GLASS SEALINGS BY SOL-GEL DERIVED ORGANICALLY MODIFIED SILICATES

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Abstract

A new material structurally related to glass and containing an inorganic as well as an organic polymeric network is prepared by the sol-gel process. The inorganic backbone is built up by hydrolysis and condensation of metal alkoxides like $Si(OR)_4$ and substituted silicoesters of the type $R'R''Si(OR)_2$ (R, R', R'': organic groupings). Additionally an organic crosslinking is achieved by use of photopolymerizable ligands R' and R''. The moisture resistant seal to glass is due to reactive bonds and structural similarities of the new material to glass (organically modified silicate). Thus, it is possible to develop glass sealings which are applicable at temperatures between -30°C and +80°C.

1. Introduction

Sealing to glass surfaces can result in problems if the moisture on glass

surfaces cannot be removed completely and if it is not possible to apply

effective adhesion promoters. Especially for this reason the moisture re-

sistance of glass seals is sometimes very poor /1/. This can lead to serious

practical problems. It was shown elsewhere that phenyl group containing orga-

nically modified silicates (ORMOSILs) exhibit extremely moisture resistant

seals to glass surfaces if used as hot melts /2,3/. This type of material

can be prepared by the sol-gel process and is based on a glass-like amorphous

inorganic network where organic instead of inorganic groupings play the role

of the network modifiers /4/.

Organic network modifiers beside their effect on structure can change the

material properties drastically compared to inorganic network modifiers.

For example materials can be prepared which are thermoplastic at low tempera-

tures (e. g. at 100°C) and soluble in organic solvents /3/. The high moisture

resistance of seals to glass with this special type of ORMOSILs described in

/3/ is interpreted by the presence of chemical bonds which are built up during

the sealing procedure and which are due to reactive groups (SiOH and SiOR)

in the sealing agent. Since materials of that type have been developed for the application in a hot sealing procedure, they have to be thermoplastic. Therefore they get soft at temperatures above 70°C. At temperatures below 0°C these materials become very brittle and therefore the actual sealing strength is very poor at these temperatures. It was shown elsewhere that it is possible to synthesize glass-like materials by the sol-gel process with organic groups used as network formers /5/. In this case the organic network was built up by methacrylate polymerization.

For outdoor applications the hot melt material properties described above are insufficient since seals have to resist temperatures from -30°C up to +80°C. In order to improve the high temperature behaviour it seems to be reasonable to develop highly crosslinked materials. However, the glass-like inorganic crosslinking via metal oxide bonds normally leads to insoluble materials brittle even at higher temperatures. Therefore it was of high interest to introduce an organic (linear) type of crosslinking which should lead to a non-thermoplastic, less brittle material without losing the good properties of the basic material with respect to adhesion to glass. From a more linear type of crosslinking it can be expected to come to less brittle products at low temperatures, too, if a "silicone rubber type" structure can be partially realized. In figure 1a-c a comparison of the idealized structures of glass (a), organically modified inorganic (b) and crosslinked organically modified inorganic (c) networks can be seen.

Therefore the use of a methylvinylsilane as a precursor was proposed because of its possibility of organic crosslinking by the addition of the methyl to the vinyl group or by vinyl polymerization as described in /6/. Materials based on the system diphenylsilane/methylvinylsilane/tetraalkoxysilane without organic crosslinking have already been used as hot melts in /2/.
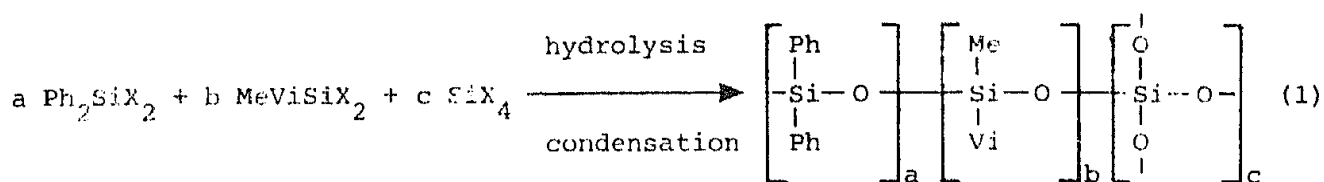
Since for glass to glass seals a hot sealing process cannot be applied the sealing material has to be used in a liquid, mostly viscous state. Parameters have to be found out in order to obtain the desired viscosities. After application a curing procedure has to be performed which leads to the desired properties of the seal.

Objective of this work was to show that it is basically possible to prepare moisture resistant and temperature resistant seals by this method and to establish the basic parameters for this procedure.

$R' = Me, CH = CH_2$

(a)   (b)   (c)

Fig.1. Comparison of the idealized structures of (a) glass, (b) inorganic network with organic network modifiers and (c) inorganic network with organic network formers. The fourth valence bond of Si directs out of the plane.

2. Experimental

Hydrolysis and condensation were carried out as described in /2,3/. Therefore dichloromethylvinylsilane (MeViSiCl$_2$), dichlorodiphenylsilane (Ph$_2$SiCl$_2$) and tetraalkoxysilane (Si(OR)$_4$) were mixed in an appropriate ratio and re-fluxed in ethanol for two hours /3/. After this treatment the solvent was removed by evaporation. To the low viscous precondensate acetone and aqueous HCl were added and the mixture was refluxed for 30 more minutes. After this procedure the solvent was removed by evaporation and further condensation was performed by heat treatment up to 200°C. The heat treatment was stopped at a viscosity of $4.8 - 7.8 \cdot 10^{-6}$ m^2/s (50% solution by volume in ethylacetate; measured by capillary viscosimetry). A polymerization catalyst was added and stirred until a homogeneous mixture was achieved. This product was de-fined as adhesive. IR spectra for controlling of the SiOH and SiOR group concentrations were performed from a capillary film between sodium chloride plates.

If thicker layers were desired for sealing, organic pre-crosslinking had to be applied in order to achieve higher viscosities. Therefore depending on the type of catalyst the adhesive was treated either by heat or by UV-light until the desired viscosities were achieved.

3. Results and Discussion

3.1. Inorganic network

The inorganic network is built up by hydrolysis and condensation of the silane components according to equation (1). The methylvinylsilane and the diphenyl-silane lead to a linear and the tetraalkoxysilane leads to a three-dimensional crosslinking. That means that by the choice of composition the inorganic cross-linking and the resulting material properties (thermoplasticity or brittleness) are expected to be adjusted.

$$a\ Ph_2SiX_2 + b\ MeViSiX_2 + c\ SiX_4 \xrightarrow[\text{condensation}]{\text{hydrolysis}} \left[\begin{array}{c} Ph \\ | \\ -Si-O- \\ | \\ Ph \end{array}\right]_a \left[\begin{array}{c} Me \\ | \\ -Si-O- \\ | \\ Vi \end{array}\right]_b \left[\begin{array}{c} | \\ O \\ | \\ -Si-O- \\ | \\ O \\ | \end{array}\right]_c \quad (1)$$

(X = Cl, OR; Ph = phenyl $(-C_6H_5)$; Me = methyl $(-CH_3)$; Vi = vinyl $(-CH=CH_2)$)

If chlorides are used as precursors for reasons of HCl production only acid catalysis can be applied. On the other hand tests with alkoxides or silanols as precursors and basic catalysis lead to almost SiOH group free materials which do not show good adhesive behaviour to glass surfaces.

Unhydrolyzed SiOR groups can be detected in the IR-spectrum. The absorption band at 2960 cm^{-1} in the IR spectrum of the condensate (see figure 2) is due to the CH stretching vibrations of the unhydrolyzed SiOR group (after removal of alcohol). It is surprising that under the applied acid conditions the SiOR group is so stable. Moreover, if alcohol and acid are added to the condensate and heated it could be proved that a reesterification process takes place and the absorption band in the IR spectrum at 2960 cm^{-1} increases. Too high amounts of SiOR group lead to non-stable products (due to slow hydrolysis and condensation from moisture of the air). On the other hand small amounts of SiOR group may form bonds to glass surface silanol groups according to figure 3 which is a well-known reaction.

The bands in the 3500 cm^{-1} range relate to OH vibrations (free and bridged SiOH groups) and the bands in the 3100 cm^{-1} region to the phenyl and vinyl groups. It was experimentally found out that for a good sealing behaviour the absorptions of certain IR bands have to be within the following limits
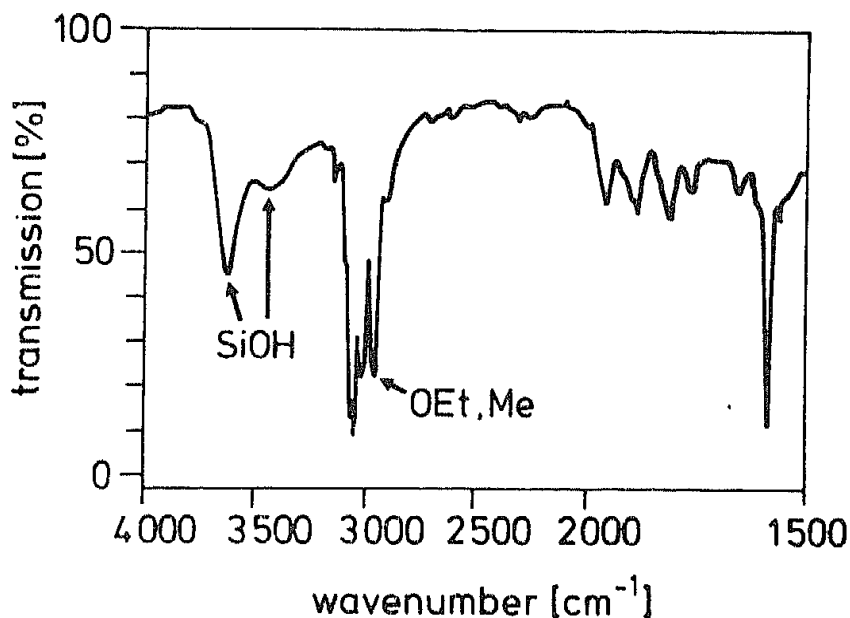
Fig.2. IR spectrum of the condensate, cured at 180°C for two hours

(whereby the 3060 cm^{-1} phenyl band and the 3010 cm^{-1} vinyl band are used as internal standards): E_{3600}/E_{3400} (SiOH) = 2,0 - 2,5; E_{3600}/E_{3060} = 0,30 - 0,38 and E_{2960}/E_{3010} = 0,95 - 1,07. Whereas the SiOH group concentration can be decreased by thermal treatment the SiOR groups were almost insensitive to thermal treatment. That means that in this system the condensation type SiOR + HOSi ⟶ SiOSi + HOR, which is reported to be very important in the pure $Si(OR)_4$ system, does not play an important role /7/. The SiOR groups have to be adjusted by hydrolysis conditions (time and temperature).
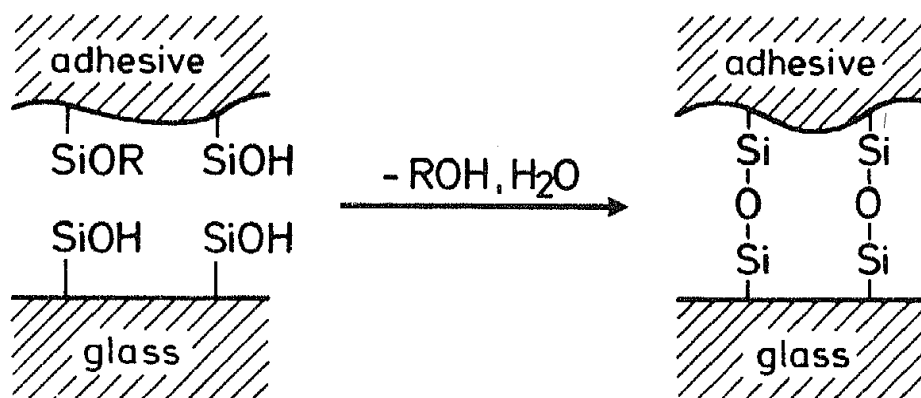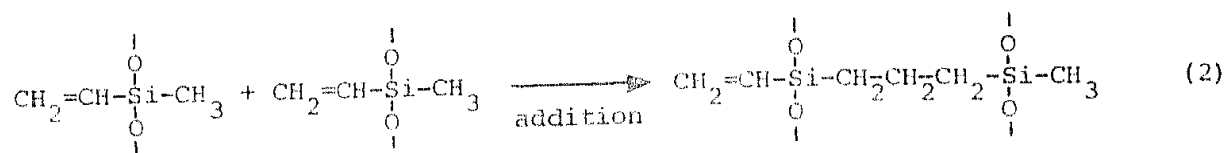

Fig.3. Covalent bond formation between the sealing agent and a glass surface

The viscosity of the condensate depends on the content of SiOH and SiOR groups, since both groups are non-crosslinking groups which affect the degree of crosslinking. If the SiOR group concentration is according to the

IR spectroscopic specification (E_{2960}/E_{3010} = 0,95 - 1,07) appropriate viscosities can be adjusted by thermal treatment via silanol condensation. The viscosity can be controlled by capillary viscosimetry. Values of about 4.8 - 7.8·10^{-6} m^2/s at 25°C are suitable for getting homogeneous mixtures with polymerization catalysts.

3.2. Organic crosslinking

For the organic crosslinking two different possibilities exist (equations 2 and 3):

$$CH_2=CH-\overset{O}{\underset{O}{Si}}-CH_3 \; + \; CH_2=CH-\overset{O}{\underset{O}{Si}}-CH_3 \quad \xrightarrow{\text{addition}} \quad CH_2=CH-\overset{O}{\underset{O}{Si}}-CH_2CH_2CH_2-\overset{O}{\underset{O}{Si}}-CH_3 \qquad (2)$$

$$-O\underset{CH_3}{\overset{\overset{CH_2}{\parallel}}{\underset{}{Si}}}O- \; + \; -O\underset{CH_3}{\overset{\overset{CH_2}{\parallel}}{\underset{}{Si}}}O- \quad \xrightarrow{\text{polymerization}} \quad -O\underset{CH_3}{\overset{CH-CH_2-CH}{Si}}O- \quad -O\underset{CH_3}{\overset{CH_2}{Si}}O- \qquad (3)$$
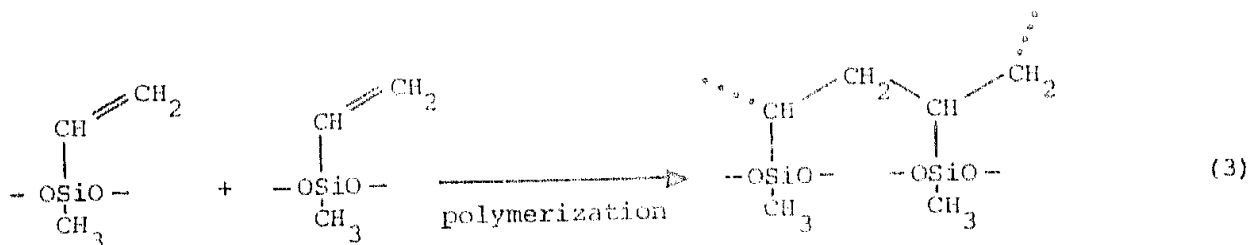
There is an evidence that by heat treatment at about 200°C a slow crosslinking takes place (loss of vinyl absorption in the IR spectrum). But that is a very ineffective method. Better results are achieved by the use of crosslinking catalysts. Therefore peroxides like tert.butylperbenzoic acid $C_6H_5COOOtBu$ or dicyclohexylperoxodicarbonate $(C_6H_{11}OCOO)_2$ are useful. The experiments show that these peroxides enable curing, but if temperatures of more than 50°C are applied gas bubbles appear inside the adhesive. They are due to the decomposition of the catalyst and the formation of gaseous or low boiling fragments like carbondioxide or acetone. Thermal shock experiments with bubble-containing adhesives show that at low temperatures the bubbles initiate cracks in the cured adhesive. For this reason catalysts without the release of volatile products are chosen. Especially some photoactive catalysts like ⍺-hydroxyketones do not produce such fragments. Moreover, the photocatalysis has the advantage that it is not necessary to heat up the seal (which may be sometimes hazardous for glass). It is of special advantage if the absorption range of the catalyst permits irradiation of the seal through glass. Therefore catalysts were chosen which become active at wavelengths above 330 nm which is suitable for the most common glasses.

3.3. Sealing

Two different types of sealing procedures were investigated. The first one was the application of thin films on glass plates with aluminum foils as counterparts. Curing was performed by irradiating the seals through the glass plates. Thereby the only inorganic crosslinked material could be used since it is a liquid of low viscosity which could be brought on the top of the glass plates by simple techniques like spraying or spreading on. The layers were covered with strips of an aluminum foil and the adhesion was performed by soft pressure. Then the plates were irradiated for some minutes by a high pressure mercury vapour lamp in the distance of about 5 cm. After this, tests showed a sealing strength of 10 N/cm. The sealing strength did not decrease after 10 temperature cycles between -30°C and +80°C.

In other experiments tests were made with tubes of about 2 mm of inner diameter. Thereby it was not possible to use the only inorganic crosslinked material since the viscosity was too low and the liquid did not remain in the tubes as plugs. Therefore the organic crosslinking step was partially performed. The adhesive was put into 2 ml medical syringes from polypropylene and irradiated for some minutes by a high pressure mercury vapour lamp in order to achieve a viscosity which was just suitable to press the adhesive into the glass tubes. The plugs did not flow out if the glass tubes were put into the vertical position and the irradiation was continued until the organic crosslinking reaction has been finished.

The seals were tested by 10 temperature cycles between -30°C and +80°C and by evacuation with respect to tight sealings. Continuous irradiation with high power UV-lamps did not change the properties of the seals. The good sealing properties are interpreted by the formation of chemical bonds between the glass-like structure of the seal and the glass surface according to figure 3.

4. Conclusions

The investigations show that it is possible to synthesize glass related, amorphous materials building up an inorganic network by the sol-gel process and an organic crosslinking via methyl-vinyl addition or vinyl polymerization. Compared to the non-organically crosslinked materials the crosslinked type shows a quite different temperature and adhesion behaviour. The materials

are still stable solids at +80°C and less brittle at temperatures below 0°C than the non-crosslinked types. Despite the change in structure they show a very good adhesion to glass surfaces and a high moisture resistance. This is interpreted as an effect of residual SiOR and SiOH groups which do not lose their effectiveness by the organic crosslinking. By variation and proper choice of reaction conditions the system can be adapted to different purposes e. g. outdoor applications. The two-step crosslinking procedure allows the adjustment of the material properties like required viscosities or of curing procedures.

5. Acknowledgements

6. References

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