and s_c stand for the coating thickness and estimated tensile strength after 500 °C densification (50 Mpa).

3.2. Development of coating sols

As already mentioned in the intro-
duction, there are several ways of
obtaining thick coatings. One way
would be the increase of the tensile
strength of the coating. However, in
three-dimensional crosslinking inor-
ganic amorphous systems, strength
and relaxation behaviour, in general,
are correlated. That means, with in-
creasing strength, a decrease of re-
laxation behaviour has to be taken
into consideration. In gels, the me-
chanical properties are the result of
colloidal particle interaction based
on van-der-Waals forces, but mainly
on chemical condensation leading to
strong bonds between the particles.

Densification of coatings requires a
considerable movement of material
due to the requirement of a uniaxial
process. The more densely the mate-
rial can be employed during the coat-
ing process (high solid content), the
smaller are the average transporta-
tion paths for colloidal particles to
get dense. Based on this considera-
tion, a process has been developed
which already has been described in
detail elsewhere [3]. For the develop-
ment, aqueous electric charge-stabi-
lised silica sols with an average par-
ticle size of 7 nm in diameter has been
chosen. To reduce the particle-to-
particle interaction after destabilisa-
tion (which, for example, takes place
automatically in processing steps like
concentration of the system or sol-
vent removal) the SiO_2 particles were
covered by methyl groups to coating
with methyltriethoxysilane.
The coverage of the particle surfaces
with CH_3 groups results in two ad-
vantages: First, the particles are pre-
vented from condensation due to the
lack of SI-OH groups, and second,
the effect of the repulsing forces is in
a much smaller range compared to
electrostatic repulsing forces. This
should lead to a higher solid content
without gelation at low viscosities.
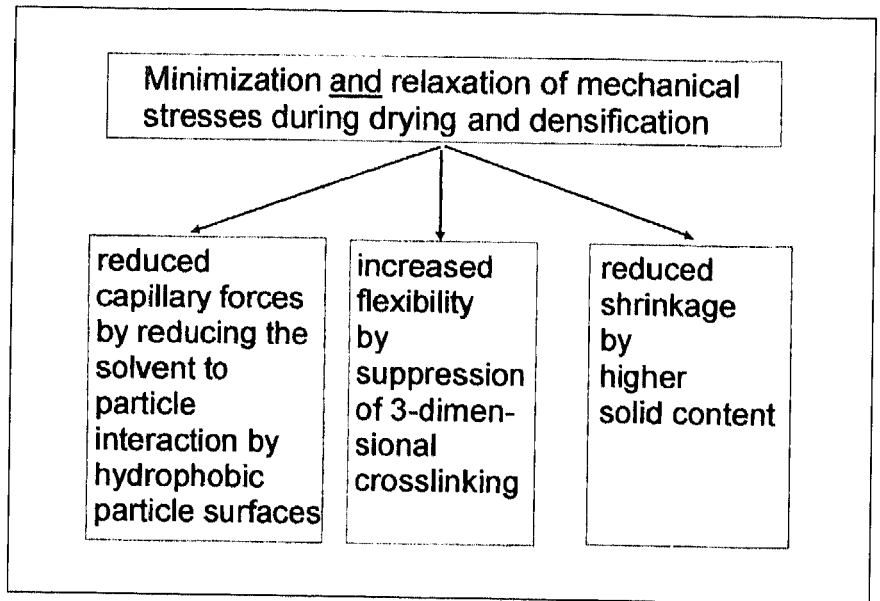In fig. 3, the strategy and the possible

Fig. 3: Schematic presentation of the keys to make thick SiO_2-
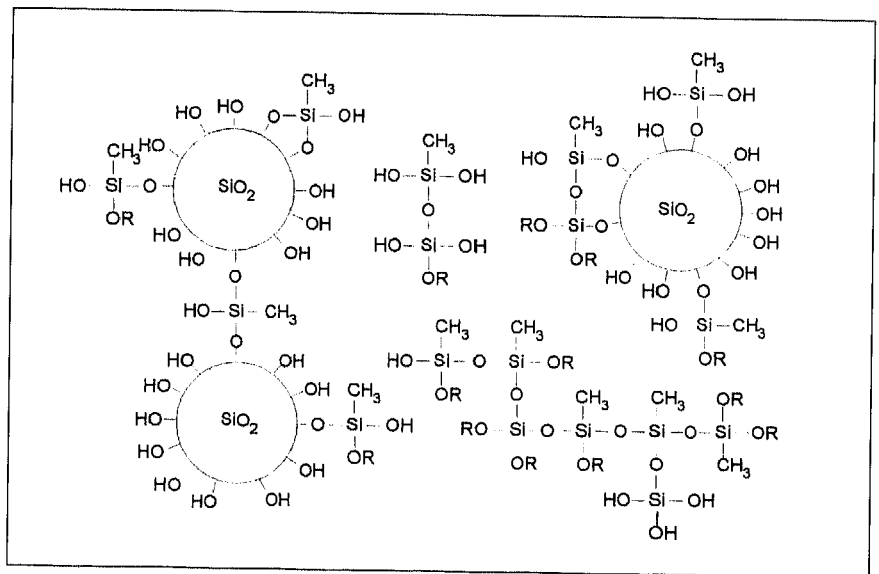Coatings with one dipcoating and densification step.

Fig. 4: Model of a MTEOS/TEOS/colloidal silica sol with a polymer/
colloidal mixed structure.

advantages of this consideration are
shown.
In fig. 4, a scheme of the process of
surface modification of nanosized
SiO_2 particles by methyltriethoxysi-
lane is shown. The process results in
an overall reduction of the particle-
to-particle interaction forces.

By the modification, the solid con-
tent of the modified polymer/colloi-
dal sol can be increased to about 50
wt.%, whereas with an unmodified
sol gelation occurs very rapidly if the
solid content exceeds 20 wt.%. The
sols are slightly opaque but yield to
clear and colourless coatings. Pure,

unmodified colloidal sols can be electrostatically stabilised at high pH values only to concentrations up to 50 wt% but it is known, that then their coating ability is generally very poor.

3.3. Coatings

In the scheme of fig. 5, the densification behaviour of modified SiO_2 sols and unmodified sols are compared. Whereas the modified sol leads to a dry, crack-free gel film which can be densified to 97 % of the theoretical density, even at a temperature as low as 500 °C (T_g value of SiO_2: ≈ 1200 °C), the unmodified gel film cracks during drying completely into small particles.

The density has been estimated from refractive index measurements.
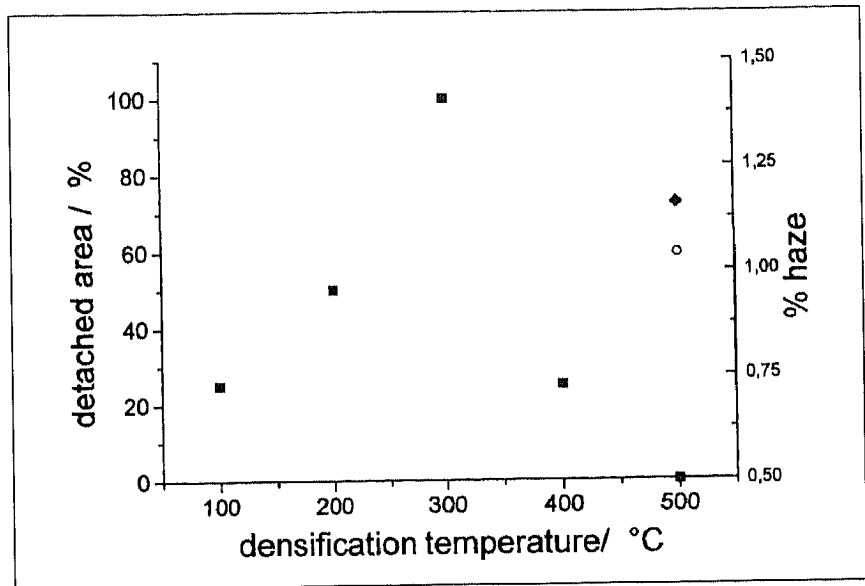
To determine the scratch resistance

Fig. 6: Detached area in % of the area covered by the Taber Abrader of a 5 μm thick SiO_2-coating on float glass due to the Taber Abrader test (100 cycles, 500 g load) as function of the densification temperature; detached area, haze, haze of the uncoated sample for comparison.
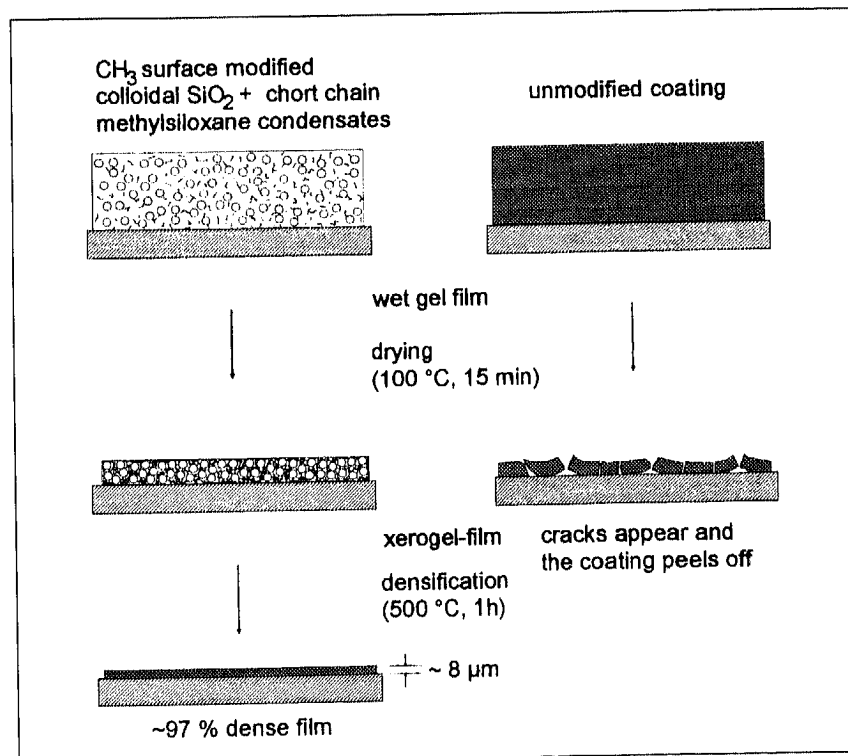

Fig. 5: Comparison of the drying and densification behaviour of modified and unmodified sol gel films. The methyl-modified colloidal/polymer film can be densified crackfree at 500 °C to approx. 8 μm thick coatings, whereas unmodified films crack upon drying or densification.

and adhesion of the coating on a float glass substrate after different temperature treatment, the Taber Abrader test was used. After the test, the glass plate was checked visually and microscopically in order to see if parts of the coating were detached. The largeness of the detached areas is attributed to the quality of adhesion. Fig. 6 shows the detached area and haze (in %) after the Taber Abrader test.

Fig. 6 shows that the adhesion undergoes a minimum at 300 °C and the maximum is reached after densification at 500 °C where no detached areas were detectable. Light scattering was determined from this sample, showing that the increase of scattered light after the Taber Abrader test was + 1.04 % in comparison to +1.16 % of the uncoated glass plate, which indicates that the coating is at least as scratch resistant or even better than the substrate. The adhesion minimum at 300 °C can be explained using thermal analysis data as shown in fig.7.
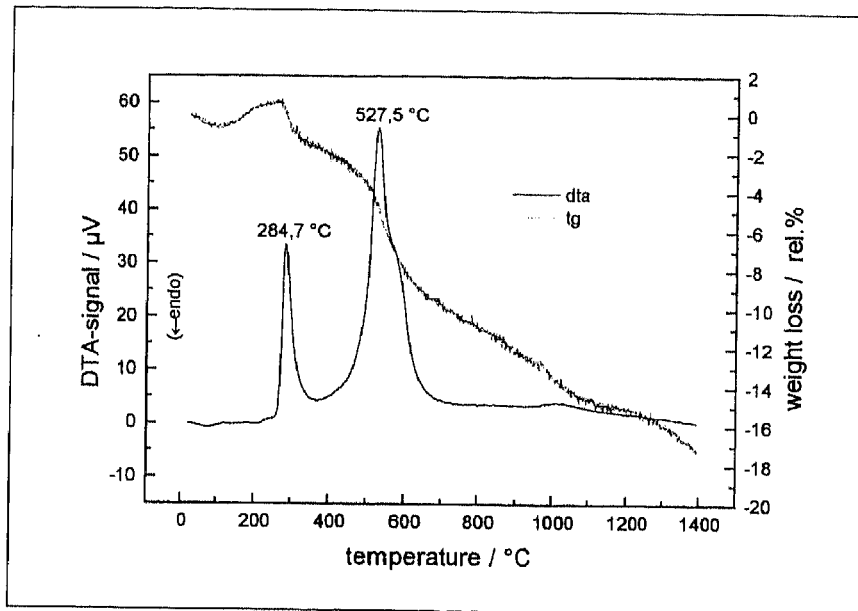
Fig. 7: DTA/TG plot of a xerogel powder consisting of MTEOS-TEOS/colloidal silica, dried at 100 °C. Heating rate: 20 K/min. Two peaks at 284,7 and 527,5 °C indicate the burning of alkoxy- and methylgroups.

soaked in by the uncoated weaving within 2 minutes whereas the coated weaving does not get wetted.

Electron microscopy shows, that the approximately 9 µm thick fibres are coated with a approximately 1.5 µm thick SiO_2-coating which builds triangular membranes between two crossing fibres as can be seen in fig. 10.

Due to the membrane-like structures the coating has a high binding ability and can also be used for the fixation of already mounted heat insulation materials.

3.3. Thermal behaviour of coated glass and fibre samples

If microscopic slides are coated with a modified sol and densified at 500 °C, it is not possible to melt them by gas burner with flame temperatures of about 1700 °C. The sample temperature in this case is above 1000 °C. In opposition to this, the uncoated slides were completely melted after 50 seconds [5] . This behaviour can be expected from the calculations shown in fig 2. However, the application of these results on larger plates is rather difficult since up to now, it was not possible to avoid the crack formation completely after heating up to 1.000 °C. If cracks are formed, the support function of the

During drying residual solvents (water, ethanol) vaporise from the gel. Further heating causes the desorption of adsorbed water (no peak detectable) and the decomposition of unhydrolized alkoxy-groups and methyl-groups indicated by two peaks at 284,7 and 527,5 °C in the DTA/TG plot of fig 7. Since it is known, that for temperatures < 400 °C adhesion of a silicate coating is dominated by hydrogen bonding interactions and not by Si-O-Si bondings to the substrate, it can be understood, that the adhesion of the coating to the substrate is weakened by the thermal treatment up to approx. 300-400 °C. Further densification at higher temperatures leads to the formation of Si-O-Si bondings to the substrate, providing again strong adhesion. Adhesion promotion due to sodium diffusion from the substrate into the coating is neglected by this consideration.

The coating already shows a good adhesion after 100 °C drying. At this temperature the coating is still rather flexible which is of special interest

for glass fibre articles which have to maintain their flexibility after coating. Fig. 8 shows the flexibility of fibres or weavings after coating and temperature treatment at 100 °C. The sample can be bend without any cracking of the coating.

Due to the remaining methyl-groups the coated weaving exhibits hydrophobic properties. As shown in fig. 9, a coloured droplet of water gets
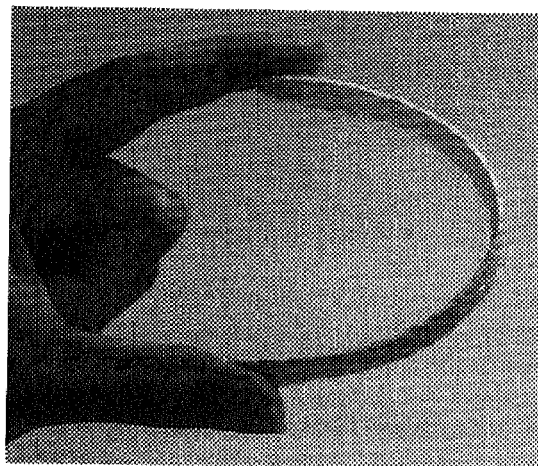

Fig. 8: Flexibility of the coated weaving. The coated weaving can be bend without cracking of the coating.
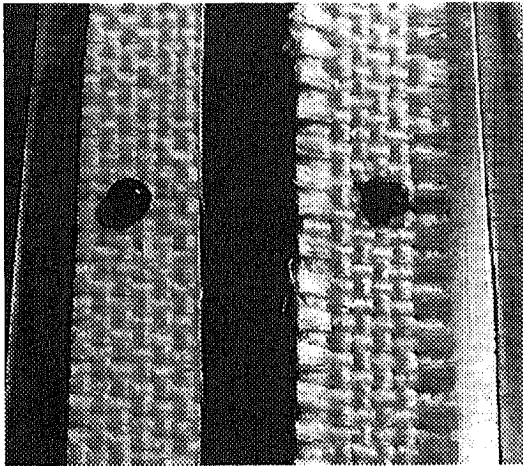
Fig. 9: Hydrophobic behaviour of a coated weaving after drying at 100 °C compared to an uncoated one. The coloured droplet of water gets soaked in by the uncoated weaving within 2 minutes, whereas the coated weaving is not wetted.

It can be seen, that the uncoated weaving melts and drops at about 800 °C. The shrinkage of the uncoated weaving before dropping is attributed to a surface tension effect of the melting horizontal fibres of the weaving (see fig. 13). The custom coated (unknown) weaving (Hellhake Hightemp 1.100 g/m) melts at about 850 °C without former contraction. This is a hint that this coating can suppress the melting-together of the fibres but is not able to prevent the weaving from elongating at temperatures higher than 850 °C.

The sol-gel coated weaving elongates at about 1050 °C. This was due to a breakage of the fibre strip and not due to a melting. The breakage was attributed to defects in the strip, and the brittleness increasing drastically with temperature. Strips heated up without mechanical load remain unchanged even after 30 minutes at 1 000 °C. In fig. 12, two strips (coated and uncoated) heated at 1000 °C for 30 minutes are shown. The uncoated piece is molten together. In this case the coating thickness is only 1.5 μm.

Fig. 10: SEM of a ca.1.5 μm thick coated E-glass fibre weaving densified at 100 °C. The coating has binding ability due to the formation of triangular membranes between two crossing fibres.

coating is interrupted, and the stabilisation effect decreases. For this reason, the coatings have to be optimised to remain crack-free even after heating up to higher temperatures.

For coated weavings, the situation is much more advantageous since the volume ratio between coating and fibre is higher than in the case of plates. For testing the heat resistance of coated glass fibre weavings, a self developed equipment was used. The samples were placed between two heating plates and a 40 g weight was applied. The elongation was measured inductively via LVDT (linear variable differential transducer) while heating up according to the standard of DIN 4102 [6]. The experimental procedure is shown in fig. 11.
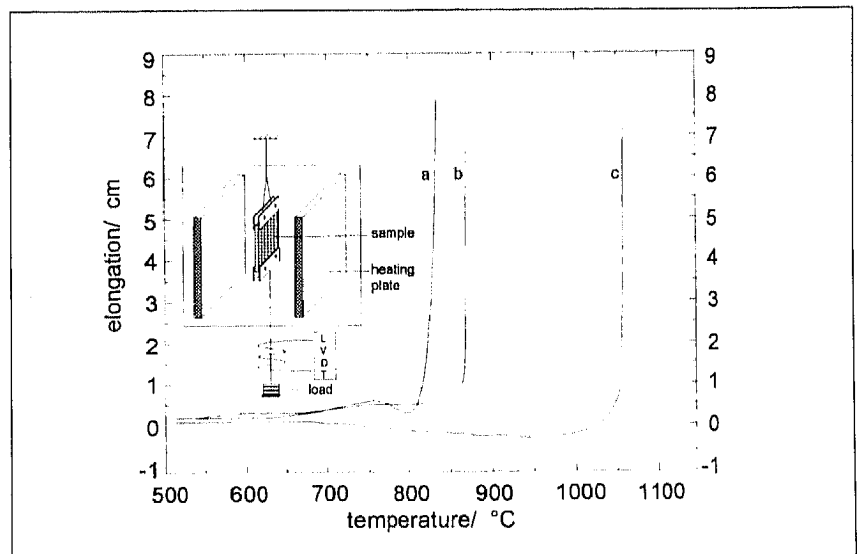

Fig. 11: Comparison of a: uncoated, b: custom coated and c: sol-gel coated E-glass fibre weaving (1.100 g/m², (5x10) cm, fibre thickness 9 μm) under both thermal and mechanical load (40 g).
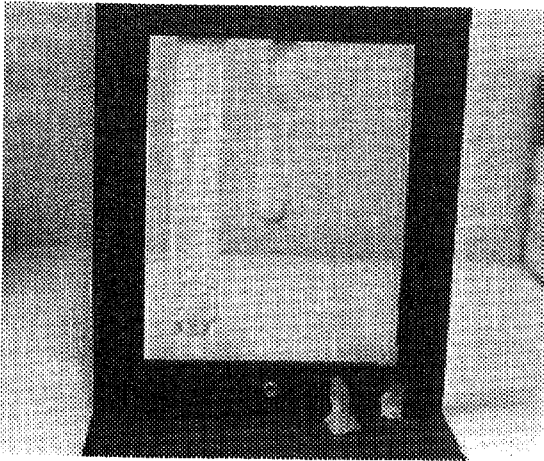
Fig. 12: A sol-gel coated, a custom coated and an uncoated (from left to right) piece of E-glass fibre weaving after 30 minutes at 1000 °C. The uncoated weaving is melted to a glass lump at the bottom.

5. Literature

[1]   F. Lange, "Liquid Precursors for Ceramic Particles, Fibres and Thin Films", Proceedings of the International Symposium on Molecular Level Designing of Ceramics, p. 14-28, March 16, 1991, Nagoya, Japan.

[2]   Offenlegungsschrift DE 421743 A1, Verfahren zur Herstellung von Glas mit verbesserter Langzeitstandfestigkeit bei erhöhten Temperaturen. Institute for New Materials, 66123 Saarbrücken, Germany.

[3]   M. Mennig, G. Jonschker, H. Schmidt, Sol-Gel Optics II, 1991, Vol. 1758, pp 125-134 J. D. Mackenzie, Ed. Bellingham: Spie- INT Soc. Optical Engineering (Series: Proceedings of the Society of Photo-Optical Instrumentation Engineers (Spie), Vol 1758).

[4]   T.A. Michalske, K.D. Keefer, "Adhesion of hydrated silica films", Mat. Res. Soc. Symp. Proc. Vol. 121 (1988) 187-197.

[5]   G. Jonschker, M. Mennig, H. Schmidt, Sol-Gel Beschichtungen zur Verbesserung des thermischen Verhaltens von Flachglas, Glastechnische Berichte, to be published.

[6]   DIN 4102, Beuth Verlag, 1990

The behaviour can be explained by the formation of a high viscosity SiO_2 coating around the fibres. The coating prevent the molten cores of E-Glass of the fibres from getting in touch with each other, and by this, from shrinking and melting together. Additionally, based on its mechanical strength, the SiO_2 coating maintains a reasonable strength of the weaving even at higher temperatures. The effect is shown schematically in fig. 13.

The picture 12 shows an 1.5 µm thick coated, an customary coated and an uncoated piece of E-glass fibre weaving after 30 minutes at 1.000 °C. The uncoated weaving is molten to a glass lump and the custom coated weaving shrank about 50 % and looks like compact glass. The sol-gel coated weaving however is nearly unchanged. After the test the weaving was brittle, but the single-fibre structure of the weaving was still preserved. Regarding the high temperature we assume that the coating is now nearly completely densified SiO2-glass which wraps the liquid glass fibre.

Therefore we can conclude that the sol-gel coating acts as an high-temperature antistick agent to prevent a contact of the low-melting fibres according to fig. 13.

4. Conclusion

The experimental results show that even relatively thin coatings on glass can change the thermomechanical properties of the whole system remarkably. The effect, of course, depends on the volume ratio of the coating to the substrate material, and for this reason, it is enhanced on parts made from glass fibres. The sol-gel process will provide an interesting route for the application of thick coatings if a coating technique for thicker coatings is available. The demonstrated route to fabricate thick coatings by surface-controlled colloidal particles as intermediates, in this case shown with silica, opens a variety of possibilities for various systems.

Authors: M. Mennig, G. Jonschker, H. Schmidt; Institute for New Materials, 66123 Saarbrücken, FRG. P. Kahanek, Bischoff Glastechnik, Bretten, FRG. Paper presented at the 1st Int. Conf. on Sol-Gel Production, Saarbrücken, Oct.93: Proceedings published by Trans Tech Publications, Zürich, Schweiz.
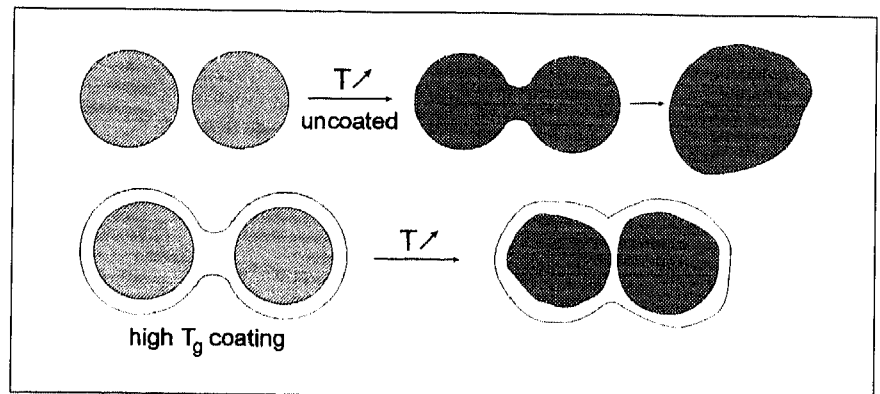
Fig. 13: Effect of the high Tg coating on temperature stability. left: solid glass phase, right: melted glass phase.