Original Paper

Development of organic-inorganic coatings for strength-preserving of glass bottles

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An amino-epoxy-silane based coating system (GAMAL) for glass surfaces was developed, which can efficiently protect bottles from the damages of a bottling plant. Testing bottles with a ramp pressure tester show an identical value of about (40 ± 4) bar for conventionally hot- and cold-end coated bottles and bottles coated with the developed organic-inorganic composite (GAMAL) system. After already 2 min of wet line-simulation testing, all species of a conventionally coated probe fall short of the critical limit of 16 bar, whereas bottles coated with GAMAL (thickness about 7 μm) show a value of (21 ± 3) bar. Coating is possible by dip and spray application on cold or hot (80 °C) substrates, the coating is cured at 120 °C for 5 to 10 min. Additional functions such as colour or UV protection can be added easily, without reduction of the protection potential. The low content of carbon (about 0.5 g per 1 l soft drink bottle) should not disturb the recycling process of such coated bottles.

Entwicklung einer festigkeitserhaltenden organisch-anorganischen Beschichtung auf Glasflaschen

Es wurde ein Beschichtungssystem auf der Basis eines Amino-Epoxy-Silans (GAMAL) entwickelt, das Flaschen effektiv vor den Beschädigungen in einer Abfüllanlage schützen kann. Herkömmlich heiß- und kaltend vergütete Flaschen zeigen mit Werten von (40 ± 4) bar Berstinnendruckfestigkeit die gleichen Werte wie GAMAL-beschichtete Flaschen. Nach nur 2 min nasser Liniensimulation fallen alle Spezies einer Probe mit herkömmlicher Beschichtung unter die kritische Grenze von 16 bar, während GAMAL-beschichtete Flaschen (Beschichtungsdicke ca. 7 μm) mit Werten von (21 ± 3) bar deutlich über dem Grenzwert liegen. Die Applikation der Beschichtung kann per Sprüh- oder Tauchverfahren auf kalte oder heiße (80 °C) Substrate erfolgen, die Schicht wird bei 120 °C zwischen 5 und 10 min ausgehärtet. Zusätzliche Funktionen, wie Farbe oder UV-Schutz, können ohne Einfluß auf die Schutzwirkung realisiert werden. Der niedrige Kohlenstoffgehalt der Beschichtung (ca. 0,5 g C pro 1-l-Softdrinkflasche) sollte zu keinen Problemen beim Recycling so beschichteter Flaschen führen.

1. Introduction

The practical strength of glass is much smaller than its theoretical one. This is due to micro flaws in the glass surface, which decrease the bending strength and lead to stress corrosion problems, depending on the environment [1 to 3]. Sol-gel derived SiO_2- [4 and 5], SiO_2-ZrO_2- [6] and multi-component glass coatings [7 and 8] have been applied to glass surfaces successfully to fill these micro flaws, which leads to an increase in the bending strength of float glass up to a factor of 4 [7]. However, such inorganic glass-like coatings are not suitable for the protection of the glass surface against mechanical load [9] because defects are generated in the coating and can propagate as micro flaws into the glass substrate easily, due to perfect chemical bonding of the coating to the substrate and similar elastic moduli of coating and substrate. It has been shown [9] that the strength-increasing effect of different SiO_2 coatings on float glass could be eliminated completely by the sand-falling test [10].

A coating protecting the glass surface and therefore preserving the strength during use would be of special interest for light weight container glass. Therefore, different organic polymer coatings have been developed [11 to 17] successfully to protect the surface of container glass against mechanical attack and to preserve its strength. The thickness of these coatings is in the range of about ≥ 50 μm [18]. This can lead to problems with recycling, because only a small amount of carbon (about 1 g carbon per 420 g glass [19]) can be tolerated in the cullet. It was proposed to grind the cullet down to an average grain size equal to the coating thickness and to separate glass and polymer by vibration [18].

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Der ausführliche Schlußbericht „Untersuchungen zur Festigkeit von Glas: Festigkeitserhaltende und festigkeitserhöhende Beschichtungen auf Glas" (AiF-Nr. 11685 N) kann bei Bedarf über die Bibliothek der Deutschen Glastechnischen Gesellschaft (DGG) bestellt werden.

Kasemann et al. have shown that the inner bursting pressure of glass bottles could be increased by about 30 % by application of an organic-inorganic (Ormocer) coating [20]. It can be assumed that this type of hybrid coating possesses an interesting potential for strength preservation, because the elastic modulus and the chemical bonding at the substrate interface could be tailored by variation of the coating composition. The interesting question is which minimum thickness would be necessary for a sufficient protection of the glass surface with respect to recycling problems.

Therefore, the aim of this paper was to develop an organic-inorganic composite coating on lab scale, which can protect the surface of one-way 1 l glass bottles against the mechanical load of a bottling plant without disturbing the recyclability. In addition, upgrading functions like colouring or UV protections should be investigated.

Float glass samples in combination with double ring bending test and sand-falling test were chosen for basic investigations [21]. The results of these investigations were then transferred to 1 l soft drink bottles and further optimized.

2. Experimental

2.1 Sol synthesis [22]

2.1.1 GPTS/APTES

354 g of 3-glycidoxypropyltrimethoxysilane (GPTS) were hydrolyzed with 40.5 g of water by stirring under reflux for 24 h. 388 g aminopropyltriethoxysilane (APTES) were hydrolyzed by adding 49 g of water and stirring for about 2 h at room temperature. Afterwards 185 g prehydrolyzed GPTS were diluted with 50 ml isopropanol (2-PrOH) and cooled down to 5 °C in an ice bath. Finally 50 g prehydrolyzed APTES was added under stirring within 5 min.

2.1.2 GPTS/APTES/ESA

The GPTS/APTES sol was synthesized as described in 2.1.1. After the addition of the prehydrolyzed APTES, the sol was warmed up to 20 °C and stirred for 20 min. Finally 4.7 ml of acetanhydride (ESA) were added.

2.1.3 GAMAL

The synthesis of this sol is based on the GPTS/APTES/ESA sol (see 2.1.2). Instead of 50 ml 2-PrOH a mixture of 50 ml 2-PrOH and 2.62 g aluminium-*sec*-butylat was used for the dilution of the prehydrolyzed GPTS (see 2.1.1).

2.1.4 GAMAL coatings with organic dyes and UV absorber

For the preparation of GAMAL (see 2.1.3) with different colours and with a UV absorber, respectively, the following organic dyes (500 mg each) were dissolved in the 50 ml 2-PrOH used for the dilution of the prehydrolyzed GPTS (see 2.1.1 to 2.1.3):

blue:	Ciba-Geigy, Blau 10336;
red:	Ciba-Geigy, Filamid Rot RG;
green:	Hoechst, Hoastatint-Grün GG30;
UV absorber:	TINUVIN 1130.

2.2 Coating process

Float glass samples ((100 x 100 x 4) mm^3) were washed manually using deionized water and dried in air at room temperature. They were coated by dipping with a withdrawal speed of 5 mm/s and cured at 120 °C for 10 min.

1 l soft drink bottles (Saint-Gobain Oberland AG, Bad Wurzach (Germany)) of one and the same mould with standard hot-end coating were taken carefully from the cooling furnace (80 °C) and coated by manual spraying using a Sata-Jet spray gun. The coatings were cured at 120 °C for 5 min.

2.3 Characterization

The mechanical damage of the float glass samples was simulated by the sand-falling method [10] by sprinkling 500 g of Al_2O_3 powder of the grain P30 from a height of 1.5 m to the rotating glass substrate (impact angle 45 °).

The bottles were damaged using a line simulation tester (AGR International, Inc., Butler, PA (USA)). This device simulates damage processes by bottle to bottle contact under wet and dry conditions characteristic of standard bottling plants.

The bending strength of float glass was measured with the double-ring bending test [23] and the results were evaluated with Weibull statistical analysis [24]. For each strength measurement 20 to 25 samples with the origin of fracture inside the small loading ring were chosen.

The strength of the bottles (inner bursting pressure) was measured using a Ramp Pressure Tester (AGR International, Inc.) and the results were evaluated by Weibull statistical analysis. For each measurement, two series of 19 bottles (capacity of line simulator) were chosen.

The friction of the coated bottles with each other was characterized by measuring the so-called slipping angle. For this, two coated float glass samples were put one on the top of the other and placed on a tiltable table. The bottom substrate was fixed and the table was tilted until the upper sample started to slip (slipping angle), which was detected by a laser light barrier.

The chemical bonds in the different coatings were characterized by ^{29}Si and ^{13}C solid state nuclear magnetic resonance spectroscopy (NMR) (Bruker MSL; magnetic field strength 4.7 T).

The optical properties of the coatings (float glass) were investigated by UV-VIS spectroscopy (Omega 30; Bruins Instruments, Munich (Germany)).

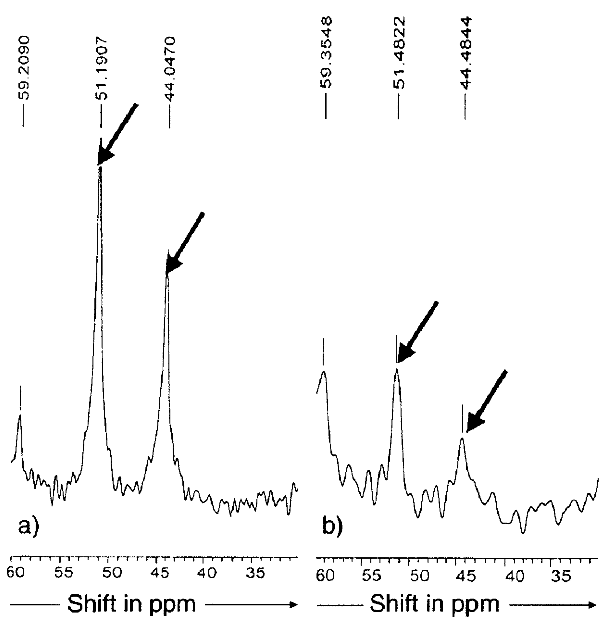
3. Results and discussion

3.1 Development of the sol synthesis

In a prior screening step [21], coatings prepared from single component GPTS sols were investigated. These coatings could not protect the surface of float glass against mechanical load of the sand falling test sufficiently, because they were not thick enough and too brittle [21].

In order to increase the critical thickness (i.e. the maximum thickness to obtain crack-free coatings after curing) and the elasticity of the coatings, APTES was investigated as a second component by organic (amino-epoxy reaction) as well as by inorganic (condensation of Si−OH groups) crosslinking. Coatings derived from GPTS/APTES sols should protect the surface of float glass samples efficiently against the damage of the sand-falling test [21]. However, the sols possessed a pot life of only about 20 min, which is not suitable for a future industrial application. The pot life of the sol could be expanded to about 100 min by addition of acetanhydride (ESA) as described in section 2.1. One might assume that the expansion of the pot life was due to a blocking of the amino group of APTES to be taken up by the oxygen group of the ESA more likely than by the oxygen in the epoxy ring of GPTS. However, detailed investigations have shown that the effect of ESA is related to a hindered condensation [25].

Bottles coated with sols derived from GPTS/APTES/ESA showed slipping angles of about 90° by measurement with a tilting table tester [26], which gives data comparable with those from the slipping angle measurements performed with the float glass as described in 2.2. [21]. This angle is unacceptably high for practical application because the strong adhesion of coated bottles with each other can cause serious problems in a bottling plant [19]. Therefore, state-of-the-art cold end coatings have been optimized to slipping angles of about 20° [19]. It was assumed that the almost sticky coating surface was due to incomplete organic crosslinking of the coating material [25]. Therefore, aluminium alkoxide was introduced into the synthesis route as a promoter for the ring opening of the peroxo group of the GPTS (GAMAL, see 2.1). In order to investigate this effect, coatings with and without aluminium alkoxide were investigated by solid state NMR. The result is presented in figures 1a and b.



Figures 1a and b. ^{13}C solid state nuclear magnetic resonance signals of the closed epoxy rings from GPTS (pointed out with the arrows); a) without addition of aluminium-*sec*-butylat b) with addition of aluminium-*sec*-butylat. (For detailed synthesis descriptions see 2.1.)

A comparison of figures 1a and 1b clearly shows that the NMR signals at about 51 and about 44 ppm, which are ascribed to the closed epoxy rings from GPTS, are significantly smaller for the coating prepared with the aluminium alkoxide. A quantitative analysis leads to the result that in figure 1a (without aluminium alkoxide) only about 63 % of all epoxy rings are opened, whereas in figure 1b about 90 % of them are opened [27]. Bottles coated with the GAMAL system showed slipping angles between 20° and 25°, which is assumed to be low enough for practical application [19].

3.2 Strength preservation

The strength-preserving effect of the GAMAL coating was first investigated on float glass samples (coating thickness 20 μm) by the sand-falling method. The result is given in figure 2.

Figure 2 shows that the float glass in the state of delivery has a bending strength of about $\sigma_0 = (174 \pm 12)$ MPa with a Weibull coefficient of about $m = 4.9$ (confidence interval 3.5 to 6.1). This is in good agreement with results obtained earlier [9]. The sand-falling test leads to a significant decrease in the bending strength to $\sigma_0 = (60 \pm 1)$ MPa and a strong increase of the Weibull coefficient to $m = 33.4$ (confidence interval 24.0 to 41.5). In the case of GAMAL-coated float glass,

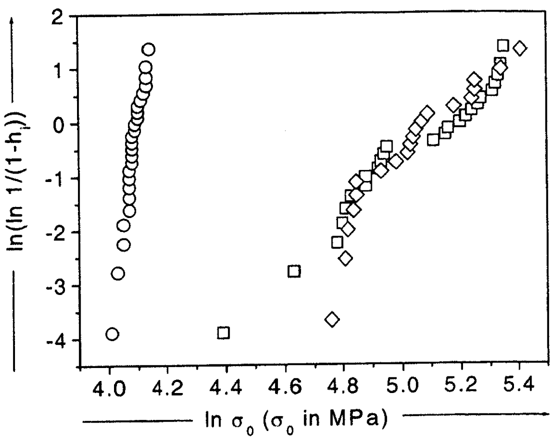


Figure 2. Weibull statistical analysis of the bending strength (investigated with double ring bending test, evaluated according to the maximum likelihood method – for details see [28]) of float glass ((100 x 100 x 4) mm^3). Plots of ln (ln (1/1 − h_i)) versus ln σ_0, where $h_i = (n - 0.5)/N$, with n = sample rank and N = total number of samples. □: on state of delivery: σ_0 = 174 MPa (163 to 186 MPa); m = 4.9 (3.5 to 6.1), ○: after sand-falling test [10] σ_0 = 60 MPa (59 to 61 MPa); m = 33.4 (24.0 to 41.5) and ◇: GAMAL-coated and damaged [10] σ_0 = 170 MPa (159 to 181 MPa); m = 5.2 (3.7 to 6.5). (Preparation see 2.3.)

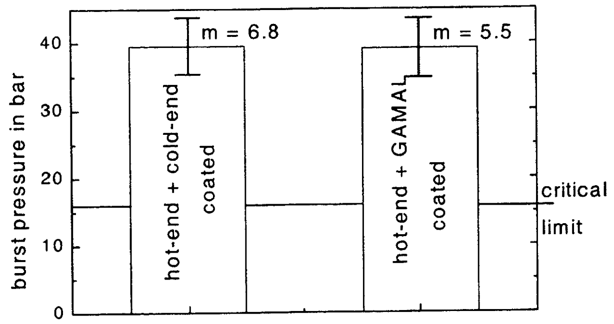


Figure 3. Comparison of the inner bursting pressure strength of conventional hot- and cold-end coated and hot-end and GAMAL-coated bottles. (Preparation see 2.3.)

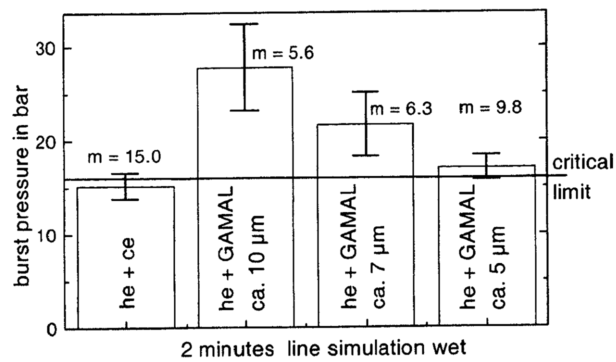


Figure 4. Comparison of the inner bursting pressure strength of conventional hot-(he) and cold-end (ce) coated and hot-end and GAMAL (with different thickness of about 10, 7, 5 µm) coated bottles after 2 min wet line-simulation test. (Preparation and test conditions in 2.1.)

no significant difference to the state of delivery is obtained after sand-falling test, because the confidence intervals of the bending strength are well overlapping (see figure 2). From this result it can be concluded that possible damages induced in the GAMAL coating are not propagating towards the glass surface and therefore a very good protection effect is obtained.

In the next step, hot-end coated bottles were coated at about 80 °C as described in 2.2. The application of the GAMAL coating to 80 °C hot bottles did not lead to any visible defect formation (bubbles, cracks) and coatings with good optical quality were obtained. However, a short post-heating at 120 °C for 5 min had to be performed for complete curing [21]. Further investigations will be necessary to eliminate this post-curing process.

The first question was whether the GAMAL coating had an influence on the inner bursting pressure strength of the bottles compared with the state-of-the-art cold end coating. The answer is given in figure 3.

From figure 3 it is obvious that there is no significant difference between both cases. This is in contrast to the results of Kasemann et al. [20], who reported a 30 % increase in the inner bursting pressure strength of glass bottles, coated with an organic-inorganic composite sol based on GPTS, compared to uncoated bottles. It is assumed that this is due to the fact that in [20] the bottles were coated after transportation from the factory to the lab which may cause defects that can be healed by the coating. In the present case, the bottles were taken very carefully from the cooling furnace belt and coated directly without any prior damage. For a more precise discussion, both coatings have to be compared under identical experimental conditions.

In the next step, the protection potential of the GAMAL coating was investigated after 2 min of wet (sprinkling the bottles with water during the test) line-simulation. For this test, 19 bottles are placed on a metal disk with a metal railing around it. The disk is rotating so that the bottles come in contact (friction, bumping) with each other. A test of 2 min wet simulation is assumed to be realistic for the simulation of a bottling plant for a one-way bottle. After the line-simulation test, the inner bursting pressure is measured and it is demanded that all tested bottles stay above a certain critical limit (16 bar in the present case). The tests were evaluated by Weibull statistics and the results are summarized in figure 4.

It is clear to be seen from figure 4 that the bottles with standard cold end coating fail the 2 min line test. The bursting pressure strength decreases from (40 ± 4) bar (see figure 3) to about (15 ± 2 bar). The increase of the Weibull parameter from 6.8 to 15.0 indicates a significant damage of the glass surface.

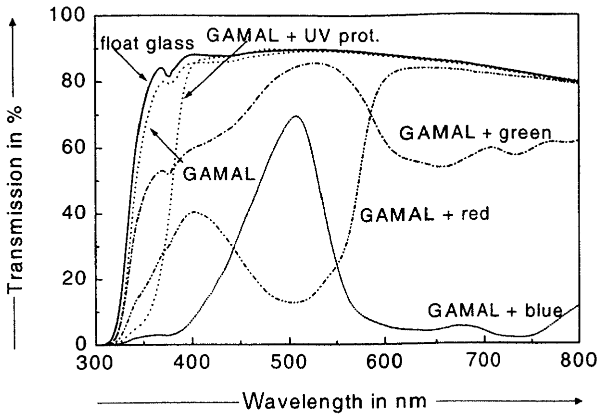


Figure 5. Transmission spectra of float glass substrates (100 x 100 x 4) mm³ uncoated and dip-coated (coating thickness about 20 µm) with GAMAL and GAMAL with colouring or UV protective additives. (For detailed synthesis information see 2.1.)

A much better protection is obtained with the GAMAL coatings. The inner bursting pressure strength decreases from about 25 to 17 bar and the Weibull parameter increases from 5.6 to 9.8 with decreasing coating thickness. From the original Weibull statistics data [21] it can be concluded that in case of coating thickness of 10 and 7 µm all individual bottles passed the test.

The carbon content of a coating with thickness in the range between 7 to 10 µm on a 1 l softdrink bottle can be calculated with a conservative guess to be in the range between 0.5 to 0.7 g/bottle, which is well below the expected limit of 1 g/bottle for recycling [19].

3.3 Additional functions

Costs are a strong issue for the production of container glass and it has to be assumed that the material costs and processing costs for the production and the application of the GAMAL coating are higher than for the standard cold end coating. Therefore, it was interesting to check whether additional functions like transparent colours or UV absorption can be realized to upgrade the GAMAL coating.

For this purpose, GAMAL sols with three different dyes and a UV absorber were prepared as described in 2.1 and float glass samples were coated by dipping. Transparent and defectfree coatings were obtained after curing. The transmission spectra of these coatings are given in figure 5.

Figure 5 shows the well-known transmission spectrum of a 4 mm thick iron-oxide containing float glass. The GAMAL coating has only a small influence on the transmission spectrum. This proves that the coating is colourless. By incorporation of a UV absorber (4 g/l coating solid) a UV absorbance edge (50 % transmission) is created at about 380 nm wavelength. The coating remains colourless as one can see from figure 5. It is also evident that the three selected colouring agents lead to transparent pastel-coloured coatings. These are only examples. By choosing other UV absorbers or colouring agents or by changing their concentration in the coating sol, a great variety of coatings with different optical properties will be possible.

It was proven that the incorporation of the colouring agents did not change the strength-preserving function of the GAMAL coating [21].

4. Conclusion

It can be concluded that the developed organic-inorganic composite coating possesses an interesting potential for industrial application, because an efficient protection of the glass surface against practically relevant mechanical damage can be obtained without disturbing the recyclability of the glass. The application technology is user-friendly, because spray coating on hot substrates without pre-treatment leads to coatings of acceptable optical quality and high functionality. Upgrading the protection coating by colouring agents or UV absorbers may be a suitable possibility to justify the coating costs. However, this question can only be answered definitely after the industrial technology has been developed, which will be subject of future work.

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