MODELLING OF ORMOCER COATINGS BY PROCESSING

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Hydrolysis, condensation and polymerization of γ-glycidyloxipropyltrimethoxysilane was studied under different reaction conditions and yields a hard coating material for polyethyleneterephthalate substrates. The progress of hydrolysis was followed by ^{29}Si-NMR spectroscopy and Karl Fischer titration. Hydrolysis proceeds very slowly at pH 5.5, but can be enhanced at pH 9. Independent from submitted water and pH the solutions only one half of hydrolyzable methoxy groups can be removed. Condensation and polymerization were investigated on coated substrates and start during thermal curing. The formation of the polysiloxane network takes place by elimination of methanol. Polymerization of the epoxy groups to polethyleneoxide units is achieved above 100°C using a special catalyst. The properties of the cured coatings depend on the free water and glycol content in the solution. Minimizing the amount of both components leads to an ORMOCER coating on polyethyleneterephthalate which features a good abrasion resistance in combination with a high flexibility.

1. Introduction

ORMOCERs (organically modified ceramics) are inorganic/organic polymers and combine the properties of ceramic with those of organic components [1–5]. Several applications of these materials have been described, especially as hard or protective coatings on organic polymers [6–9]. Hard coating systems are based on Al_2O_3, ZrO_2, TiO_2 or SiO_2 as network formers and epoxy or methacrylate groups bonded to Si via a $\equiv$Si–C$\equiv$ bond. These compositions have been successfully applied on polycarbonate (PC), but problems arise for the application on polyethyleneterephthalate (PET). In order to get sufficient adhesion and protective function of the ORMOCER coating on this polymer, substrates have to be pretreated either with a primer or a corona discharge. However, hard coatings on PET show poorer mechanical properties compared with PC substrates. These differences may be due to insufficient processing during sol preparation and may be improved by a better reaction control. In order to test this assumption, the hydrolysis, condensation and polymerization of γ-glycidyloxipropyltrimethoxysi-

lane, an important precursor and ORMOCER coatings was studied. The results of these investigations and a comparison with the mechanical properties of the coating on PET and PC are presented in this paper.

2. Experimental

The development of a coating material from γ-glycidyloxipropyltrimethoxysilane was carried out as a two-step process. First, the silane was prehydrolyzed with differing amounts of water, varying the water concentration between 1.5 mol (S 1.5) and 3.0 mol (S 3.0) per mol silane. The pH of the solution was adjusted at 5.5 by bubbling CO_2 through it. After the addition of water, the mixture was stirred for 16 h at 25°C. The hydrolysis was followed by ^{29}Si-NMR spectroscopy during this time and the residual water after 16 h was determined by Karl Fischer titration. The epoxy content after prehydrolysis was controlled by a titration technique described in ref. [10]. In the second step, the pH was adjusted to 9 by addition of another catalyst. Coating experiments were carried out after a reaction time of 3 h on polyethyleneterephthalate and polycarbonate by dip coating. The coated substrates were dried at 130°C
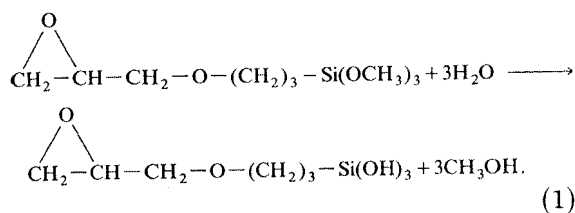
for 3 h and the mechanical properties were investigated.

3. Results and discussion

3.1. Hydrolysis

The complete hydrolysis of γ-glycidyloxipropyltrimethoxysilane requires 3 mol of water as shown in eq. (1):

$$CH_2-CH-CH_2-O-(CH_2)_3-Si(OCH_3)_3 + 3H_2O \longrightarrow$$

$$CH_2-CH-CH_2-O-(CH_2)_3-Si(OH)_3 + 3CH_3OH. \tag{1}$$

According to the hydrolysis of tetraalkoxysilanes [11] the rate of hydrolysis of the precursor should be rather slow at pH = 7, but could be enhanced under acidic conditions. In most cases, inorganic acids such as hydrochloric or sulfuric acid are used to promote the hydrolysis of alkoxysilanes, but these catalysts exhibit one general disadvantage: they could not be removed from the solution. Therefore, CO_2 was chosen as a catalyst, since it gives an acidic reaction with water (eq. (2)) and can easily be removed:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H_3O^+. \tag{2}$$
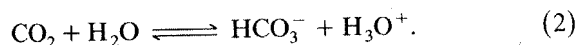
Hydrolysis was carried out at pH = 5.5 with varying amounts of water. The progress of hydrolysis with time for S 3.0 was followed by ^{29}Si-NMR spectroscopy (fig.1). The assignment of the observed signals is given in table 1.

The precursor gives an intense signal at -37.4 ppm which shifts to higher field with increasing number of hydroxyl groups attached to the silicium atom. Similar results were reported for partially hydrolyzed tetraalkoxysilanes [11]. Condensation products are indicated by a signal around -44 ppm. However, the ^{29}Si-NMR spectra clearly demonstrate that the hydrolysis of γ-glycidyloxipropyltrimethoxysilane at pH = 5.5 with a stoichiometric amount of water is rather slow. Even after a reaction time of 16 h the precursor is still present together with partially hydrolyzed
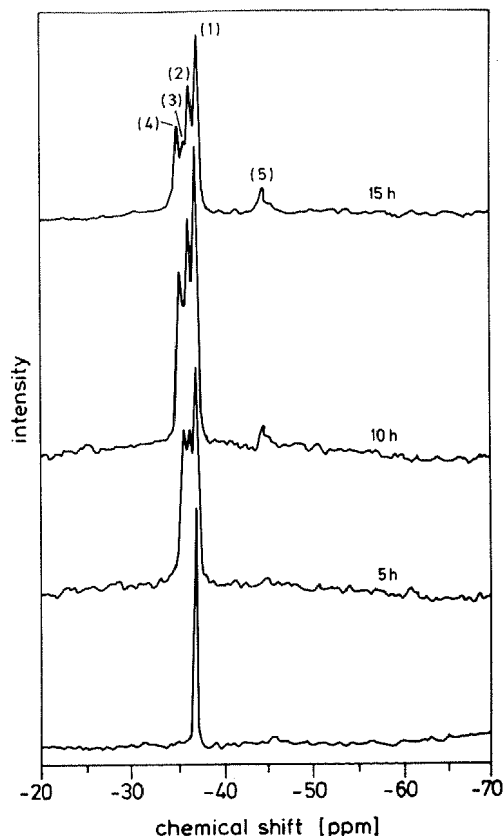

Fig. 1. ^{29}Si-NMR spectra of the hydrolysis of S 3.0; pH: 5.5.

species. The first signal of a condensed species could be detected after 10 h, but did not increase very much in intensity with increasing time. Therefore, the rate of condensation of the hydro-

Table 1
Assignment of the signals detected by ^{29}Si-NMR spectroscopy during hydrolysis of γ-glycidyloxipropyltrimethoxysilane

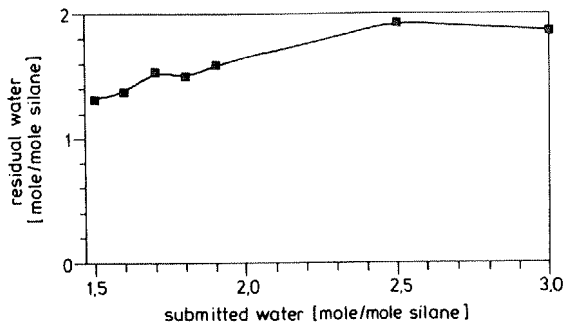| Compound	Chemical shift relative to internal TMS [ppm]
(1) R–Si(OCH$_3$)$_3$	-37.4
(2) R–Si(OH)(OCH$_3$)$_2$	-36.6
(3) R–Si(OH)$_2$(OCH$_3$)	-36.1
(4) R–Si(OH)$_3$	-35.3
(5) ≡Si–O–Si≡	-44.0

R: $CH_2-CH-CH_2O-(CH_2)_3-$
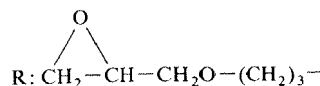
Fig. 2. Water content as a function of the submitted water for the hydrolysis of γ-glycidyloxipropyltrimethoxysilane after a reaction time of 16 h; pH: 5.5.

lyzed precursor seems also to be rather slow. The residual water after a reaction time of 16 h was determined by Karl Fischer titration. A value of 1.9 mol of free water per mol silane was found, clearly indicating that the hydrolysis is incomplete. The results of hydrolysis with less than the stoichiometric quantity of water are shown in fig. 2.
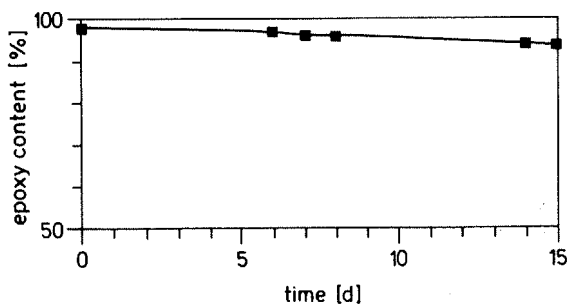

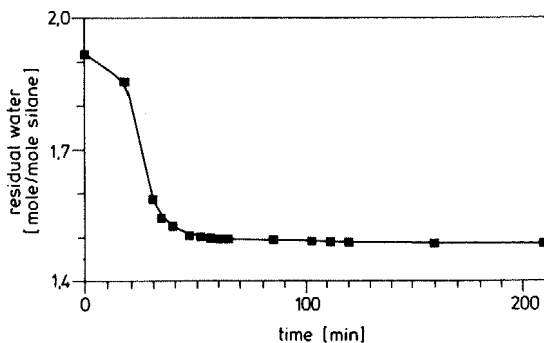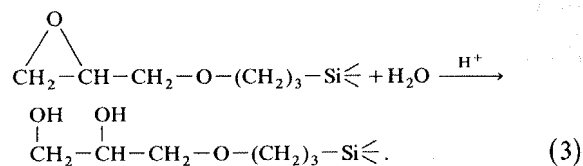Fig. 3. Change of epoxy content of prehydrolyzed S 3.0; pH: 5.5.

With a decreasing quantity of water used for hydrolysis the amount of free water dramatically increases. For comparison, hydrolyzing the precursor with 3 mol water leads to 1.9 mol (63%) of free water, whereas the hydrolysis with only 1.5 mol water results in 1.3 mol (87%) of free water.

Beside the degree of hydrolysis, another important question is the content of epoxy groups in the solution. Epoxy groups react with water under acidic conditions forming glycols (eq. (3)) which no longer can form a polyethyleneoxide network:

$$CH_2-\overset{O}{\overset{\diagup\diagdown}{CH}}-CH_2-O-(CH_2)_3-Si \leqslant + H_2O \xrightarrow{H^+}$$

$$\underset{|}{\overset{OH}{CH_2}}-\underset{|}{\overset{OH}{CH}}-CH_2-O-(CH_2)_3-Si \leqslant . \qquad (3)$$

Since hydrolysis was performed at pH = 5.5 the epoxy content was controlled by titration. The change of epoxy content during ageing of S 3.0 for 15 days is shown in fig. 3. The epoxy content decreases only slightly from 98% to 93% within 15 days and therefore the formation of glycol can be neglected at this state of hydrolysis.

In order to obtain a completely hydrolyzed precursor, the pH of the solution was changed by the addition of a second catalyst adjusting the pH at 9. The water consumption of S 3.0 and S 1.5 are shown in figs. 4 and 5, respectively. A comparison of the results in figs. 4 and 5 clearly shows that a complete hydrolysis of the precursor was not obtained. In both cases only 50% of hydrolyzable methoxy groups were transfered to hydroxyl groups. However, differences arise from the con-

Fig. 4. Water concentration as a function of time for the prehydrolyzed sol S 3.0 at pH 9.
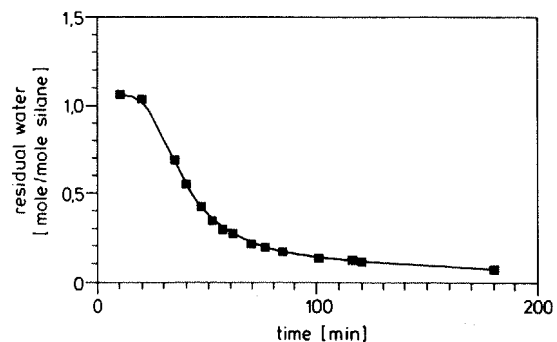

Fig. 5. Water concentration as a function of time for the prehydrolyzed sol S 1.5 at pH 9.
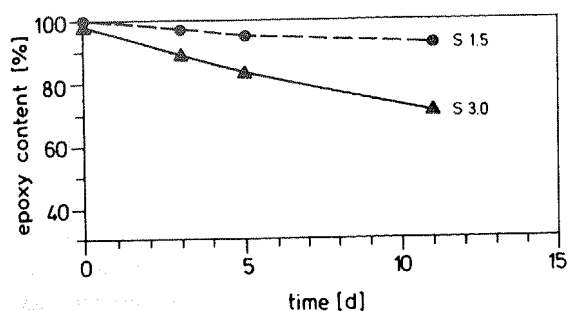
Fig. 6. Change of epoxy content with time of S 3.0 and S 1.5; pH: 9.

tent of free water in the solution. Whereas S 1.5 contains less than 0.1 mol water/mol precursor after 3 h, the water content of S 3.0 was 1.5 mol/mol precursor and did not change with time. In addition, the change of pH can tremendously increase the formation of glycol (eq. (3)) and therefore the change of epoxy content with time was determined (fig. 6).

Compared with the acidic hydrolysis with excess water (fig. 3) the epoxy content decreases faster at pH = 9 and after a reaction time of 10 days only 70% of unreacted epoxy groups remain in solution. A parallel determination of the glycol content gave a value of 25% after 10 days, which corresponds to the loss of epoxy (30%).

In contrast, the initial epoxy content in S 1.5 decreases only slightly within 10 days (fig. 6) and strongly displays the role of free water in the coating solution. From this point of view, it is quite clear why the hydrolysis with only 1.5 mol water/mol precursor was preferred.

Table 2
Properties of the coating material S 1.5 and S. 3.0 on polycarbonate (PC) and polyetheleneterephthalate (PET)

| Substrate	Coating sample	Thickness (μm)	Humidity resistance [a]	Haze [b] (%)	Cross cut [c]
PC	S 1.5	10	not cracked	0.8	0/0
PC	S 3.0	17	cracked	1.5	1/1
PET	S 1.5	10	not cracked	1.0	0/0
PET	S 3.0	15	cracked	2.1	1/1

[a] $T = 40\,^\circ$C, 100% humidity, 14 days.
[b] Haze measured per 100 cycles.
[c] Before/after test.Present address: INM gem. GmbH, Uni-

3.2. Condensation

The prehydrolyzed γ-glycidyloxipropyltrimethoxysilane was transfered to an ORMOCER coating by curing at 130°C. During this procedure siloxane-bonds are formed by the condensation of hydroxyl groups as well as of methoxy groups (eq. (4) and eq. (5)):

$$R: CH_2-CH-CH_2-O-(CH_2)_3, \qquad (4)$$

$$R: CH_2-CH-CH_2-O-(CH_2)_5. \qquad (5)$$
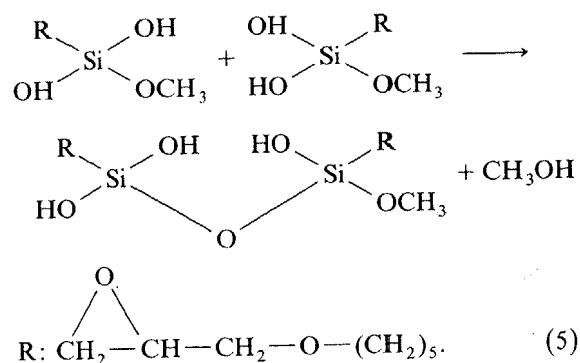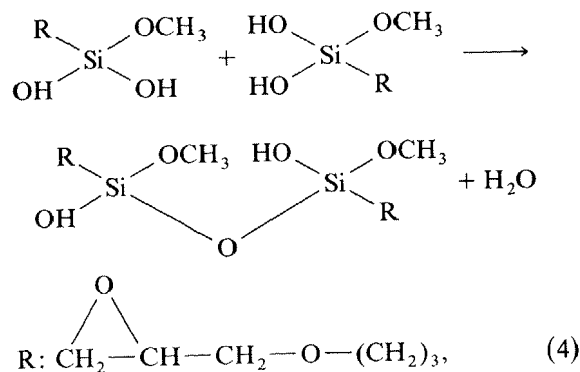
These reactions may take place simultaneously and, in order to get some information about the preferred reaction, the evaporated water as well as the total weight loss during curing was determined. For the determination of the evaporated water a programmable furnace was coupled with the Karl-Fischer-apparatus and the water evaporated at 130°C was carried by a stream of dry nitrogen into the titration solution. Using this technique, an average value of 0.01 mol water/mol precursor for S 1.5 was found whereas S 3.0 lost 1.3 mol water/mol precursor. In addition, the total weight loss corresponds to 2.9 mol methanol/mol precursor (S 1.5) and 2.8 mol methanol/mol precursor (S 3.0). These results clearly show

that the elimination of methanol is preferred compared to the elimination of water.

3.3. Coatings

Coating experiments were carried out with S 1.5 and S 3.0 on polycarbonate (PC) and polyethyleneterephthalate (PET). The properties of the coated substrate are summarized in table 2.

The results in table 2 clearly display the influence of processing on the properties of the coatings. Whereas the coating S 1.5 was not attacked by water vapor within 14 days, cracks appear in coating 3.0 during this period of time. Adhesion tests, crosscut in combination with a tape test, also indicate better properties of S 1.5 compared with S 3.0. In addition, S 1.5 exhibits a very good flexibility on PET, whereas S 3.0 cracked off during bending. Additionally, a good abrasion resistance of coating S 1.5 on PET was maintained. These differences can be explained from a structural point of view. Thermal curing of S 1.5 can lead only the condensation and polymerization, whereas curing of S 3.0 can be accompanied also by the formation of glycol. These different reaction behaviors can be expected in order of the different water content of the coating solution, as mentioned above. However, glycol groups possibly also increase the hydrophilicity of the coating and the permeability of water. Therefore, the humidity resistance as well as the adhesion of coating S 3.0 is less compared with S 1.5. This assumption also explains the flexibility of S 1.5 on PET. A good flexibility requires a high degree of polymerization of the epoxy groups to polyethyleneoxide chains which can only be obtained in absence of glycol groups.

4. Conclusions

A coating material was developed from γ-glycidyloxipropyltrimethoxysilane by controlling hydrolysis, condensation and polymerization of the precursor. The material can be applied to polycarbonate as well as to polyethyleneterephthalate and features a superior abrasion resistance. The adhesion could be improved by minimizing the free water in solution. In addition the coatings on polyethyleneterephthalate exhibit a very good flexibility.

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