HOT MELT ADHESIVES FOR GLASS CONTAINERS BY THE SOL–GEL PROCESS

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Based on organically modified silicates prepared by the sol–gel process, a sealing medium for glass surfaces was developed which overcomes basic difficulties of a hot sealing process performed with conventional thermoplastic organic polymers. The new polymers form a moisture resistant bond to the glass surface and the sealing strength is not affected by water layers usually present on those surfaces. The mechanical and thermal properties can be tailored by composition of the multicomponent system and by reaction conditions. A technical procedure based on the new material can be performed.

1. Introduction

Sealing to glass surfaces is a procedure of high technical importance, as known for example from car windshields or insulating glasses. The basic process includes the formation of adhesion mechanisms from an organic polymer to an inorganic, generally a siliceous surface. Since organic polymers in most cases are hydrophobic, and glass surfaces due to surface hydroxyl groups are hydrophilic, wettability problems may occur and the formation of strong bonds will become difficult. Moreover, more problems may arise from the fact that the state of a glass surface depends strongly on its history, since as a function of time and environmental conditions, an ion exchange process between alkaline ions and protons takes place, producing a more or less thick leached surface layer. This surface layer generally is covered with a strongly adsorbed water layer which may affect diffusion of more water into the boundary layer with time and a decrease of the adhesion strength [1], especially under wet conditions. In order to perform good adhesion despite these facts, in the past efforts were made to overcome the problem by modifying the glass surface by compounds which are able to form covalent bonds to the glass surface and at the same time can form bonds to a polymer. If the polymer is able to take up the water adsorbed on the glass surface or the modifying agent consumes the water by reaction, as known from different hydrolyzable silanes, good sealing strength that is resistant against moisture can be obtained.

The use of hot melts for technical purposes, especially for sealing food

containers, has to face even more difficulties. Since short sealing times have to be applied, the chance to dissolve the adsorbed water layer into the polymer is very low and, on the other hand, the use of primers to treat the glass surface is hardly possible for reasons of health hazard. In order to develop a procedure suitable for wet-resistant hot melts for food container sealing, polymers had to be developed which, based on their chemistry, are able to form resistant bonds to the glass surface by chemical reaction during the sealing procedure. Therefore organically modified silicates (ORMOSILs) prepared by the sol–gel process were chosen, since this group of materials allows a wide variation of their properties including the chance of tailoring the desired properties.

2. Experiments

For the technical application the hot melt was dissolved in acetone or ethyl acetate (50 wt%) and aluminum foils were coated with the sealing agent by use of common lacquer techniques (layer thickness about 15 μm). After drying, suitable caps were punched out and pressed onto the glass container with a hot sealing device (heated metal block with a silicone rubber cover) at temperatures between 100 and 200°C. Measurements of the tightness are carried out by evacuating the closed containers in a water bath; leaks can be indicated by air bubbles.

For the hot melt optimization procedure, simple tests were used to determine sealing strength and water resistance. Therefore 1 cm wide stripes of a prepared sealing foil were sealed on small glass plates. Measurements of the adhesive strength are made with a test equipment measuring the peeling strength (90°). The water resistance was tested by storing the sealed plates in moisture or water for several days before measuring the adhesive strength again.

The hot melt viscosities as a function of temperature were measured by rotation viscosimetry. The synthesis and condensation reactions are controlled by IR spectroscopy in the range of 4000 to 2000 cm^{-1}. Therefore, NaCl IR windows were coated with thin films of the hot melt from solution.

3. Results

3.1. Chemical modification of glass surfaces

First it was important to know the behavior of conventional hot melts under wet conditions in order to create a standard comparison with optimized products. Second it was important to know the effect of the glass surface treatments with different silanes on the moisture resistance of the seal. Therefore, glass plates were treated with different types of silanes. As

Table 1
Adhesive strength (N/cm) of some hot melt foils before and after treatment in moisture (40°C/92% r.h.)

Foil	Before	After 600 h	
		with epoxysilane	without epoxysilane
Polyamide	12	12	8
Ethylene–vinyl–acetate	9	5	3
Surlyn	18	18	13

hot melts, three different types of polymers were used (polyamide, ethylene–vinyl–acetate, and Surlyn (registered trade name)). In a series of rough experiments the epoxysilane

$$CH_2-CH_2-CH_2-OC_3H_6-Si(OR)_3$$
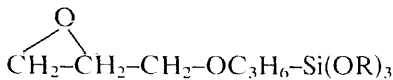
was found to be most effective as a coupling agent. Table 1 shows the sealing strength (measured in N/cm) as a function of the polymer used.

The experiments show a more or less strong decay of the sealing strength after exposure to moisture. In another experiment the seals were deposited under water and the decay of the sealing strength was measured. The results are shown in fig. 1.

These experiments show that there is a clear effect of pretreatment of glass surfaces with a reactive silane. But it shows, too, that the moisture resistance is not good enough for practical use.

3.2. Chemistry of the hot melt

ORMOSILs can be prepared by hydrolysis and condensation of different alkoxides, where at least one is a silicic acid ester containing a $\equiv$Si–C$\equiv$ bonded organic group. An example is shown here:

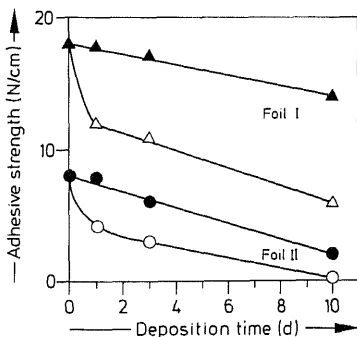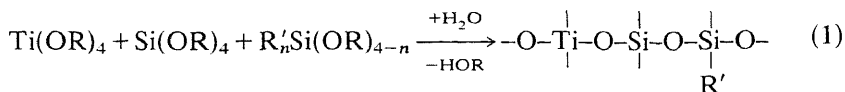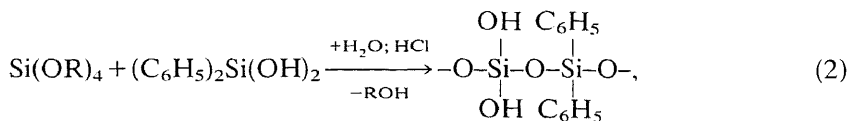Fig. 1. Adhesive strength of two different commercial sealing foils after storage in water with ($\blacktriangle$,$\bullet$) and without ($\triangle$,$\bigcirc$) pretreatment of the glass surface with epoxysilane.

$$Ti(OR)_4 + Si(OR)_4 + R'_n Si(OR)_{4-n} \xrightarrow[-HOR]{+H_2O} \quad -O-\overset{|}{\underset{|}{Ti}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{\underset{R'}{|}}{Si}}-O- \quad (1)$$

R = alkyl; R' = organofunctional group. Since R' acts as a network modifier, the type and amount of R' effects structures strongly. As shown in ref. [2], the use of phenyl groups as R' can lead to thermoplastic and soluble polymers which can be prepared with variable amounts of uncrosslinked $\equiv$Si–OH groups as a function of curing temperature. These $\equiv$Si–OH groups should be able to form stable $\equiv$Si–O–Si$\equiv$ bonds with surface silanols during a heat treatment of the sealing step, and, moreover, should create a sufficient solubility of water. These considerations led to an optimization procedure of thermoplastic ORMOSILs, based on the $(C_6H_5)_2SiO$ group as the key unit.

3.3. Optimization of the sealing properties

The condensation reaction of diphenylsilanediol by itself does not lead to polymers. Even refluxing with water and HCl only leads to soluble trimers, as proved by molecular weight determination. Systematic investigations of the cocondensation of $(C_6H_5)_2Si(OH)_2$ and $Si(OR)_4$ according to (2),

$$Si(OR)_4 + (C_6H_5)_2Si(OH)_2 \xrightarrow[-ROH]{+H_2O;\, HCl} \quad \overset{\overset{\textstyle OH}{|}\ \overset{\textstyle C_6H_5}{|}}{-O-\underset{\underset{OH}{|}}{Si}-O-\underset{\underset{C_6H_5}{|}}{Si}-O-,} \quad (2)$$

show that thermoplastic products could be prepared up to contents of 40 mol% SiO_2 from $Si(OR)_4$. Infrared spectra of compositions cured at 150°C for 2 h show two types of OH vibrations in the 3500 cm^{-1} region which are assigned to bridged and unbridged Si–OH groups (fig. 2).

The material is still soluble in acetone and can be used for coating aluminum foils. The coated foils were sealed to glass at 100°C. Underwater treatment of such samples does not show any decay of sealing strength with time, but the sealing strength itself is poor (<3 N/cm). This is a result of the brittleness of the material at room temperature.

In order to increase the elasticity, efforts were made to decrease the degree of crosslinking by introduction of two-fold bonding silane monomers of the type $R'_2Si(OR)_2$. While $(CH_3)_2Si(OR)_2$ leads to a strong decrease of sealing strength, the use of methyl–vinyl–silane $(CH_2=CH)(CH_3)Si(OR)_2$ increases the sealing strength without affecting the moisture resistance. The sealing strength of these compositions is 7 to 8 N/cm which is enough for practical use.

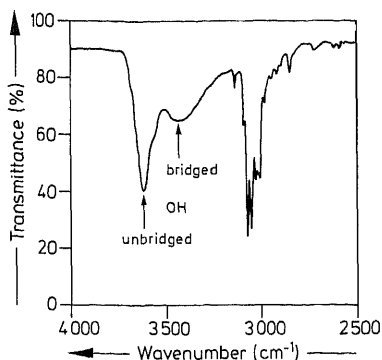During the thermal curing process an additional crosslinking proved by IR takes place after (3):

$$\equiv Si-CH_3 + CH_2=CH-Si\equiv \rightarrow \equiv Si-CH_2-CH_2-CH_2-Si\equiv \quad (3)$$
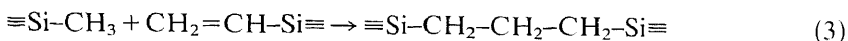
Fig. 2. IR transmission spectra of a new sealing polymer based on organically modified silicates.
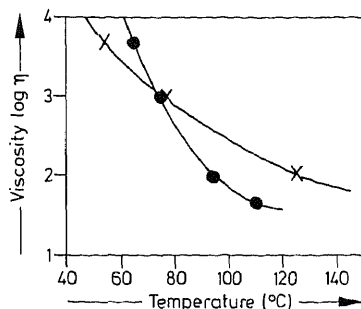
Fig. 3. Log η/T plot of two different compositions with low (O) and high (×) methyl-vinyl-silane content.

This second type of crosslinking strongly affects the viscosity on temperature dependence of the cured materials. The log η/T plot (fig. 3) shows that with the higher content of methyl-vinyl-silane the curve becomes more flat. This means that the hot melt behavior of the sealing medium can be tailored and it is possible to adjust the temperature dependence of viscosity (and sealing strength) to practical problems.

The number of OH groups in the sealing materials depends strongly on the thermal treatment. The concentration of OH groups in coatings can be quantitatively computed from the IR spectra, if an independent internal standard is used. For this purpose phenyl groups are used, since their concentration is defined by the composition. Fig. 4 shows the decrease of the OH concentration at 150°C curing temperature. The marked area represents the range of usable practical sealing properties. Too high curing times cause strongly crosslinked materials, since the decrease of OH concentration is related to condensation:

$$\equiv SI-OH + HO-Si\equiv \rightarrow \equiv Si-O-Si\equiv + H_2O \qquad (4)$$
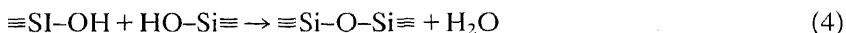
The IR spectra permit one to recognize unhydrolyzed $\equiv Si(OR)$ groups, too. These groups cannot condense with themselves and act as network modifiers, lowering the viscosity. Unhydrolyzed $\equiv SiOR$ cannot be effectively removed at temperatures up to 300°C, since the $\equiv Si-O-C\equiv$ bond has a good thermal stability. In order to get reproducible products, an IR controlled hydrolysis had to be applied. The calibration of the IR determination of $\equiv SiOR$ was performed by chemical analysis [3]. Based on this method an optimal control of sealing properties is possible.

The optimal OH concentrations can be adjusted by thermal curing, as mentioned above, however, also by 'chemical curing'. Theoretically, a crosslinking of $\equiv Si-OH$ groups should be possible by the use of reactive crosslinking agents like $Ti(OC_2H_5)_4$ after (5):
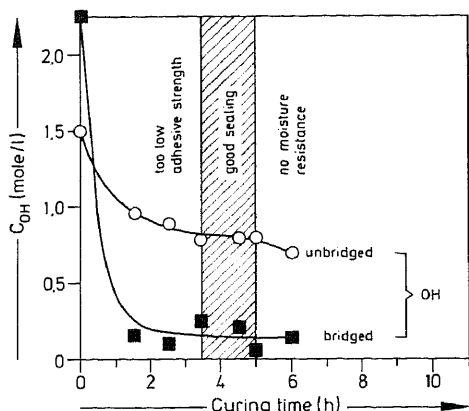
Fig. 4. Influence of thermal treatment at 150°C on OH concentration of the sealing polymer.

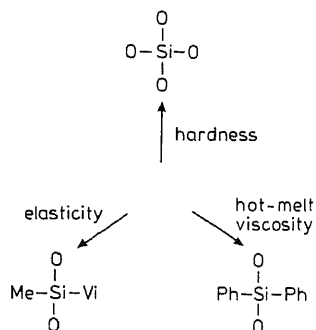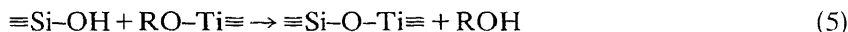Fig. 5. Structural elements of sealing polymers and their influence on main properties.

$$\equiv Si-OH + RO-Ti \equiv \rightarrow \equiv Si-O-Ti \equiv + ROH \qquad (5)$$

Experiments show that $Ti(OR)_4$ affects the viscosity very similar to the effect of thermal curing. This economizes the production procedure by saving time and energy. An optimized sealant composition can be obtained from (in mol%): $5Si(OC_2H_5)_4$; $60(C_6H_5)_2Si(OH)_2$; $5Ti(OC_2H_5)_4$ and $30(CH_2=CH)(CH_3)Si(OC_2H_5)_2$ as chemical curing agent.

Summarizing these data, a sketch can be drawn which shows the main tendencies of how the properties of the hot melt can be influenced (fig. 5).

In order to perform a sealing process, the material which shows a resin-like appearance at room temperature has to be dissolved in an organic solvent (e.g., ethylacetate) to an amount of 40 to 60 wt%. The liquid then can be used for coating aluminum foils by industrial techniques, applying film thicknesses of about 10 to 15 μm. After coating, the films have to be dried at 170°C for 20 s. The foils then can be used for sealing glass containers which show no decay of sealing strength after one year in use.

In conclusion, we would like to say that a new type of hot melt adhesive for the sealing of glass containers could be developed by using the manifold possibilities of the organically modifier silicates, prepared by the sol–gel process. Due to the reactive binding to the glass surface, an extremely good moisture resistant sealing can be achieved. This technique opens new possibilities for applications to glass.

References

[1] D.E. Schaudel, Adhäsion 9 (1978) 70, 107, 145, 252, 288.
[2] H. Schmidt. G. Tünker and H. Scholze, Europ. Patent 36 648 (1984).
[3] A.L. Smith, ed., Analysis of Silicones (Wiley, New York–London–Sydney–Toronto, 1974).