

USE OF NEW SILICA FILLERS AS ADDITIVES FOR POLYMERS USED IN PACKAGING OF FRUIT

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The objective of this work was to synthesize nanosilicas with different degree of hydrophobicity by the sol-gel method, using tetraethyl orthosilicate as a precursor. For this purpose, 3-aminopropyl triethoxysilane (APS) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS), were added during synthesis as modifiers. A commercial biopolymer (Hexamoll Dinch, BASF) intended for packaging of apples, was added to the new nanosilicas. The materials obtained were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, potentiometric titration, porosity, specific surface area and hydrophobicity/hydrophilicity by wetting test. Colorimetry was used to evaluate change in apple pulp color after contact with the different silicas.

Keywords: modified silica; SEM; TEM.

INTRODUCTION

Consumers demand food products that preserve their health value and retain their natural color, flavor, aroma and texture yet contain fewer additives. These requirements constitute new challenges for the processing and packaging of fruit and vegetables.¹ Currently, the polymeric films used in natural food packaging are not efficient enough creating the need to develop more environmentally friendly packaging materials able to extend durability and be recyclable.²

Silica and biopolymers are attractive for the preparation of multi-functional and high performance hybrid materials by using the sol-gel method.³ With the fast development of sol-gel chemistry in recent decades, most silica gels are now prepared using alcoxide precursors such as tetramethyl orthosilicate (TMOS, $\text{Si}(\text{OCH}_3)_4$) and tetraethyl orthosilicate (TEOS, $\text{Si}(\text{OCH}_2\text{CH}_3)_4$). The latter has been widely used as a silica precursor for the preparation of several biopolymer-silica hybrids,^{4,6} in which the organosiloxanes with non-hydrolysable organic groups contribute to build the structural units of silica as well as the surface functional groups. Sol-gel chemistry based on these compounds prevents the formation of unwanted products and, in addition, provides much greater control over the final product. On the other hand, gels prepared from TEOS with acid or basic catalyst in a "one step" reaction have the advantage of being produced in a single container.

The preparation of hybrid nanomaterials is increasingly attractive due to the unique physical and chemical properties attained. It is well known that the intrinsic properties of nanoparticles associated with their composition, size and shape, enhance the properties of polymers and even generate new properties.⁷ It should be noted that the synthesis of modified nanosilicas can be considered environmentally friendly because the properties of fruits are not modified.

The objective of this work is to synthesize and characterize nanosilicas with different hydrophobicity by using the sol-gel method with TEOS as a precursor. Two modifiers, 3-aminopropyl triethoxysilane (APS) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS), were added during the synthesis. These modifiers were chosen because they

have different structures and react differently with the surface and between themselves. The new silicas were added to a commercial biopolymer (Hexamoll Dinch, Basf) for use as packaging film for apples and pears. The extent of damage/deterioration of the fruit, placed in contact with silica, was evaluated.

EXPERIMENTAL

Synthesis of modified silica

The silicas were obtained by the sol-gel method, under a nitrogen atmosphere. Firstly, pure silica (S1 sample) was prepared using tetraethyl orthosilicate, TEOS (98%, Aldrich) as a precursor in absolute ethanol (EtOH 99.9%, Carlo Erba), and acetic acid (AcH, Anedra) was used as the hydrolysis catalyst. The silica was then washed with ethanol. To synthesize the modified silicas, 3-aminopropyltriethoxysilane, $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, (APS, 98%, Sigma) and 1,1,1,3,3,3-hexamethyldisilazane, $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$, (HMDS, 97%, Aldrich) were used as modifiers. The synthesis of some silicas was carried out in the presence of different amounts of biopolymer (Hexamoll® Dinch, Basf), whose formula is $\text{C}_{26}\text{H}_{48}\text{O}_4$, molecular weight of 424.7, and form is a clear liquid oil, free of foreign material. The quantity of the modifiers was changed in order to obtain different silica gel structures. The alcoxide:ethanol:acetic acid:modifier volumetric ratio used in the silica synthesis was 3.4:1.35:1:0.5-2. The samples without biopolymer were named S2, S3, S4, S5, S6, S7 and S8, while the silica-biopolymer samples were named A, B, C and D. Tables 1 and 2 show the nomenclature and composition of the samples.

To prepare the silicas, 13.5 mL of absolute ethanol was added to 10 mL of acetic acid, with subsequent addition of TEOS. Afterward, the modifiers were added to the mixture. Lastly, 30 mL of ethanol and 10 mL of water were added. All silicas and silica-biopolymer materials were left to dry at room temperature.

Fruit samples

The fruit was washed with cold distilled water, treated for 1 min with diluted chlorine cold water solution (0.3 g/L) and rinsed

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Table 1. Nomenclature and synthesis parameters of silicas

Chemical	S1	S2	S3	S4	S5	S6	S7	S8
TEOS (mL)	34	24	19	14	9	19	14	9
APS (mL)	-	5	5	5	5	10	15	20
HMDS (mL)	-	5	10	15	20	5	5	5
Total (mL)	34	34	34	34	34	34	34	34
Total EtOH (mL)	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5
AcH (mL)	10	10	10	10	10	10	10	10
Water (mL)	10	10	10	10	10	10	10	10

Table 2. Nomenclature and synthesis parameters of silica-biopolymer samples

Chemical	A	B	C	D
TEOS (mL)	16	16	16	16
APS (mL)	2.5	2.5	2.5	2.5
HMDS (mL)	1.5	2.5	3	5
Biopolymer (mL)	1.5	2.5	3	5
Total EtOH (mL)	43.5	43.5	43.5	43.5
AcH (mL)	10	10	10	10
Water (mL)	10	10	10	10

by immersion in distilled water for a further 1 min.⁸ The fruit was then peeled with a sharp knife, and cut into 2 x 2 x 1 cm pieces, which were placed in contact with 0.2 g of the synthesized silica or silica-biopolymer material, left for 1 h at room temperature, and the surface color measured.

Characterization

Textural properties of the silicas or silica-biopolymer materials were determined from N₂ adsorption-desorption isotherms at 77 K on a Micromeritics Accusorb 2100 device (USA). X-ray diffraction (XRD) patterns were obtained on Philips (Holland) PW-1390 (channel control) and PW-1394 (motor control) equipment coupled to a scanning graphical recorder. Cu K_α (λ = 1.5417 Å) radiation was employed using an Ni filter, 20 mA and 40 kV voltage source, a 5-60° 2θ scanning angle range, a scanning rate of 2°/min and 2000 counts/s for the amplitude of the vertical scale. Potentiometric titration with n-butylamine was carried out with a digital Hanna Instrument pH 211 microprocessor (Switzerland), and a double-junction electrode calibrated with pH 7.01 and 4.01 buffer solutions. 0.025 mL/min of n-butylamine in acetonitrile (0.05 N) was added to 0.05 g of sample previously suspended in acetonitrile (90 mL) and stirred for 3 h. Scanning electron microscopy (SEM) micrographs were obtained with a Philips Model 505 apparatus (Holland), using a voltage of 15 kV; samples were supported on graphite and metallized with sputtered gold films. The images were obtained with ADDAII (Soft Imaging System acquisition). Transmission electron microscopy (TEM) micrographs were obtained with a Jeol JEM-2010 device (Tokyo, Japan). A cellulose acetate butyrate film dissolved in ethyl acetate was placed on the microscope grid along with some glycerin drops. For the wetting test, the silica or silica-biopolymer samples were examined with different solvents to characterize their hydrophobic or hydrophilic behavior. Bidistilled water and ethanol were used. A 0.25 g sample was weighed in a Petri plate and 2.5 mL of solvent was added dropwise.

Cut-apple surface color was measured with a handheld tristimulus reflectance spectrophotometer Minolta Model CR-300

(Minolta, Japan). The CIE (Commission Internationale d'Éclairage) color components, L* (lightness or luminance), a* (chromaticity on a green (-) to red (+) axis), b* (chromaticity on a blue (-) to yellow (+) axis), were recorded. The numerical values were converted into "Hue angle" (h*), which is the color function, using $h^* = \tan^{-1}(b/a)$ when $a > 0$ and $b > 0$ or $h^* = 180 + \tan^{-1}(b/a)$ when $a < 0$ and $b > 0$. Color was evaluated after 1 h of contact of the fruit with the silica or silica-biopolymer material. The results were expressed as the average of two replicates.

RESULTS AND DISCUSSION

The specific surface area, pore volume and average pore size of the silicas and silica-biopolymer materials are given in Table 3. The S1 sample has an adsorption isotherm corresponding to Type I according to the classification given by Brunauer *et al.*,⁹ characteristic of microporous solids. Compared to the S1 sample ($S_{\text{BET}} = 517.4 \text{ m}^2/\text{g}$), a high decrease in the specific surface area is observed in the S2 sample (Figure 1, $S_{\text{BET}} = 133.1 \text{ m}^2/\text{g}$) which was prepared with APS and HMDS; furthermore, the adsorption isotherm is different (Type IV) and shows hysteresis, indicating the existence of slit-shaped mesopores.

Table 3. Textural properties of the silicas and silica-biopolymer materials

Sample	S_{BET} (m ² /g)	Pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Average pore size (Å)
S1	517.4	0.24	0.17	18.5
S2	133.7	0.11	0.02	32.5
S3	69.3	0.13	-	75.6
S4	2.5	-	-	42.1
S5	3.1	0.01	-	88.9
A	29.3	0.18	0.01	207.4
B	7.3	0.08	-	281
C	3.5	0.03	-	322.9
D	2.9	0.02	-	217.8

For the S3 sample (higher HMDS, constant APS, lower TEOS, compared to S2 sample), S_{BET} decreases more (69.3 m²/g), and the pore diameters correspond to mesopores, although macropores can also be present. The S4 and S5 samples show very low S_{BET} values, 2.5 and 3.1 m²/g, and are mainly mesoporous. On the other hand, for the samples obtained by increasing the amount of APS (S6, S7 and S8 samples), the textural properties cannot be measured because they resembled elastic gum.

The characterization of the textural properties of the silica-biopolymer materials shows adsorption isotherms with similar hysteresis of Type A, typical of the presence of cylindrical pores with very

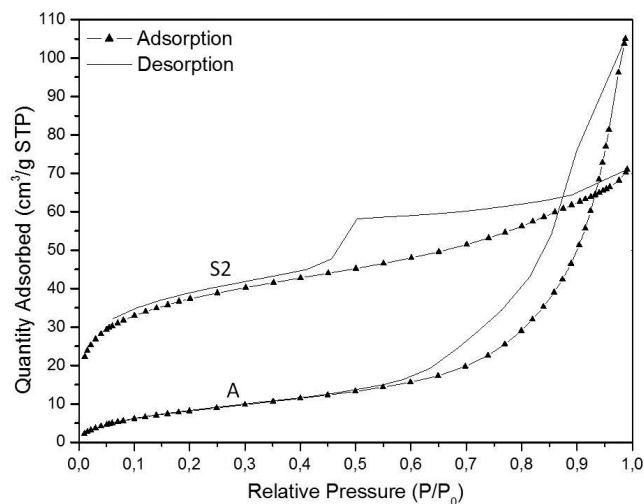


Figure 1. N_2 adsorbed vs. relative pressure of S2 and A samples

similar average diameter. In addition, they are mesoporous solids with an average pore size of between 20 and 32 nm, although macropores might also be present. Moreover, low values of specific surface area were obtained for all the samples. S_{BET} of the A sample (Figure 1) is $29.3 \text{ m}^2/\text{g}$, while for the B sample, in which the amount of biopolymer and HMDS is greater, S_{BET} decreased to $7.3 \text{ m}^2/\text{g}$. S_{BET} values are very low, 3.5 and $2.9 \text{ m}^2/\text{g}$, for C and D samples, synthesized with higher amount of biopolymer and HMDS with respect to APS.

The titration of the acid sites of the silicas does not follow a unique pattern. The S1 sample has a very strong initial acid strength (initial electrode potential, $E_i = 540 \text{ mV}$), while for the S2 sample E_i decreased sharply to 40 mV . Hence, the decrease could be due to the presence of APS and HMDS on the silica surface, because certain sites can be covered by hydrophobic moieties such as HMDS. Similar behavior is found in the S3 sample, in which HMDS amount increases while APS remains constant, and E_i decreased to 10 mV . The S4 sample has an anomalous behavior with respect to the other silicas ($E_i = 60 \text{ mV}$). For the S6 and S7 samples, with APS increasing while HMDS is constant, the values of E_i increased from 32 to 62 mV . This could be associated to the presence of some hydrophilic sites on the surface, increasing interaction with the modifiers.

The titration of the acid sites of the silica-biopolymer materials synthesized follows a unique similar pattern. The E_i values are 50 (A sample), 60 (B sample), 55 (C sample) and 52 (D sample) mV. These values suggest that, when TEOS volume is maintained, the formation of particles is unaffected, whereby the effect of the modifiers is the same independently of the amount added.

On the SEM micrographs, the characteristic morphology of bulk silica in the S1 sample is observed. The S2 sample (Figure 2) shows spherical particles that become faint in the S3 sample when the amount of HMDS increases and that of TEOS decreases. The S4 and S5 samples are similar in granulometry, showing that when a very high amount of HMDS is present with respect to that of APS, the particle shape is laminar. The S6 sample (Figure 3) shows evidence of formation of spherical particles due to the presence of APS, but when the APS amount increases up to the same TEOS volume, the laminar shape is predominant. The SEM micrographs obtained for the silica-biopolymer materials (Figure 4) exhibit similar morphology. The presence of biopolymer increases the formation of clusters.

The TEM micrograph of the S1 silica is shown in Figure 5 and has spherical or oval shaped particles, with a primary particle size of close to 12 nm (nanoparticles). To maintain the nanometric particle size, the amount of water, acetic acid and ethanol were kept constant

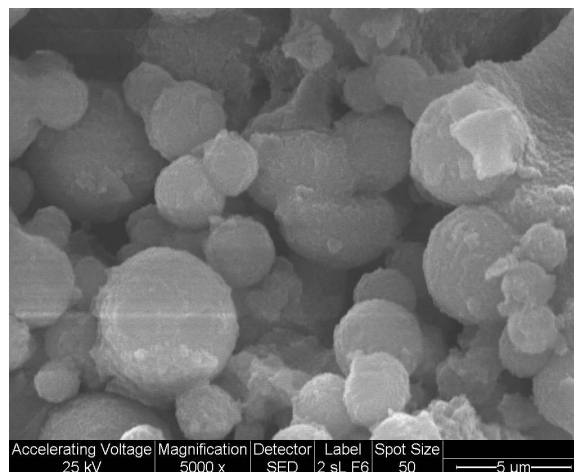


Figure 2. SEM micrograph of S2 sample. Magnification: $5000 \times$

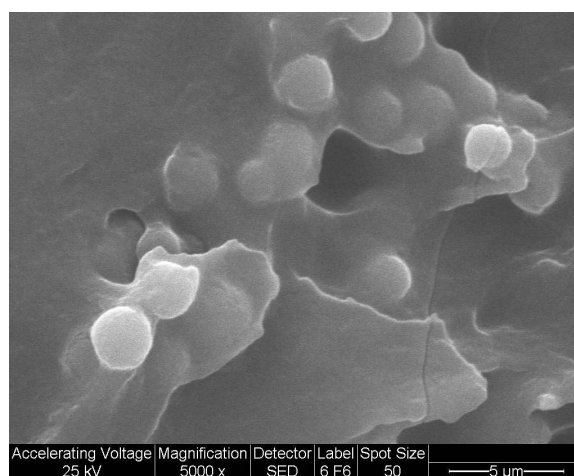


Figure 3. SEM micrograph of S6 sample. Magnification: $5000 \times$

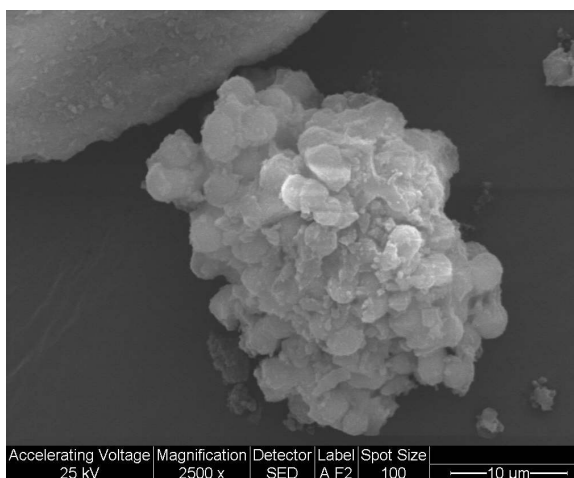


Figure 4. SEM micrograph of A sample. Magnification: $2500 \times$

in the synthesis of the modified silicas. TEM micrographs of S2, S3 and S4 samples show that the shape of the S1 silica particles is maintained, though there is some agglomeration of particles, and the particle size is greater. In addition, the presence of floccules in the crystalline network of the silicas can be partially seen.

These formations lead to a visible deformation of the particles, as can be observed in the micrograph of the S5 sample (Figure 6).

When the TEM micrographs of S2 and S6 samples are compared, the deformation of the particles produced in the silicas prepared

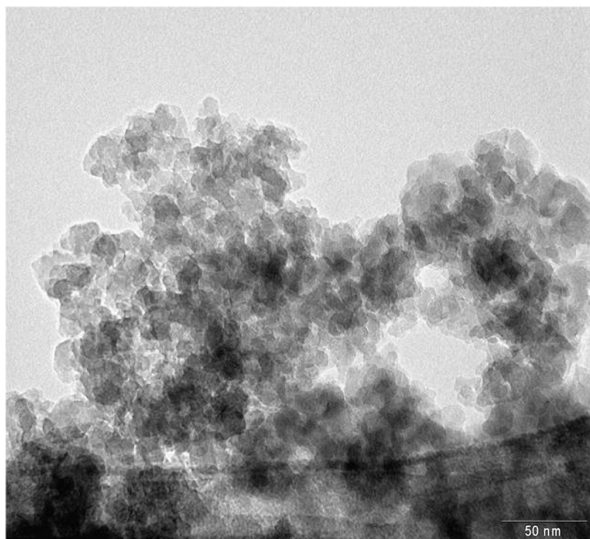


Figure 5. TEM micrograph of S1 sample. Scale: 50 nm

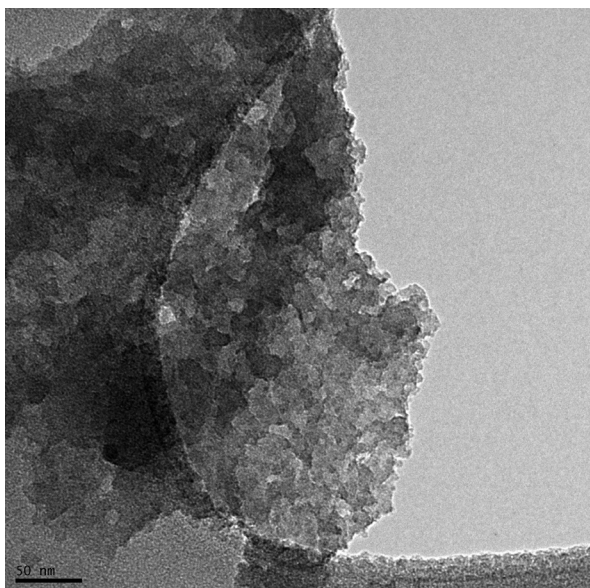


Figure 6. TEM micrograph of S5 sample. Scale: 50 nm

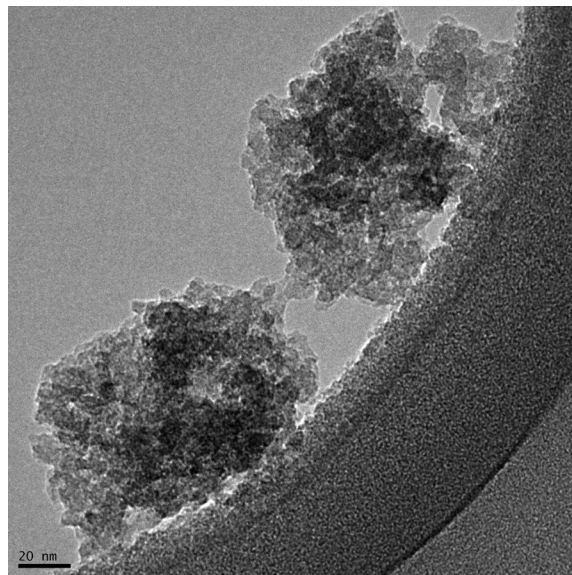


Figure 7. TEM micrographs of D sample. Scale: 20 nm

The X-ray diffraction patterns of S1, S2, S3, S5 and S6 samples show that all solids are amorphous. This uniform characteristic is independent of the compound used during the synthesis,¹⁰ evidenced by the fact that the S1 sample was prepared using only TEOS while the others were modified by addition of APS and HMDS. The same behavior was observed for the A, B, C and D samples.

In relation to wettability, it is known that solid surface wetting by a liquid is governed by the chemical properties of the solid and its surface morphology.¹¹ The modified silica shows a loss of hydrophilicity when the amount of HMDS increases, as HMDS reacts with the silanol groups of the silica, readily replacing them and surrounding the particles.¹² This interaction acts like an umbrella over the silanols of pure silica. Xu *et al.*¹² found that the enrichment of methyl groups on the particle surface influences its hydrophobicity. For S6 and S7 samples, hydrophobicity using ethanol as the wetting agent was measured, and the formation of an emulsion due to the mixture of APS and HMDS in the silica can be observed.

The wettability using water for the silica-biopolymer materials produces a suspension due to the hydrophobicity caused by HMDS, and a strengthening of this property due to the biopolymer characteristics.

Finally, the parameters obtained on the CIE scale of the samples at room temperature, are shown for control, S1, S2 and S6 samples (Table 4), which allows analysis of the changes in color over time. The results showed a correlation between the control parameter values and the browning that apples suffered. The L^* coordinate (luminosity) is associated with global dimming of the product. It was noted that these values decreased at 1 h of contact in all analyzed cases, and this is related to the browning of apples over time.

It was observed that a^* parameter showed negative values (-6.78 and -2.18 range) in all cases, this indicates the green color of the pulp. These values after 1 h of contact become less negative, reflecting a decrease in green color with time. Many authors have reported a decrease in L^* value and an increase in a^* value as indicative of browning.¹³⁻¹⁵ Therefore, the simultaneous change obtained in both values, L^* and a^* might be a good indicator of the apple browning over time. According to the variations of a^* and b^* , there are slight changes in Hue values after 1 h. Hue values decrease as apples darken. It was also noted that S1 silica was the sample which produced less loss of light, the one that least affected the Hue angle and did not change the background color of the apple. The S1 sample

with higher amount of APS, at a constant HMDS content, is clearly observed. It can be assumed that the modifier is not only on the silica surface, but also forms part of its crystalline network. The flocules are likely produced by the excess of the modifier interacting with silanol and siloxane groups in the gel network. This different morphology could be associated to the APS compound, which can produce higher interaction through its amine group. The deformation confers a gummy texture to the solid, seen partially in the S7 sample and completely visible in the S8 sample, which is an elastic gum and could not be observed by TEM. The TEM micrograph of the S7 sample shows that the oval shape of the particles is lost, and instead a laminar shape is observed.

The TEM micrograph of the silica-biopolymer D sample is given in Figure 7 as a typical example. This solid contains the highest amount of biopolymer. By increasing the magnification, it can be noted that the regular spherical particle shape is retained, but slight deformation in the primary particles is evident. The biopolymer helps maintain the spherical particle shape of the silica. The low amount of APS helps to minimize particle deformation due to low quantity of amine groups interacting with TEOS.

Table 4. Colour parameters L*, a*, b* and hue angle of cutted apple surface before and after of the contact with the selected silica

	Control		S1		S2		S5	
	t = 0	t = 1 h	t = 0	t = 1 h	t = 0	t = 1 h	t = 0	t = 1 h
L*	77.75	73.51	80.14	79.66	79.66	75.94	81.86	74.24
a*	-6.02	-3.07	-6.42	-4.5	-5.96	-2.81	-6.26	-2.18
b*	22.74	31.71	19.8	21.26	19.95	27.31	18.81	30.56
Hue	105.04	96.18	107.97	102.29	106.66	95.87	108.42	94.2

provides moisture due to the amount of isolated silane groups that it presents. Nevertheless, the aim of the present work was to control this moisture, thus APS and HMDS are incorporated into the structure, although the most effective relationships have not yet been found. The b* value appears to be unrelated to the extent of browning, in agreement with other results reported in the literature.¹⁵

CONCLUSIONS

The specific surface area and average pore size of the synthesized silicas using HMDS and APS modifiers were severely affected. However, when the biopolymer was added, more uniform textural characteristics were obtained, because the N₂ adsorption-desorption isotherms were similar, and also presented similar hysteresis, associated with cylindrical pores, with all the samples being mesoporous solids. On the other hand, more hydrophobic silicas were obtained when APS and HMDS were added as modifiers whereas the addition of biopolymer, due to its properties, increased hydrophobicity.

Titration of the acid sites of the silica modified with APS and HMDS showed a sharp decrease in acidity compared to that of the unmodified silica, while the silica-biopolymer materials followed a similar pattern. When the amount of HMDS increased, the initial acid strength or total number of present sites was lower, due to the hydrophobic characteristics of this compound. On the other hand, the increase in APS led to a slight increase in initial acid strength, due to the presence of some hydrophilic sites that increase interaction.

Silica modified with APS and HMDS showed similar morphology by SEM with respect to bulk silica and increase in the amount of modifiers. The silica-biopolymer materials showed similar morphology, forming clusters.

TEM analysis of the samples prepared with APS and HMDS showed that the increase in HMDS content led to retention of the spherical particle shape of the silica with the biopolymer helping to maintain it. On the other hand, the increase in APS amount led to a visible deformation. It can be assumed that the modifier is not only on the silica surface, but also forms part of its polymeric network, and can produce higher interaction through its amine group. The deformation conferred a gummy texture to the solid.

All the synthesized solids presented amorphous characteristics by XRD.

The surface color using the CIE scale showed a loss of brightness of the pieces of apple pulp in contact with the modified silica which was slightly higher than for the unmodified silica, without organic modifiers. Similar behavior was observed for the Hue angle.

Finally, suitable selection of the modifier and its concentration allowed the obtention of silicas that could be used as fillers in films for packaging to help retain the characteristics of the fruit pulp.

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