

Mechanical behavior of glass reinforced with SiO₂ hybrid sol–gel coatings

S. Pellice^a, U. Gilabert^b, C. Solier^b, Y. Castro^c, A. Durán^{c,*}

^a INTEMA-Conicet., Av. J.B. Justo 4302, B7608FDQ Mar del Plata, Argentina

^b INTEMIN (SEGEMAR), C.C 327, San Martín, Buenos Aires, Argentina

^c Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Kelsem sln, 28048 Madrid, Spain

Abstract

Hybrid sols were prepared from tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and 3-(methacryloxypropyl) trimethoxysilane (γ -MPS) in an acid medium at different TEOS/MTES and TEOS/ γ -MPS ratios. An organic monomer, 2-hydroxyethyl methacrylate (HEMA), was free-radical co-polymerized with γ -MPS, with 2,2'-azobis(isobutyronitrile) (AIBN) as initiator. We report the preparation of coatings from different sols on amber beer bottles and soda-lime glass rods and slides by a dipping process. Various withdrawal rates and heat treatments (from 150 to 500 °C) were used to prepare the coats in order to determine the best conditions as a function of composition. In all cases, transparent and crack-free coatings with good adhesion were obtained. Rods and slides of soda-lime glass were mechanically tested using four-point flexure and ring-on-ring tests. The results indicate that the TEOS/ γ -MPS coated rods and slides treated at 150 °C show the best behavior. The scale factor was increased by 26.5% and 22.8% in rods and slides, respectively. In the case of beer bottles, two different types of container were used: untreated and protected bottles with a hot-end SnO₂ coating. The bottles were tested using the normal standards of hollow glass: scratch resistance, sliding angle, and internal pressure. Mechanical properties of the coated bottles were analyzed for possible industrial application. The internal pressure of TEOS/ γ -MPS coatings is similar to standard values, while especially good scratch resistance was observed for TEOS/ γ -MPS/HEMA/PEG coatings, more than 15 cycles at 294 N.

© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Brittleness is one of the most important problems of glass materials due to the presence of superficial defects and micro-cracks [1]. Brittle materials strengths are a bulk property, which is limited by the surface state. The difference between the strength of glass usually achieved in practice and that theoretically calculated is due to micro-flaws in the glass surface [1]. It is usually assumed that in a brittle material failure occurs when the stress intensity (K_I) exceeds the critical stress inten-

sity, K_{IC} . At the tip of a surface flaw of length c , the mode I stress intensity, K_I , under an applied tensile stress σ_a , can be expressed as [1,2]:

$$K_I = \sigma_a \sqrt{\pi \Omega c}, \quad (1)$$

where Ω is a geometric factor, which depends on the shape of the flaw tip, σ_a is applied tensile stress and c is length of the surface flaw.

Sol–gel coatings could increase the strength of glasses and other brittle materials by the following mechanisms or by any combination of them [2,3]:

- filling in surface micro-flaws, reducing c .
- blunting crack tips, decreasing Ω .

* Corresponding author. Tel.: +34 91 735 5840; fax: +34 91 735 5843.

E-mail address: aduran@icv.csic.es (A. Durán).

- adding a compressive stress to the surface to decrease the net σ_a .
- protecting the material from fatigue, with an effective increase in K_{IC} .

A glass surface protective coating preserving strength during use would be of interest for lightweight glass containers.

Glass bottles are not an exception, in most cases they need protection to confront the mechanical exigencies imposed by industrial procedures such as the filling line, packaging and the market cycle. On the other hand, there is tendency to reduce weight and thickness of bottles at same time that the rhythm of production and the filling line speed become faster [4]. Thus, the development of methods to increase the mechanical resistance is a key factor for the glass industry. The minimum requirements that one bottle should support are usually established by different standard tests. Measurement of scratch resistance, slide angle and internal pressure are the typical parameters used by bottles factory labs. The minimum values of these parameters accepted are a scratch resistance of 245 Newton (N), a slide angle from 10° to 15° and an internal pressure greater than 245 N/cm².

The standard treatment used at present is a coating system in two steps called hot-end coating, applied at the entrance of the annealinglehr, and the Cold-End coating, at the exit of the annealinglehr [4,5]. The hot-end coating is a SnO₂ coat of ~10 nm, deposited from different precursors and sprayed at ~500 °C. The cold-end coating consists of a layer of paraffin or polyethylene (PE), also sprayed at approximately 80 °C.

Several attempts have been made with the application of sol–gel derived SiO₂, SiO₂–ZrO₂ and multi-component glass coatings [6–8]. Although these experiments led to increasing the bending strength of glass specimens, such inorganic coatings are not suitable for the protection of the glass surface against mechanical load. Besides, the thickness of these coatings is limited by residual stresses that can conduct to cracking and delamination above a critical thickness. The introduction of organic groups can produce the build up of residual stresses and therefore help the preparation of thicker coatings.

Recently hybrid organic–inorganic SiO₂ coatings have been used for strengthening soda-lime glass containers [9,10]. Mennig et al. [9] found similar results in the ramp pressure tester for conventionally coated and hybrid coated bottles, but after two minutes of wet simulation testing, better results were found for the hybrid coated bottles. On the other hand, Verganelakis et al. [10] found that hybrid coated bottles showed a 160% strength increase with respect to the uncoated bottles.

The aim of this work was to develop new hybrid coatings by the sol–gel method as substitute of one or both

of the standard coatings actually used. This kind of coatings has the advantage of easy elaboration [11] and low production costs [11,12] along with adjustable properties of the material like surface tension or hardness [13], depending on the starting reactants and preparation methods. Rods and sheets of the same type of glass were tested to study the reinforcement produced by these coatings.

2. Experimental

2.1. Preparation and characterization of sols

Tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and 3-(methacryloxypropyl) trimethoxysilane (γ -MPS) from ABCR were used as precursors. 2-hydroxyethyl methacrylate (HEMA, Aldrich) was alternatively utilized for free-radical co-polymerization of γ -MPS adding 2,2'-azobis (isobutyronitrile) (AIBN, Aldrich) as initiator.

Two groups of sols were prepared one for coatings densified at high temperature, 450 °C, and another for coatings densified at 150 °C. In all cases, the hydrolysis and condensation reactions were produced by adding diluted HNO₃ (0.1 N). Particular synthesis conditions are shown in Table 1.

The synthesis and physical characterization of TEOS/ γ -MPS and TEOS/MTES sols were reported in previous works [14,15]. In sols containing HEMA, co-polymerization reaction was carried out after hydrolysis at 65 °C during 4 h.

The C=C groups polymerisation was followed throughout the evolution of C=C peak at ~1635 cm⁻¹, referred to the C=O peak at ~1725 cm⁻¹, during the synthesis and thermal treatment using Fourier transformed infrared spectroscopy (FTIR) (Perkin-Elmer Spectrometer 1760X) in transmittance mode for TEOS/ γ -MPS/HEMA system.

To determine the remaining polyethyleneglycol (PEG) in TEOS/MTES/PEG coatings after densification treatment, thermogravimetric analysis (TGA) (Shimadzu TGA50) was performed on gelled self-supported films in air with a heating rate of 10 °C/min up to 450 °C, and 30 min at this temperature.

2.2. Preparation and characterization of coatings

Coatings were obtained on glass slides by dip-coating at different withdrawal rates and sol concentrations. The films were dried at room temperature and densified during 30 min at 150 °C or 450 °C, depending on their compositions, with a heating rate of 10 °C/min in air. The thicknesses of the coatings were measured by profilometry (Talystep, UK).

Table 1
Parameters used to prepare the hybrid sols

Composition	Molar ratios	H ₂ O/alcoxides molar ratios	Hydrolysis T, t	[SiO ₂] g/l
<i>Hybrid SiO₂ coatings, T = 450°C</i>				
TEOS/MTES	40/60	1.7	40°C, 3 h	180
TEOS/MTES/PEG	39/58/3	1.7	40°C, 3 h	180
<i>Hybrid SiO₂ coatings, T = 150°C</i>				
TEOS/PEG	95/5	2	50°C, 3 h	150
TEOS/ γ -MPS	65/35	1.8	50°C, 3 h	150
TEOS/ γ -MPS/HEMA	60/10/30	1.9	50°C, 3 h	150
TEOS/ γ -MPS/HEMA/PEG	54/9/27/10	1.9	50°C, 3 h	150

Preliminary tests by spray deposition were performed onto glass slides at room temperature and 500°C, with further evaluation of the coating.

Soda-lime glass substrates were used for testing, in particular: 50 × 50 × 2 mm slides and 5 mm diameter rods. Samples were coated by dipping to obtain films 1 μ m thick.

After coating, the samples were treated in air at a constant heating rate of 10°C/min to two temperatures for each sol: 450 and 500°C for TEOS/MTES, and 150 and 200°C for TEOS/ γ -MPS. Uncoated slides and rods were used as control specimens, which were run side-by-side with the coated samples through all treatments steps except coating, so as to separate annealing from coating effects.

Amber beer bottles of 250 ml volume with and without SnO₂ treatment were coated by dip-coating and tested in pilot plant applying scratch and sliding angle tests, and internal pressure before and after impact in-line test.

2.3. Mechanical tests

Ring-on-ring test: glass slides were tested by the ring-on-ring method using 30 samples for each composition and treating temperature. The load was applied using 5000 N Instron equipment. In these tests the cross head speed was kept equal to 0.2 mm/min. Since the glass commercial slides are usually rectangular, it was necessary to cut them to the square dimensions required by this test. Thus, higher data dispersion is expected taking into account this previous handling of samples.

Four-point flexure test: glass rods were tested by four-point bending with a mechanical testing apparatus (Netzsch 401), using 30 samples for each condition. In these tests, a 200 N/min loading rate was used.

Scratch resistance: this test consists on rubbing two bottles subjected to increasing load until the glass substrate is scratched. In case a load reaches 294 N the test is repeated until scratch occurs, recording how many times the test was repeated at this maximum load. This test is closely related to mechanical resistance and aesthetic appearance of bottles after a market cycle. The acceptable lower load limit for typical bottles is 245 N.

Sliding angle: two bottles are placed parallel to the axis of a slating moving plane and a third bottle is situated over the others. Sliding angle is defined as that angle at which the upper bottle displaces respecting to the fixed two underneath bottles. This test relates with hydrophilic and lubricant character of the coatings. Typical angles are between 10° and 15°, although in certain circumstances a 30° sliding angle can be useful. The usual notation in factory labs is an angle range, e.g. 10–12 or 12–14.

Internal pressure: a standard test [16] was used to determine the strength of glass containers when subjected to internal pressure. Forty bottles were used to obtain well determined statistic parameters. Weibull analysis was applied for each test. To evaluate the residual resistance after a market cycle, the test was repeated onto bottles subjected to an impact in-line test that simulates a turn over the market. These bottles will be referred from here on as ‘over-used bottles’.

Errors in ring on-ring tests, four-point tests and internal pressure tests have been calculated from mean square scatter.

3. Results

3.1. Characterization of sols and coatings

Homogeneous and transparent sols were obtained in all the cases with high wettability. All the compositions were stable at least for two months at 8°C.

Transparent and crack-free coatings with good adhesion were obtained by dipping.

Preliminary tests showed that spray method is also applicable to obtain coatings with these solutions. TEOS/MTES sol was successfully sprayed onto both cold and hot substrates, at room temperature and 500°C respectively. Moreover, a substantial increase in thickness was observed comparing to the dip-coating method. Crack-free coatings without border effects and 4 μ m thick were obtained from TEOS/MTES sol onto glass slides after sintering at 450°C, compared with the critical thickness of 2 μ m obtained by dip coating [15].

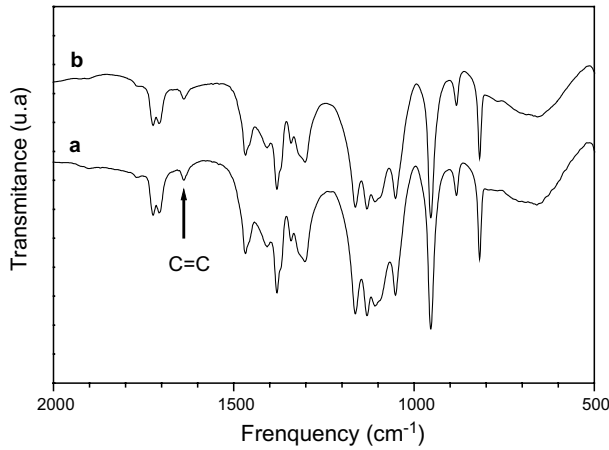


Fig. 1. FTIR spectra of TEOS/ γ -MPS/HEMA sol (a) before and (b) after pre-curing step of 4 h at 65°C with AIBN.

FTIR spectra of sol TEOS/ γ -MPS/HEMA reveal that the free-radical polymerization of C=C groups reached approximately 7% during the pre-curing step; upper conversion rates produce an irreversible gelling of hydrolyzed sol. Fig. 1 shows the conversion reached after pre-curing treatment detected in C=C peak at 1635 cm^{-1} .

The thermogravimetric analysis (TGA) of a TEOS/MTES/PEG gel reveals the almost complete elimination of organic compounds during the heating step.

3.2. Mechanical properties of coated rods and slides

Table 2 shows the results of the mechanical testing for the coated and the uncoated specimens. Both tests were analyzed using the Weibull procedures. The Weibull analysis [2], is based on the ‘weakest link theory’ of Pierce [6], has been widely used for modeling the inherent scatter of the brittle material strength. Pierce carried out some research on the development of reliable procedures for the testing of yarn and stated that ‘It is a truism, of which the mathematical implications are of no little interest, that the strength of a chain is that of the weakest link’. Unlike Pierce, who assumed a normal distribution of strength, Weibull supposed a unique proba-

bility density function which is known as a Weibull distribution. A two parameter Weibull distribution is given by

$$P_i = 1 - e^{-(\sigma/\sigma_0)^m}, \quad (2)$$

in which P_i represents the probability to failure at a stress level equal to σ , σ_0 is the scale factor and m is the Weibull modulus. The modulus m and the scale factor σ_0 were determined from the slope and intersection of the plot between $\ln(\ln(1/(1 - P_i)))$ versus $\ln \sigma$ since:

$$\ln \left(\ln \left(\frac{1}{1 - P_i} \right) \right) = m \ln \sigma - m \ln \sigma_0. \quad (3)$$

Since it is not possible to know the true value of P_i for each σ_i from the experiments, a prescribed function should be employed to calculate the P_i value. Such a function is usually called the probability index. Several forms of probability indexes have been used by different authors. In this work we used:

$$P_i = \frac{i}{n + 1}, \quad (4)$$

where n is the sample size.

The physical meaning of the Weibull modulus and scale factor can be appreciated in the Fig. 2, where the

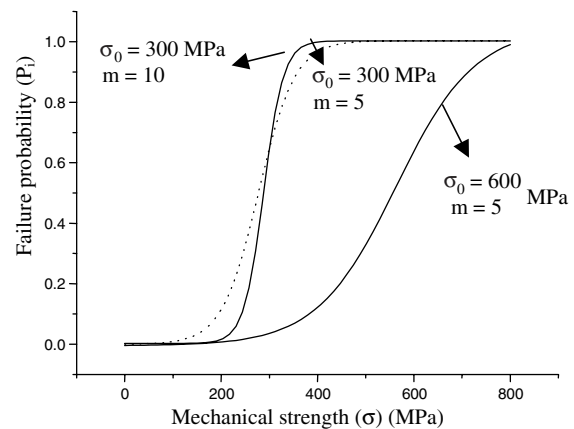


Fig. 2. Cumulative distribution function for Weibull distributions with various values of m and σ_0 . P_i is the probability of failure and σ is the mechanical strength.

Table 2
Results of rods and slides mechanical testing

Sol	TEOS/ γ -MPS				TEOS/MTES			
	150°C		200°C		450°C		500°C	
Samples	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated
<i>Slides</i>								
$m \pm \Delta m$	3.7 ± 0.4	3.5 ± 0.3	4.4 ± 0.4	3.3 ± 0.4	4.3 ± 0.3	4.6 ± 0.4	3.9 ± 0.3	4.1 ± 0.4
$\sigma_0 \pm \Delta \sigma_0$ (MPa)	200 ± 8	253 ± 10	202 ± 10	240 ± 12	164 ± 10	187 ± 11	177 ± 10	198 ± 10
<i>Rods</i>								
$m \pm \Delta m$	8.0 ± 0.5	9.5 ± 0.3	7.6 ± 0.5	8.8 ± 0.3	6.0 ± 0.5	5.5 ± 0.3	6.1 ± 0.3	6.5 ± 0.5
$\sigma_0 \pm \Delta \sigma_0$ (MPa)	145 ± 9	178 ± 11	148 ± 10	180 ± 11	150 ± 11	189 ± 12	145 ± 11	191 ± 11

Weibull cumulative distribution function (CDF) has been plotted for different values of m and σ_0 . The scale factor affects CDF location and steepness, while m only affects the steepness of CDF Weibull distribution.

Figs. 3 and 4 show the probability to failure (P_i) as a function of the mechanical strength (σ) for TEOS/MPS and TEOS/MTES coated rods and slides compared with uncoated ones.

3.3. Mechanical properties of coated bottles

Table 3 shows the results of sliding angle, scratch resistance and internal pressure tests before and after impact in-line test (named Over Used) as a function of composition, thermal treatment, pre-treatment of the substrate and thickness of sol-gel coatings. All the tests were performed on untreated (NT) bottles, SnO₂ hot-end treatment and standard coated bottles (SnO₂+PE) to be taken as reference of the new coating system.

4. Discussion

4.1. Mechanical properties of rods and slides

As observed in Table 2, in all cases, coated samples have a greater scale factor than the uncoated ones but no analogous variation was observed in the Weibull modulus. For low temperature coatings, the best results were obtained with coated TEOS/ γ -MPS specimens treated at 150°C. The scale factor increased by 26.5% and 22.8% in rods and slides, respectively. Slightly smaller scale factors were obtained for samples treated at 200°C, which augment by 21.6% for rods and 18.8% for slides.

In the case of TEOS/MTES coatings, treated at 450 and 500°C, a different property was observed, the best results depending on the test. In fact, coatings fired at 450°C show an increase of scale factor by 14% and 26% in slides and rods, respectively, while the higher

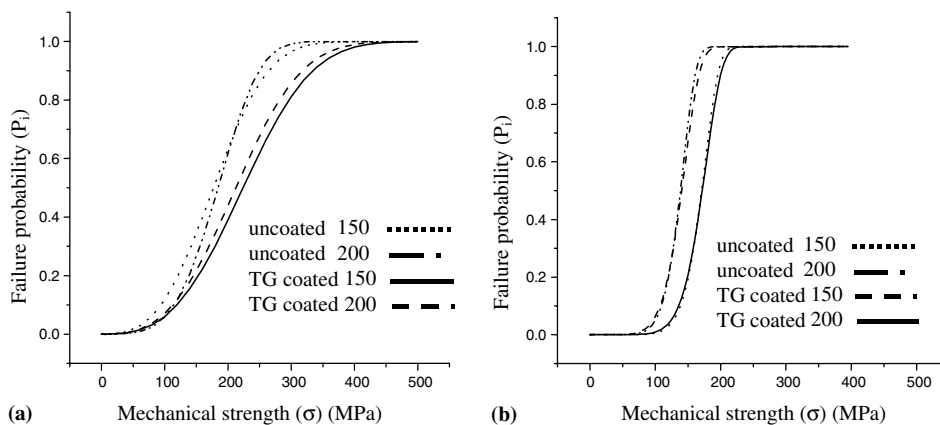


Fig. 3. Failure probability (P_i) as a function of the mechanical strength (σ) for TEOS/ γ -MPS coatings compared with uncoated samples on: (a) slides, and (b) rods.

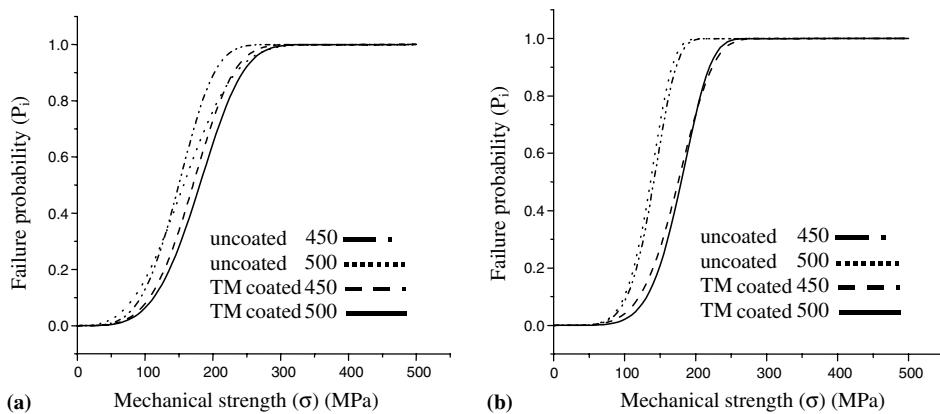


Fig. 4. Failure probability (P_i) as a function of the mechanical strength (σ) for TEOS/MTES coatings compared with uncoated samples on: (a) Slides, and (b) Rods.

Table 3
Mechanical tests on coated bottles

TT (°C)	Coating	Substrate pretreatment	Coating thickness (nm)	Sliding angle α (°)	Scratch resistance		Internal pressure resistance (N/m ²)		
					(N)	Cycles at 294N	Initial bottles ($\times 10^4$)	Over-used bottles ($\times 10^4$)	
450	TEOS/MTES	NT	1000	32–34	245–294	–	239 \pm 46	158 \pm 20	
	TEOS/MTES/PEG	NT	500	29–30	118	–	245 \pm 56	150 \pm 38	
		SnO ₂	500	29–30	137	–	272 \pm 59	149 \pm 30	
150	TEOS/ γ -MPS	NT	200	33–35	78	–	296 \pm 67	167 \pm 26	
			500	25–26	245	–			
			1000	24–26	98	–			
	SnO ₂	200	33–34	>294	4	5	–	–	
			500	28–30	>294				5
			500	12–14	49				–
	TEOS/PEG	SnO ₂	200	9–12	245	–	–	–	
			500	12–14	196	–			
			500	9–10	>294	5			
	TEOS/ γ -MPS/HEMA	NT	350	34–35	59	–	222 \pm 63	127 \pm 21	
			SnO ₂	350	33–35	>294	5	277 \pm 61	189 \pm 43
			SnO ₂	350	32–35	>294	15	–	–
Substrate pre-treatment			Reference parameters						
NT			0	27–30	10	–			
SnO ₂ (hot end)			8–10	30–32	10	–	279 \pm 70	150 \pm 28	
Standard (SnO ₂ + PE)			8–10	12–14	>294	8	311 \pm 59	220 \pm 34	

temperature treatment led to an augment of 11.9% in the scale factor of slides but a larger increase of 31.7% for rods. The smallest scale factors obtained for ring-on ring tests on glass slides are probably produced by cutting samples to fit the required dimensions.

Figs. 3 and 4 summarise the mechanical effect of TEOS/ γ -MPS and TEOS/MTES coatings on glass rods and slides with respect to uncoated ones. As observed, rod mechanical strength improvement results were more meaningful compared to slide strengths, most likely due to the handling of the glass sheets. Besides, the difference between samples with the same coatings but fired at different temperatures is less for rods. So, the fired temperature selection for each coating is apparently an industrial process matter.

The improvements obtained in this work in the mechanical properties of glass rods and slides are less than some other reported data [17,18]. However, we have separated the contributions of annealing, produced by thermal treatment, from the effects of coatings. Thus, although modest improvements of mechanical properties have been obtained, these increases may be important suffice for substituting for some of the standard coatings if applied on bottles.

4.2. Mechanical properties of coated bottles

One purpose of this work was to develop new hybrid coatings to partial or total substitution of the standard coating system of bottles used at present. These coatings

should give adequate response to requirements imposed by the industry; especially the rods angle, scratch resistance, and internal pressure resistance, resulting in an effective increase of bottle mean life times.

Sliding angle and scratch resistance tests were performed on untreated (NT) bottles, SnO₂ hot-end treatment, and standard coated (SnO₂+PE) bottles to be used as reference to further tests. Five series of bottles were used to perform the tests. The results revealed the importance of coatings in improvement of both mechanical and superficial properties. Untreated and single SnO₂ coated bottles have neither scratch resistance nor an adequate slide angle, Table 3. Only a combined double coating SnO₂+PE fulfils minima requisites for industrial bottles.

At the beginning, two types of hybrid sol-gel coatings were studied; TEOS/MTES sintered at 450°C, and TEOS/ γ -MPS cured at 150°C. In both cases the sliding angle obtained when applied onto untreated or SnO₂ coated bottles was around 30°, similar to those corresponding to NT or single coated bottles, but greater than the standard requirements of 10–15° obtained with SnO₂+PE double coating. The sliding angle was reduced to around 25° when coating thickness increased to 1 μ m but this thickness is till now far from the standard bottle.

With the aim of decreasing the sliding angle two OH containing polymers, PEG and/or HEMA were added to the initial sols. Only in the case of TEOS/PEG coatings cured at 150°C was a decrease in the angle to

$\sim 10^\circ$ observed. For the other compositions, no effect was observed and the sliding angle maintained around 33° . On one hand, PEG has been totally eliminated during heat treatment at 450°C in the TEOS/MTES/PEG system as shown by TGA test. On the other systems, cured at 150°C , the hydrophobia of the coating surfaces, related to their organic content, probably inhibits the adsorbency of OH groups on the surface thus avoiding a decrease of the sliding angle.

Both, NT and SnO_2 coated bottles have scratch resistance less than 10 N. On the contrary, the standard industrial coat $\text{SnO}_2 + \text{PE}$ resists eight cycles at 294 N before scratching.

The original coatings TEOS/MTES and TEOS/ γ -MPS applied on NT bottles showed a scratch resistance around 245–294 N, larger than SnO_2 coat but not enough for the standard resistance. However, when these coatings are applied onto SnO_2 single coat, they both fulfill the industrial requests, reaching 4–5 cycles at 294 N. Specially good scratch resistance was observed for TEOS/ γ -MPS/HEMA/PEG coatings, with more than 15 cycles at 294 N. However, the thickness of the coating was too large revealing surface stripes when scratch test was applied.

Although good results were obtained with sol–gel coatings, superficial stripes appear before the glass is scratched, this being a problem of aesthetic appearance that has to be solved if industrial application is desired. This effect is probably related to an excessive thickness compared to the traditional coating used in bottles.

The final test applied to sol–gel coated bottles was internal pressure (IP), performed on sets of 80 bottles for each composition, 40 bottles after suffering an impact in-line test that simulates a market cycle, and the other 40 bottles without any additional treatment.

The reference values were obtained from $\text{SnO}_2 + \text{PE}$ standard coat and also on single SnO_2 coated bottles. The internal pressure, IP, of standard coat is around 311 kg/cm^2 that falls around 30% (to $216 \times 10^4 \text{ N/m}^2$) when testing-used bottles. The SnO_2 single coat has an IP larger than standard bottles (around $279 \times 10^4 \text{ N/m}^2$), but this resistance decreases approximately 50% for over-used bottles. These results indicated that SnO_2 single coat provides the mechanical strength necessary while PE coat provides good sliding angle and, combined with SnO_2 coat increases scratch resistance.

This test has been performed on NT bottles with TEOS/MTES, TEOS/MTES/PEG, TEOS/ γ -MPS, and TEOS/ γ -MPS/HEMA as single coatings and onto SnO_2 coated bottles with TEOS/MTES/PEG and TEOS/ γ -MPS/HEMA. All the coatings, independent from the composition and thermal treatment, give similar results when applied to NT bottles, with values around $226\text{--}294 \times 10^4 \text{ N/m}^2$ with a decrease around 40% ($127\text{--}157 \times 10^4 \text{ N/m}^2$) for over-used bottles. The

best result was obtained for TEOS/ γ -MPS coatings on NT bottles, with IP's less than standard ones ($294 \times 10^4 \text{ N/m}^2$), with a resistance decrease of 40%, down to $167 \times 10^4 \text{ N/m}^2$, after impact in-line tested bottles, better than SnO_2 treated bottles.

When sol–gel coatings are applied onto SnO_2 coated bottles, only TEOS/ γ -MPS/HEMA sol–gel coatings provide an increase in the IP resistance. The IP's for this sol–gel coating increase up to $294 \times 10^4 \text{ N/m}^2$ from $275 \times 10^4 \text{ N/m}^2$ for SnO_2 bottles, although the resistance decreases 40% when testing over-used bottles.

The individual deposition of sol–gel coatings and the further handling of bottles imposed by lab conditions may be one source of defects that produces a decrease of mechanical properties. Further work is in progress to apply the best compositions by spraying simulating an industrial line.

5. Conclusions

TEOS/MTES and TEOS/ γ -MPS coatings produced similar improvements on the mechanical performance of glass rods and slides. The change in treatment temperature did not affect these properties.

Preliminary tests showed that coatings prepared by spray method could be deposited onto hot and cold substrates. An increase in critical thickness was observed, compared to dip-coating method.

TEOS/MTES and TEOS/ γ -MPS sols deposited onto NT and SnO_2 coated amber beer bottles increased the sliding angle from $\sim 12^\circ$ for standard bottles to 30° . The incorporation of polymers with OH groups like PEG in TEOS/PEG coatings reduces the sliding angle. When using PEG or HEMA for the rest of compositions, the hydrophobia of the coating surfaces probably inhibits the adsorbance of OH groups on the surface, avoiding a decrease of the sliding angle.

Scratch resistance, with more than 15 cycles at 294 N, was observed for TEOS/ γ -MPS/HEMA/PEG coatings, larger than standard industrial (8 cycles at 294 N). However, superficial stripes appeared after the glass was scratched.

TEOS/ γ -MPS coatings onto NT bottles presented internal pressure (IP) less than standard bottles ($294 \times 10^4 \text{ N/m}^2$), with a resistance decrease of 40% after impact in-line test. When applied onto SnO_2 treated bottles the coatings increase the mechanical properties but not surpassing the standard system.

Acknowledgments

This work has been developed in the frame of the CYTED project VIII.9 and the Spanish project MAT2003-05902-C02-01.

References

- [1] L.D. Pye, H.J. Stevens, W.C. LaCourse, *Introduction to Glass Science*, Plenum Press, New York, USA, 1972, p. 451.
- [2] B.D. Fabes, D.R. Uhlmann, *J. Am. Ceram. Soc.* 73 (4) (1990) 978.
- [3] L. Nikolic, L. Randonjic, *Ceram. Internat.* 24 (1998) 547.
- [4] J.M.F. Navarro, Consejo Superior de Investigaciones Científicas, third ed., *El Vidrio*, Madrid, España, 2003, p. 561.
- [5] E.A. Mari, Editorial Americalee, *Los Vidrios*, Buenos Aires, Argentina, 1982, p. 401.
- [6] B.D. Fabes, W.F. Doyle, B.J.J. Zelinski, *J. Non-Cryst. Solids* 82 (1986) 349.
- [7] A. Maddalena, M. Guglielmi, A. Racanelli, *J. Non-Cryst. Solids* 100 (1986) 461.
- [8] B.D. Fabes, G.D. Berry, *J. Non-Cryst. Solids* 121 (1990) 357.
- [9] M. Mennig, A. Gier, D. Anshütz, H. Schmidt, *Glastech. Ber. Glass Sci. Techn.* 74 (8) (2001) 217.
- [10] V. Verganelakis, P.D. Nicolaou, G. Kordas, *Glass Techn.* 41 (1) (2000) 22.
- [11] J.D. Mackenzie, *J. Non-Cryst. Solids* 48 (1982) 10.
- [12] C.J. Brinker, G.W. Scherer, *Sol-gel Science: The Physics and Chemistry of Sol-gel Processing*, Academic, San Diego, USA, 1990.
- [13] J.D. Mackenzie, E.P. Bescher, *J. Sol-gel Sci. Techn.* 19 (2000) 23.
- [14] S. Pellice, P. Galliano, Y. Castro, A. Durán, *J. Sol-gel Sci. Techn.* 28 (2003) 81.
- [15] P. Innocenzi, M.O. Abdirashid, M. Guglielmi, *J. Sol-gel Sci. Techn.* 3 (1994) 47.
- [16] ASTM C 147-86. Standard test method for internal pressure strength of glass containers.
- [17] X.M. Chen, B. Ellis, F. Wang, A.B. Seddon, *J. Non-Cryst. Solids* 185 (1995) 1.
- [18] G. de With, R.H. Brzesowsky, J.G. Van Lierop, I.J.M. Snijkers-Hendricks, N.A.M. Sweegers, *J. Non-Cryst. Solids* 226 (1998) 105.