New Silica Fillers for Polymers used in Food Packaging

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Summary: Several nanosilicas with different degree of hydrophobicity were prepared from tetraethyl orthosilicate (TEOS) by using the sol-gel method. Two modifiers, 3-aminopropyl triethoxysilane (APS) and 1,1,1,3,3,3–hexamethyldisilazane (HMDS), were added during the synthesis. The nanosilicas were added to commercial biopolymer (Hexamoll Dinch, BASF) intended for packaging of apples and pears. The nanosilicas were characterized by X-ray diffraction, transmission and scanning electron microscopies, potentiometric titration, porosity and specific surface area, and hydrophobicity/hydrophilicity by wetting tests. Colorimetry was used to assess the effect of the nanosilica in contact with apple pulp as the change in color with time was related to the efficiency of the packaging material. Addition of nanosilicas obtained with HMDS and APS increased the hydrophobicity of the biopolymer. The APS modified nanosilica showed an abrupt decrease in acidity as compared to the unmodified silica (i.e. the one prepared with only TEOS). On the other hand, the increase in HMDS maintained the spherical shape of the silica which also was maintained into the biopolymer. On the other hand, the nanosilica morphology was similar in the biopolymer materials, forming clusters or agglomerates. Finally, the brightness of the pieces of apple pulp in contact with the modified nanosilicas slightly increased with respect to the unmodified silica, and similar behavior was observed in the Hue angle.

Keywords: APS; HDMS; modified nanosilica; packaging; sol–gel method; TEOS

Introduction

The consumers demand food products that preserve their healthy value and save their natural color, flavor, aroma and texture but containing fewer additives. These requirements constitute new challenges for the processing and packaging of fruits and vegetables.[1] Currently, the polymeric films used in natural food packaging are not efficient enough and more environmental-friendly packaging materials able to extend the durability and, at the same time, be recyclable, need to be developed.

Silica and biopolymers are attractive for the preparation of multifunctional and high performance inorganic-organic hybrid materials by using the sol-gel method.[3] With the fast development of the sol-gel chemistry, in recent decades, most silica gels are prepared today using alcoxide precursors such as tetramethyl orthosilicate (TMOS, $Si(OCH_3)_4$) and tetraethyl orthosilicate (TEOS, $Si(OCH_2CH_3)_4$). The latter has been widely used as silica precursor for the preparation of several biopolymer-silica hybrids[3–5] in which the organosiloxanes with non-hydrolysable organic groups contributed to build the structural units of silica and the surface functional groups too. Sol-gel chemistry based on these compounds prevents the formation of unwanted products and, in addition, provides much greater

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control over the final product. On the other hand, the gels prepared from TEOS with acid or basic catalyst have the advantage of being produced in "one step".

There is an increased attraction toward the preparation of hybrid nanomaterials, 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, amplify the properties of polymers and even generate new properties.[6] It must be remarked that the synthesis of the modified nanosilicas can be considered as environmentally friendly because the properties of fruits should not be modified.

The objective of this work is to synthesize nanosilicas with different degree of hydrophobicity by using the sol-gel method. Two modifiers, 3-aminopropyl triethoxysilane (APS) and 1,1,1,3,3,3–hexametyldisilazane (HMDS), were added during the synthesis. The new nanosilicas 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 fruits, placed in contact with the nanosilicas, was evaluated.

Experimental Part

Synthesis of the Nanosilicas

The nanosilicas were obtained by the sol-gel method, under nitrogen atmosphere. Firstly, nanosilica was prepared using tetraethyl orthosilicate, TEOS (98%, Aldrich) as precursor in absolute ethanol (EtOH 99.9%, Carlo Erba), and acetic acid (AcH, Anedra) was used as hydrolysis catalyst (S1 sample). Then, the nanosilica was washed with ethanol.

To synthesize the modified nanosilicas, 3-aminopropyltriethoxysilane, APS (98%, Sigma) and 1,1,1,3,3,3-hexamethyldisilazane, HMDS (97%, Aldrich) were used as modifiers. The synthesis of some of these nanosilicas was carried out in the presence of different amounts of a polyester-based biopolymer (Hexamoll® Dinch, Basf). The amount of the modifiers was changed in order to obtain different silica gel structures. The alcoxide:ethanol:acetic acid:modifier volumetric ratio used in the nanosilica synthesis was 3.4:1.35:1:0.5-2. The samples without biopolymer were named as S2, S3, S4, S5, S6, S7 and S8, and the silica-biopolymer samples were named as A, B, C and D. Tables 1 and 2 show the nomenclature and composition of the samples.

To prepare the modified nanosilicas, 13.5 ml of absolute ethanol were added to 10 ml of acetic acid, and then TEOS was added. Afterward, the modifiers were added into the mixture. Lastly, 30 ml of ethanol and 10 ml of water were added. All nanosilicas and nanosilica-biopolymer materials were left to dry at room temperature.

Fruit Samples

The fruits were washed with cold distilled water, treated for 1 min with diluted chlorine cold water solution (0.3 g/l) and rinsed by immersion in distilled water for 1 min more.[8] Then, the fruits were peeled with a sharp knife, and cut into $2 \times 2 \times 1$ cm pieces, which were placed in contact with 0.2 g of the synthesized nanosilicas or

Table 1.
Nomenclature and synthesis parameters of the nanosilicas.

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
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 of the nanosilica-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
EtOH (ml)	43.5	43.5	43.5	43.5
AcH (ml)	10	10	10	10
Water (ml)	10	10	10	10

nanosilica-biopolymer materials, left in contact for 1 h at room temperature, and then the surface color was measured.

Experimental Techniques

Textural properties of the nanosilicas or nanosilica-biopolymer materials were determined from N_2 adsorption–desorption isotherms at 77 K in Micromeritics Accusorb 2100 equipment (USA).

X-ray diffraction (XRD) patterns were obtained in Philips (Holland) PW-1390 (channel control) and PW-1394 (motor control) equipment coupled to a scanning graphical recorder. The Cu K_α ($\lambda = 1.5417$ Å) radiation was used using 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/sec for the amplitude of the vertical scale.

The potentiometric titration with n-butylamine was carried out with a digital Hanna Instruments pH 211 microprocessor (Argentine), a double-junction electrode calibrated with pH 7.01 and 4.01 buffer solutions was used. 0.025 ml/min of n-butylamine in acetonitrile (0.05 N) was added to 0.05 g sample previously suspended in acetonitrile (90 ml) and stirred for 3 h.

Scanning Electron Microscopy (SEM) micrographs were obtained in Philips 505 equipment (Holland), using a voltage of 15 kV; samples were supported on graphite and metallized with sputtered gold films. The micrographs were obtained with ADDAII (Soft Imaging System acquisition).

Transmission Electron Microscopy (TEM) micrographs were obtained in Jeol JEM-2010 instrument (Tokyo, Japan). On the microscope grid, a cellulose acetate butyrate film dissolved in ethyl acetate was placed, and then some glycerine drops were put on.

For the wetting test, the nanosilicas or silica-biopolymer samples were examined with different solvents to characterize their hydrophobic/hydrophilic behavior. Bidistilled water and ethanol were used as test solvents. 0.25 g sample was weighed in Petri plate and 2.5 ml of solvent was dropwise added.

Cut-apple surface color was measured with a handheld tri-stimulus reflectance Minolta CR-300 colorimeter (Minolta, Tokyo, Japan). The CIE (Commission Internationale d'Eclairage) 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 related to the color change, 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 of the fruit was evaluated after 1 h in contact with the silica or silica-biopolymer material. The results were the average of two replicates.

Results and Discussion

The porosity and specific surface area of the nanosilicas and silica-biopolymer materials are given in Table 3. S1 sample has an adsorption isotherm (Figure 1) corresponding to type I according to the classification given by Brunauer et al.,[8] characteristic of microporous solids. Compared to S1 sample ($S_{BET} = 517.4\ m^2/g$), a high decrease in the specific surface area is observed in S2 sample (Figure 1, $S_{BET} = 133.1\ m^2/g$) that was prepared with APS and HMDS; furthermore, the adsorption isotherm is different (type IV) and shows hysteresis (Figure 1) indicating the existence of mesopores of slit shape. For the S3 sample (higher HMDS content, similar APS, and lower TEOS as compared to S2 sample),

Table 3.
Textural properties of the nanosilicas and nanosilica-biopolymer materials.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore size (Å)
S1	517	0.24	0.17	19
S2	134	0.11	0.02	33
S3	69	0.13	0.004	76
S4	3	0.002	–	42
S5	3	0.01	–	89
A	29	0.18	0.01	207
B	7	0.08	–	281
C	4	0.03	–	323
D	3	0.02	–	218

S_{BET} decreases more ($69.3\ m^2/g$), and the pore diameter correspond to mesopores, although macropores can also be present. S4 and S5 samples show very low S_{BET} values, 2.5 and $3.1\ m^2/g$, and they are mainly mesoporous. On the other hand, for the nanosilicas obtained by increasing the APS amount (S6, S7 and S8 samples), the textural properties cannot be measured because they were gels.

The characterization of the textural properties of the nanosilica-biopolymer materials shows adsorption isotherms with similar hysteresis of type A, typical of cylindrical pores with very similar average diameter. In addition, they are mesoporous solids with average pore size 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 (Table 3) is $29.3\ m^2/g$, while for the B sample, in which the amounts of biopolymer and HMDS are higher, the S_{BET} decreases to $7.3\ m^2/g$. The S_{BET} values are very low, 3.5 and $2.9\ m^2/g$, for C and D samples respectively, and they were synthesized with higher amount of biopolymer and HMDS with respect to APS.

The nanosilicas have different acidity. The S1 sample has a very strong initial acid strength (initial electrode potential (Ei) = 540 mV), while for the S2 sample Ei decreased abruptly to 40 mV. This decrease could be due to the presence of APS and HMDS on the S2 nanosilica surface, as some sites can be covered by hydrophobic moieties. The potentiometric curves of the S1 and S2 samples are shown in Figure 2a and 2b, respectively. Similar behavior is found in the S3 sample, in which HMDS amount increases keeping APS constant, and E_i decreased to 10 mV. The S4 sample has an anomalous behavior with respect to the other nanosilicas showing higher acidity ($E_i = 60$ mV). For the S6 and S7 samples,

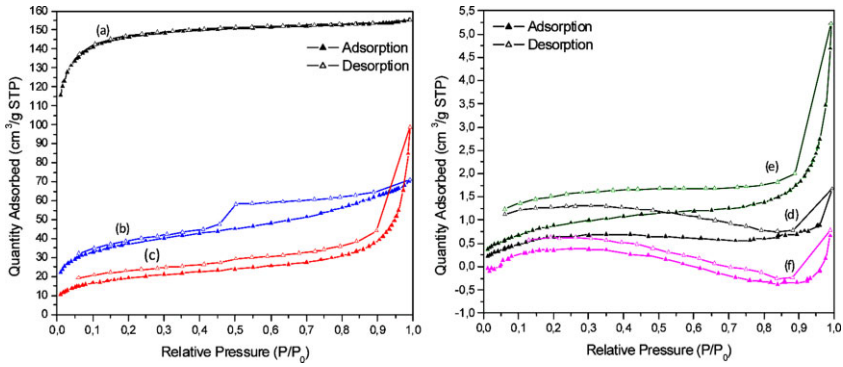

Figure 1.
N_2/77K adsorption isotherms of S1(a), S2 (b), S3 (c), S4 (d), S5 (e) and S6 (f) nanosilicas.

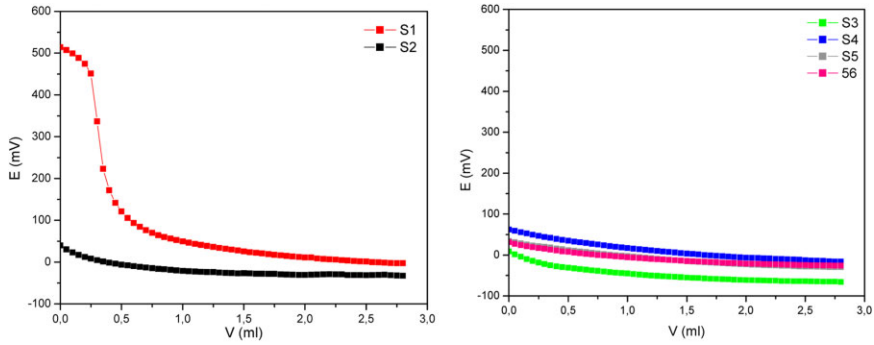

Figure 2.
Potentiometric curves of nanosilicas.

with increasing APS content and similar HMDS amount, the values of E_i increased from 32 to 62 mV. This can be associated to the presence of some hydrophilic sites on the nanosilica surface.

The titration of the acid sites of the nanosilica-biopolymer materials follows the same pattern. The Ei 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 acidity is not affected, irrespective of the amount and nature of the APS and HDMS modifiers.

The characteristic morphology of bulk nanosilica in the S1 sample is shown in the SEM micrograph of Figure 3.

The S2 sample shows spherical particles that become faint in sample S3 when the amount of HMDS increases and that of TEOS decreases. The S4 and S5 samples have similar laminar particle size, likely causes when the HMDS amount is high with respect to that of APS. The S6 sample shows evidence of formation of spherical particles due to the APS, but when the APS amount increases up to the same of TEOS, the laminar shape is dominant. On the other

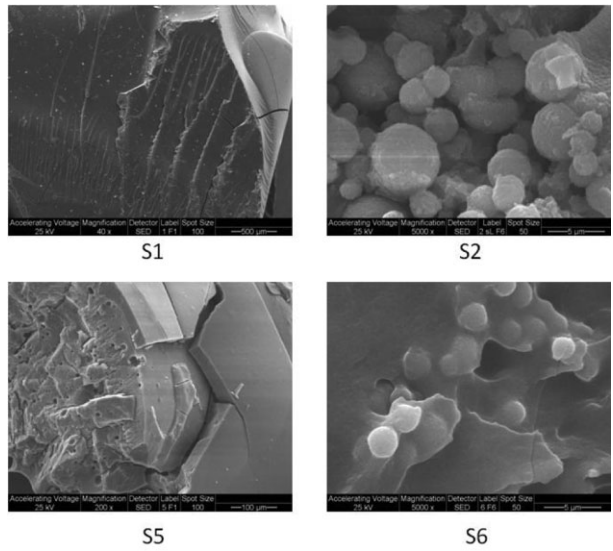

Figure 3.
SEM micrographs of S1, S2, S5 and S6 nanosilicas.

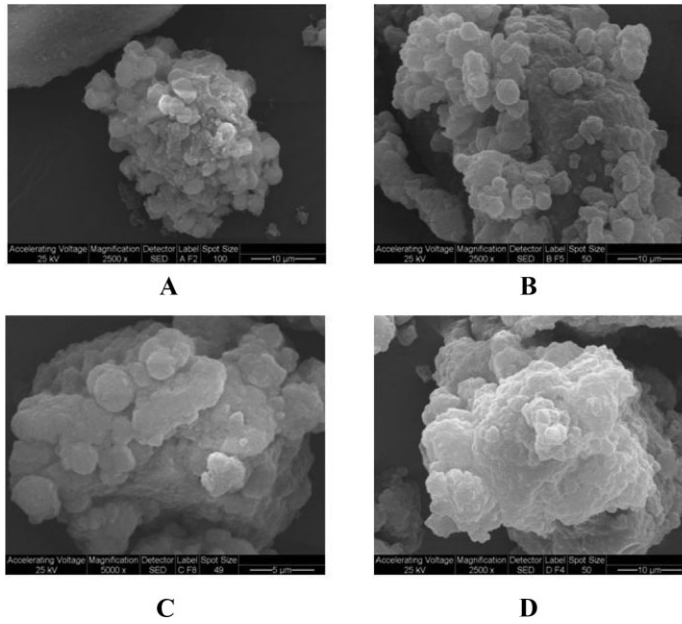

Figure 4.
SEM micrographs of A, B, C and D nanosilica-biopolymer materials.

hand, the SEM micrographs of the nanosilica-biopolymer materials (Figure 4) have similar morphology. The presence of biopolymer increases the formation of nanosilica clusters.

The TEM micrograph of the S1 silica is shown in Figure 5 and it has spherical or oval shaped particles, with a primary particle size near 12 nm. To maintain the nanometric particle size, the amount of water, acetic acid and ethanol were maintained constant 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 higher. In addition, the presence of floccules in the crystalline network of the silicas can be glimpsed. These formations lead to a visible deformation of the particles, as can be observed in the micrographs of S5 sample (Figure 5). When the TEM micrographs of S2 and S6 samples are compared (Figure 5), the deformation of the particles produces in the silicas prepared with higher amount of APS, at a constant HMDS content, is clearly observed. It can be assumed that the modifier is not only located on the silica surface, but also it is forming part of its crystalline network. Likely the floccules are 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 that can produce higher interaction throughout its amine group. The deformation provides a gummy texture, glimpsed in the S7 sample and completely visible in the S8 sample, which is an elastic gum and could not be observed by TEM.

TEM micrograph of the S7 sample shows that the oval shape of the particles is lost, and in turn a laminar shape is observed.

TEM micrograph of the nano silica-biopolymer sample D is given in Figure 6 as typical example. This sample contains the highest amount of biopolymer. At high magnification, it can be noticed that the regular spherical nanosilica particle shape is kept, but a small deformation in the primary particles is observed. The biopolymer helps to maintain the spherical nanosilica particle shape. The low amount of APS helps to minimize particle deformation due to low

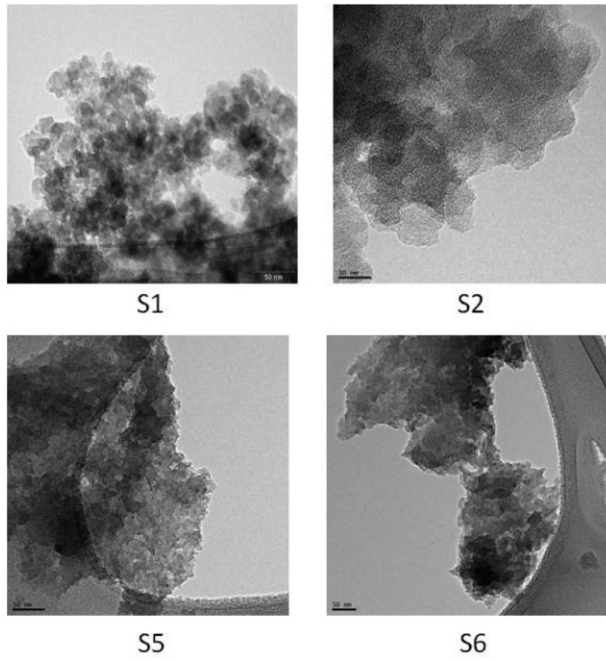

Figure 5.
TEM micrographs of S1, S2, S5 and S6 nanosilicas.

quantity of amine groups interacting with TEOS.

The X-ray diffraction patterns of A, B, C and D nanosilica-biopolymer materials are given in Figure 7. Similar X-ray diffraction patterns were obtained in S1, S2, S3, S5 and S6 samples too. All solids are amorphous irrespective of the compound used during the nanosilica synthesis, in agreement with earlier results.[9]

It is known that the solid surface wetting by a liquid is governed by the chemical properties of the solid and its surface morphology.[10] The wetting by water of the modified nanosilicas show loss of hydrophilicity when the amount of HMDS increases (Figure 8), as HMDS reacts with the silanol groups of the nanosilica.[11] This interaction is like an umbrella over the silanols of unmodified silica. Xu *et al.*[11] found that the enrichment of methyl groups on the silica particle surface influences its hydrophobicity. For S6 and S7 samples, the hydrophobicity measured by wetting with

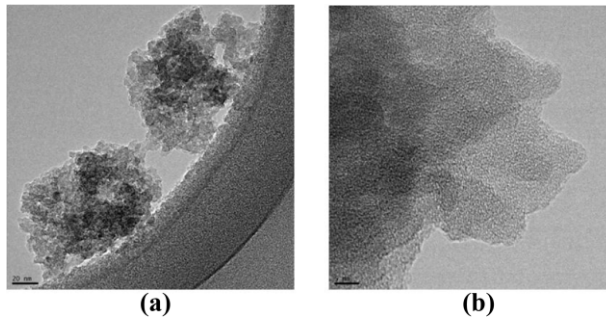

Figure 6.
TEM micrographs of nanosilica-biopolymer D at different magnifications (a) scale: 20 nm, and (b) scale: 5 nm.

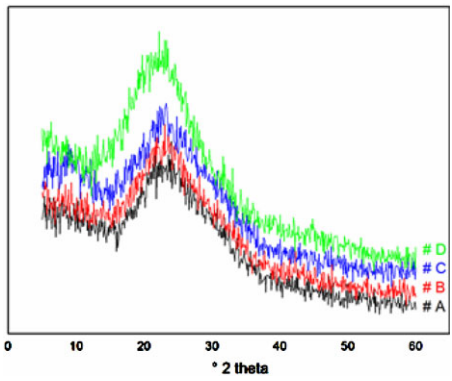

Figure 7.
X-ray diffractograms of the nanosilica-biopolymer materials.

ethanol shows the formation of an emulsion likely due to the existence of both APS and HMDS on the nanosilica surface (Figure 9). The wettability measured with water for the nanosilica-biopolymer materials provides a suspension due to the hydrophobicity caused by HMDS, more enhanced due to the biopolymer characteristics.

Finally, the parameters obtained in the CIE scale, which allows analyzing the changes of color suffered with time, of the samples at room temperature are shown in Table 4 for control, S1, S2 and S6 samples. The results show a relationship between the control parameter values and the browning of the apples pieces. The L^* coordinate (luminosity) is associated with global dimming of the product. These values decrease to 1 h of contact of nanosilica with the apple pieces in all samples, and this is also related to the browning of apples suffering over time. On the other hand, the a^* parameter has negative values (-6.78 to -2.18) in all cases which is related to the green color of the apple pulp. The a^* parameter values after 1 h of assay become less negative, indicating a loss in green color with time. Some authors[12–14] have reported that a decrease in L^* value and an increase in a^* value is indicative of browning in fruits. Therefore, the simultaneous change obtained in both values, L^*

Figure 8.
Water wetting test of S2 and S5 nanosilicas.

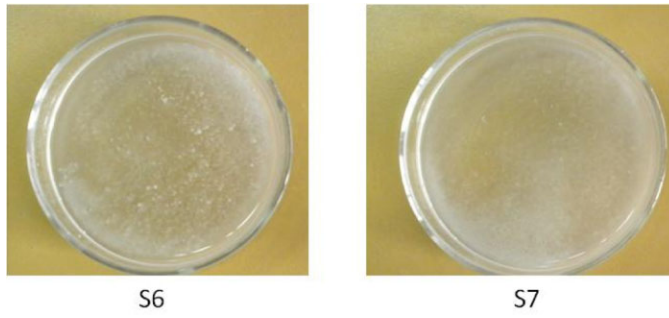

Figure 9.
Ethanol wetting test of S6 and S7 nanosilicas.

Table 4.
Colour parameters L*, a*, b* and hue angle of cutted apple pieces surface before and after being in contact with nanosilica.

	Control		S1		S2		S5		S6	
	t = 0	t = 1 h	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	79,16	75,71
a*	−6,02	−3,07	−6,42	−4,5	−5,96	−2,81	−6,26	−2,18	−6,78	−3,34
b*	22,74	31,71	19,8	21,26	19,95	27,31	18,81	30,56	21,53	29,55
Hue	105,04	96,18	107,97	102,29	106,66	95,87	108,42	94,2	107,42	96,37

and a*, might be a good indicator of the apple browning suffered over time. According to the variations of a* and b* values, there are small changes in the Hue values after 1 h. Hue values should decrease as apples darken. On the other hand, the S1 silica causes less loss of light, the one that affects less the Hue value and it does not change the background color of the apple. The b* value appears to be unrelated to the extent of apple browning, in agreement with the existing literature.[14]

Conclusion

The porosity and specific surface area of the nanosilicas modified with HMDS and APS were severely affected with respect to that obtained with TEOS only. When the nanosilica was produced in the presence of the biopolymer, more uniform porosities and specific surface areas were obtained. On the other hand, more hydrophobic nanosilicas were obtained when APS and HMDS were added but the addition of biopolymer increased their hydrophobicity.

The acidity of the modified nanosilicas with APS and HMDS decreased abruptly as compared with the unmodified nanosilica, while the nanosilica-biopolymer materials followed similar acidity. Modified nanosilicas with APS and HMDS showed similar morphology with respect to that of the unmodified nanosilica and by increasing the modifiers content. On the other hand, the nanosilica-biopolymer materials showed similar morphology, forming silica clusters. Furthermore, the spherical particle shape of the APS and HMDS modified nanosilicas was maintained and the addition into the biopolymer helped to maintain that shape.

The surface color using the CIE scale showed a loss of brightness of the apple pulp pieces in contact with the modified nanosilicas in a slightly greater extent than for the unmodified nanosilica. Similar behavior was observed for the Hue angle.

Finally, a proper selection of the modifier and its concentration allowed obtaining nanosilicas that could be used as fillers in films for packaging to help keeping the characteristics of the apple pulp.

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