

Organic–Inorganic Hybrid Films Based on Hydroxylated Soybean Oils

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Abstract Hybrid organic–inorganic films were prepared using four different hydroxylated soybean oils (HSO) or epoxidized soybean oil as organic precursor and tetraethyl orthosilicate (TEOS) as inorganic precursor in a mass ratio of HSO:TEOS of 90:10. The films were macroscopically homogeneous and were characterized by swelling and extraction in solvent, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) including energy dispersive spectroscopy (EDX), adhesion and hardness. Their properties varied as a function of the number of OH groups present in the HSO. The best hybrid system was HSOF198/TEOS, with an OH value of 198 mg of KOH/g, which presents lower swelling coefficient, very good adhesion on aluminium surface and good hardness.

Keywords Hydroxylated soybean oil · Film · Organic–inorganic hybrid · Sol–gel · TEOS

Introduction

Environmentally safe coatings have been the subject of much research, due to the urgency of replacing the usual chromium (VI) treatment on metallic surfaces [1–3].

Sol–gel inorganic coatings present interesting properties such as chemical and thermal stability [4, 5], however, films prepared in this way may present cracking problems and are also still expensive. Organic–inorganic hybrid coatings combine the good properties of inorganic components such as hardness and mechanical resistance with those of organic ones, such as flexibility and impact resistance. These final properties can be achieved through the sol–gel process at mild temperatures [6, 7]. The use of modified vegetable oils as organic precursors for ceramer coatings offers the use of renewable materials and the preparation of environmental friendly films. Hybrid films have been prepared using different sol–gel precursors and typical *drying* vegetable oils such as linseed and sunflower oils [8–12] or *semi-drying* vegetable oils such as soybean oil [13, 14], blown soybean oil [15], and epoxidized soybean oil [8], as well as castor oil [16]. Their properties—surface adhesion, flexibility, hardness and impact resistance—varied with the amount of sol–gel precursor, especially their flexibility and rupture tension.

In this work, various hydroxylated soybean oils (HSO) were synthesized and used as organic precursors in the preparation of organic–inorganic hybrid films using tetraethyl orthosilicate (TEOS). The goal was to use an organic precursor containing OH groups that could condense with the hydrolyzed tetraethoxysilane resulting in an organic–inorganic hybrid film. The films were studied as a function of the nature of HSO employed. They were characterized by degree of swelling, extraction in toluene, thermogravimetric analysis, adhesion, pencil hardness and scanning electron microscopy (SEM) analysis.

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Materials and Methods

Commercial soybean oil (SO) was purchased from Oleoplan SA (Veranópolis, Brazil) and epoxidized soybean oil (ESO) EDENOL D81 from Cognis (Jacareí, Brazil). TEOS was purchased from Aldrich Chemical (Milwaukee, WI, USA). *Meso*-erythritol (99%) was obtained from Acros (Geel, Belgium), formic acid and diethyl ether were purchased from Synth (São Paulo, Brazil). Hydrogen peroxide (30%), sodium hydrogen carbonate, sodium bisulfite, sulfuric acid and anhydrous sodium sulfate were purchased from Nuclear (Diadema, São Paulo, Brazil). Boron trifluoride etherate (48% in BF_3), absolute ethanol (98%), toluene, hexane and ethylene glycol were obtained from Merck (Darmstadt, Germany). All chemicals were analytical grade and were used without further purification.

Hydroxylated Soybean Oils (HSO)

Four different HSO were synthesized to be used as organic precursors in the preparation of the hybrid films: HSOF198 (soybean oil fully hydroxylated with formic acid/hydrogen peroxide, having an OH value of 198 mg of KOH/g), HSOF75 (soybean oil partially hydroxylated with formic acid/hydrogen peroxide, having an OH value of 75 mg of KOH/g), HSOEG (HSO from epoxidized soybean oil and ethylene glycol), and HSOMeso (HSO from epoxidized soybean oil and *meso*-erythritol).

Preparation of HSOF198 and HSOF75 [17]

Refined soybean oil (70 g, 0.37 mol of double bonds) was mixed with 43 mL (1.11 mol) of formic acid. A solution of 32% H_2O_2 (50.5 mL, 0.56 mol) was added dropwise to the mixture at room temperature for 30 min, under strong mechanical stirring. When the H_2O_2 addition was completed, the mixture was heated to 65 °C, and stirred strongly for different times depending on the hydroxylation level to be reached. After the required time, the product was washed, firstly with a sodium bisulfite 10% w/v solution to remove peroxide, followed by a sodium bicarbonate 10% w/v solution until the pH of the aqueous layer was neutral.

Afterwards, ethyl ether was added and the organic phase was separated and dried overnight with sodium sulfate. After filtration, the solvent was removed in vacuum.

Preparation of HSOEG

A solution of epoxidized soybean oil (20 g, 0.086 mol of epoxy groups) and ethylene glycol (14.4 mL, 0.26 mol) was prepared and 0.05 mL of sulfuric acid was added. The mixture was heated at 80 °C, for 24 h, under mechanical stirring. Afterwards, ethyl ether was added and the organic phase was separated, washed with a sodium bicarbonate 10% w/v solution until neutralization and with a saturated NaCl solution, and dried overnight with sodium sulfate. After filtration, the solvent was removed in vacuum.

Preparation of HSOMeso

A solution of *meso*-erythritol (7.86 g, 0.064 mol) in 30 mL of water was prepared and added to the epoxidized soybean oil (15 g, 0.064 mol of epoxy groups). Then 0.70 mL of sulfuric acid was added. The mixture was heated to 80 °C, for 24 h, under mechanical stirring. The remaining of the procedure was the same as for the preparation of HSOEG.

Organic Precursor Characterization

The four HSO organic precursors used in the preparation of organic–inorganic hybrid films were characterized by ^1H NMR, ^{13}C NMR [attached proton test (APT)], and by the determination of the OH value. ^{13}C NMR (APT) spectra were obtained in a Varian Inova 300 MHz using CDCl_3 as solvent and tetramethylsilane (TMS) as standard. The APT experiment is a multiplet detection technique in carbon-13 NMR. It consists of a 90° pulse that creates transverse magnetization, followed by a 180° pulse in the middle of the evolution period. The APT experiment yields methine (CH) and methyl (CH_3) signals positive and quaternary (C) and methylene (CH_2) signals negative.

OH values of the soy polyols were determined according to the American Oil Chemists' Society (AOCS) official method Tx 1a-66 [18]. The hydroxyl value is defined as the number of milligrams of KOH equivalent to the hydroxyl content of 1 g of sample of fatty oils and their derivatives.

Films Preparation

The films were prepared using TEOS as inorganic precursor with a mass ratio of organic precursor to TEOS of 90:10.

HSOF75 and HSOF198, HSOEG and HSOmeso Films

Absolute ethanol (4.5 mL) and 0.18 mL of deionized water were added to 4.5 g of each HSO. Formic acid was added to a pH of 2.1 followed by the addition of 0.54 mL (2.42 mmol) of TEOS. The mixture was left at room temperature for 1–2 h under mechanical stirring. Afterwards 6 g of the mixture was placed in a teflon Petri dish, partially covered and left for 72 h at room temperature. The resulting gel was cured at 160 °C for 48 h. For the HSO198 film a cure schedule consisting of 2 h at 35–40 °C, 2 h at 60–65 °C and 105 h at 160–170 °C was used.

HSO–BF₃ Films

ESO (4.5 g, 12.9 mmol of epoxy groups) was dissolved in 2.5 mL of absolute ethanol, to which 2.0 mL of an ethanolic solution containing four drops of BF₃·OEt₂ was added. The mixture was stirred during 30 min followed by the addition of 0.18 mL of deionized water and 0.54 mL (2.42 mmol) of TEOS to the mixture. For the gel preparation, 6 g of the mixture was placed in a teflon Petri dish, partially covered and left for 72 h at room temperature. The cure schedule employed was 2 h at 35–40 °C, 2 h at 60–65 °C and 105 h at 160–170 °C.

Film Characterization

The films were characterized by the determination of swelling coefficient, extraction in hexane, thermogravimetric analysis, adhesion, pencil hardness and SEM analysis.

Swelling Coefficient

The swelling coefficient was determined by soaking the films in toluene in a thermostatic bath at 30 °C for at least 48 h. The mass of the swelled samples was determinate (m), they were dried and the mass of the dried samples were also measured (m_o). The swelling coefficient, Q (g/g), was calculated according to Eq. (1)

$$Q = \left(\frac{m - m_o}{m_o} \right). \quad (1)$$

Extraction in Hexane

The extraction test was performed in a Soxhlet extractor for 3 h using hexane as solvent. The films

were weighed before and after the treatment to calculate the mass extracted. The resulting solution was evaporated and the residue was analyzed by ¹H NMR.

Thermogravimetric Analysis (TGA)

TGA was performed in a 2950 Thermogravimetric Analyzer Mod 2050, from TA Instruments, with a temperature change of 20 °C per minute in the temperature range of 25–600 °C under nitrogen and up to 1,000 °C under oxidative atmosphere.

Adhesion

Film adhesion was evaluated in films applied on aluminium surfaces, by the standard test method for measuring adhesion by the tape test (ASTM D-3359–95a) [19], in the cross-cut mode. This test method covers procedures for assessing the adhesion of coating films to metallic substrates by applying and removing pressure-sensitive tape over cross cuts made in the film and inspecting the grid area for removal of coating from the substrate. The adhesion is evaluated by comparison with descriptions and illustrations and the results are reported according to the adhesion rating (5B corresponds to 0%, 4B less than 5%, 3B from 5 to 15%, 2B from 15 to 35%, 1B from 35 to 65% and 0B greater than 65% of area removed).

Pencil Hardness

Film hardness was evaluated in films applied on aluminium surfaces, by the standard test method for film hardness by the pencil test [20] (ASTM D-3363–92a). This test method covers a procedure for rapid, inexpensive determination of the film hardness of a coating on a substrate in terms of pencil leads of known hardness. Pencil hardness varies from the hardest (6H) to the softest (6B) according to the following scale: 6H > 5H > 4H > 3H > 2H > HB > 2B > 3B > 4B > 5B > 6B. The pencils are used in succession to determine the hardness at which the film is not cut or scratched.

Scanning Electron Microscopy (SEM) Analysis

The morphology of the cryogenically fractured samples was examined by SEM (JEOL JSM 6060) on Au-coated surfaces. Energy-dispersive spectrometry (EDX) analysis (JEOL JSM 5800) was also performed on selected samples.

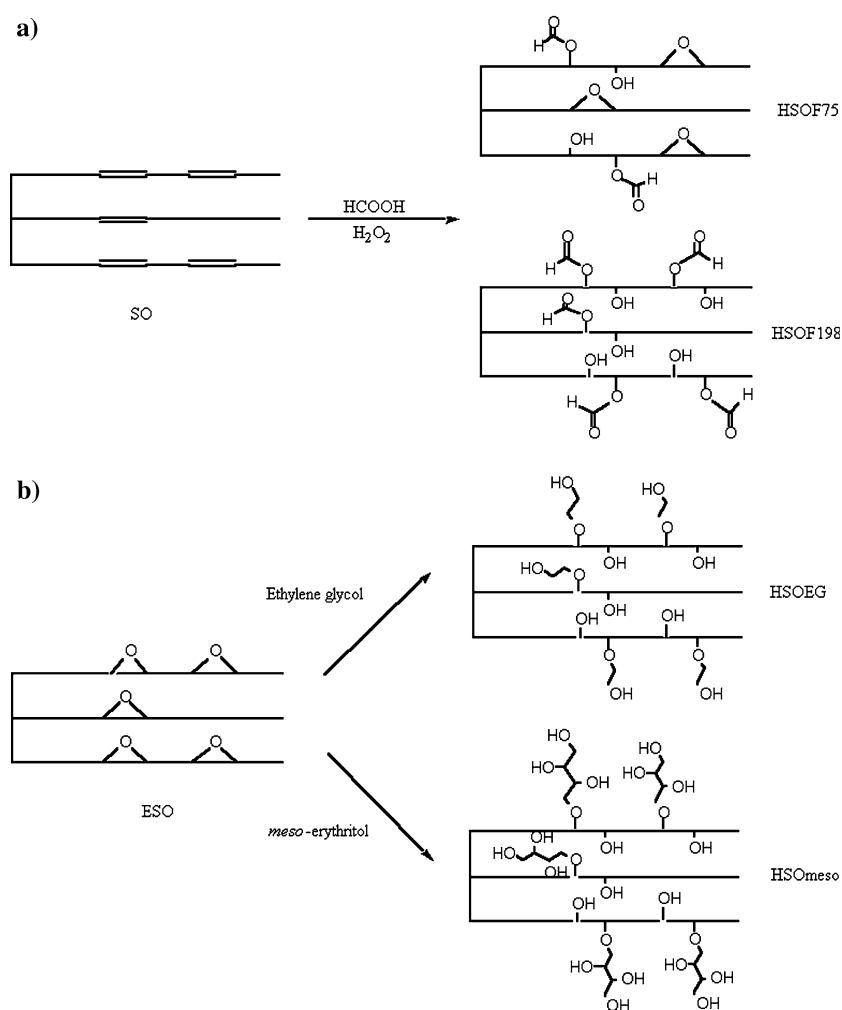
Results and Discussions

In this work four different HSO were synthesized and characterized prior to being used in the preparation of hybrids films. HSOF198 was obtained from refined soybean oil in a one-pot reaction with $\text{H}_2\text{O}_2/\text{HCOOH}$, resulting in a fully formiated soy polyol with an OH value of 198 mg KOH/g. HSOF75 was also prepared from soybean oil following the same conditions described previously but with a shorter reaction time, producing a formiated epoxy soy polyol with an OH value of 75 mg of KOH/g. HSOEG and HSOmeso were prepared by the reaction of epoxidized soybean oil (ESO) with ethylene glycol and *meso*-erythritol, respectively, in the presence of sulfuric acid. These two last reactions were carried out in such conditions that all epoxy rings were opened, resulting in products with OH values of 188 and 169 mg KOH/g, respectively. The four functionalized HSO synthesized have different functionalities, HSOF198 presents only secondary

–OH groups, HSOF75 shows epoxy and secondary –OH groups, while HSOEG and HSOmeso present primary and secondary –OH groups. Figure 1 presents the schematic chemical structures of these HSO.

It is important to point out that hydroxylated vegetable oils have an inhomogeneous distribution of OH groups because the triacylglycerol (TAG) molecules are composed of different saturated and unsaturated fatty acids. Therefore, the OH value determined for each sample is an average distribution of the OH groups present in the TAG. This inhomogeneous distribution contributes to the different properties and characteristics of the vegetable polyols compared with petrochemical ones. The occurrence of etherification reaction is another factor that can be responsible for the inhomogeneous distribution of the OH groups in HSO, due to the formation of intra- or intermolecular ether groups. As a result of the occurrence of this reaction, a sharp increase in the viscosity and a decrease of the number of OH groups are expected.

Fig. 1 Schematic reactions for the preparation of hydroxylated soybean oil: **a** from soybean oil hydroxylated with formic acid/hydrogen peroxide (HSOF75 and HSOF198) and **b** from epoxidized soybean oil hydroxylated with ethylene glycol/sulfuric acid (HSOEG) and with *meso*-erythritol/sulfuric acid (HSOmeso)



HSOEG and HSOMeso present OH values much lower than the theoretical values as well as higher viscosities, therefore it is acceptable to presume that intra and/or intermolecular etherification has occurred [17].

For the four HSO organic precursors, the ^1H NMR spectra were not useful to quantitate the amount of hydroxyl groups in the HSO precursors since the hydrogen bonded to the carbon of the alcohol group was masked by other signals. APT spectra were therefore obtained and are presented in Fig. 2.

In all spectra, the presence of signals at 62.0 and 68.4 ppm were assigned to the carbons of the glycerol group of the TAG. Also, the disappearance of the signals at 54.1 and 56.6 ppm of the carbon epoxy group region, except for the HSOF75, demonstrates that the epoxy ring opening reaction was complete. In the HSOF75 and HSOF198 spectra the negative signals in the 70–85 ppm region were assigned to the secondary alcoholic carbon, $-\text{CH}-\text{OH}$. In the HSOEG and HSOMeso spectra, besides the signals of the secondary alcoholic carbons, there are positive signals in the 60–70 ppm region, which were assigned to the primary carbon of $-\text{CH}_2-\text{OH}$ and/or to ether groups, $-\text{CH}_2-\text{O}-\text{CH}_2-$.

Hybrid films were prepared from the different HSOs and TEOS. Also, a hybrid film from ESO and TEOS was prepared adding the Lewis acid $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to the reaction. The purpose of the preparation of this film

was to promote an in situ opening of the epoxy groups and compare its final properties with those of the previously formed HSO/TEOS films. All the organic–inorganic hybrid films obtained were yellow, transparent and macroscopically homogeneous.

The swelling coefficients found for the organic–inorganic films are shown in Table 1. It is evident that, the higher the OH value, the lower the swelling coefficient. The lowest swelling coefficient was obtained for the system HSOF198, which presents the highest OH value, and therefore has formed a more closed network.

The HSOF198/TEOS and HSOEG/TEOS hybrid films presented lower values of extracted mass in hexane, suggesting again the existence of a stronger interaction between the organic and inorganic components when the HSO has a higher OH value.

TGA were carried out to evaluate the stability of the films as well as to infer silicon incorporation. TGA curves for the organic–inorganic films present a residue indicating an effective incorporation of Si. Nevertheless, sometimes they were not white, suggesting that they were not transformed into pure silica as expected, but probably into an amorphous silicon oxycarbide structure built by a random array of silicon oxycarbide units $\text{SiC}_x\text{O}_{4-x}$, with $0 \leq x \leq 4$ [21].

All of the organic–inorganic films presented excellent adhesion to metal surfaces, as can be observed

Fig. 2 **a** ^{13}C NMR (APT) spectra of the four organic precursors obtained for soybean oil hydroxylated with formic acid/hydrogen peroxide (HSOF75 and HSOF198), epoxidized soybean oil hydroxylated with ethylene glycol/sulfuric acid (HSOEG) and with *meso*-erythritol/sulfuric acid (HSOMeso). **b** The presence of primary and secondary $-\text{OH}$ groups can be better seen in the 60–80 ppm expanded region

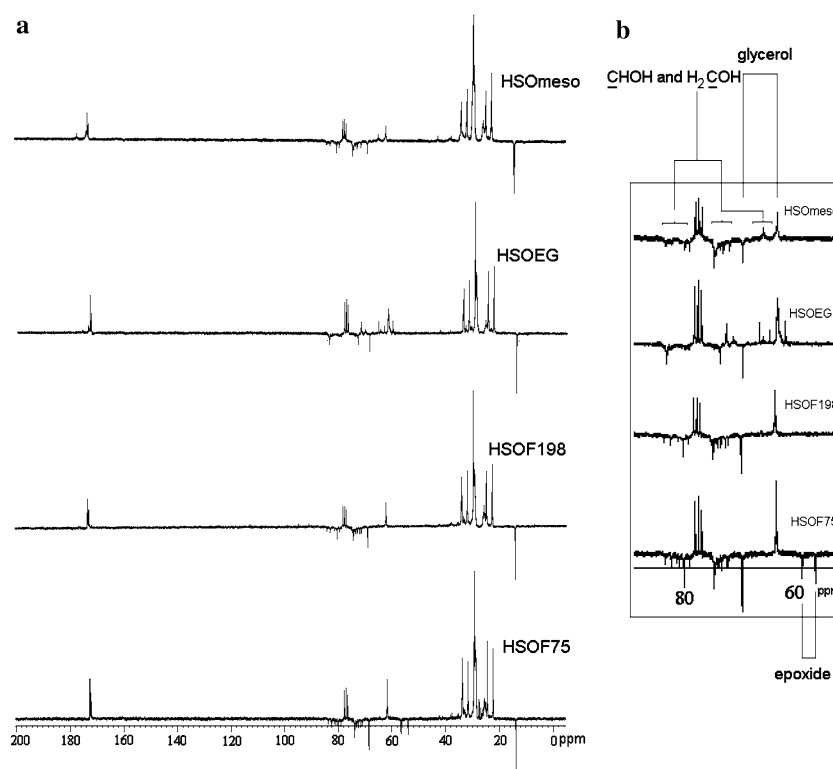


Table 1 Characterization of hybrid films

Hybrid films ^a	OH value (mg of KOH/g)	Swelling coefficient (g/g)	Extracted mass (%)	Adhesion	Pencil hardness	EDX (%Si)
HSOF75	75	2.8	15	5B	3B	2.2
HSOF198	198	1.3	9	5B	HB	7.3
HSOEG	188	1.9	9	5B	HB	2.8
HSOmeso	169	1.8	11	5B	HB	1.5
HSO–BF ₃	–	1.7	12	5B	5H	7.3

^a Hybrid films formed of HSO (hydroxylated soybean oil) and TEOS (tetraethylorthosilicate) with a mass ratio of HSO to TEOS of 90:10. For abbreviations see [Materials and Methods](#)

from the results of the crosshatch adhesion presented in Table 1, where 5B means 100% adhesion.

The property that varied the most as a function of the nature of the HSO used was the hardness, as observed in the results of the pencil hardness test presented in Table 1.

Morphologic characterization was carried out by SEM analysis of the micrography of the fractures of the films. Figure 3 shows an SEM image of the HSO/TEOS films. It can be observed that, even though some films present distinct fracture patterns, most of them are microscopically homogeneous for the amount of inorganic precursor studied and the observed magnifications.

SEM–EDX analysis was also performed to study the real percentage of TEOS incorporated into the systems. The EDX results are also presented in Table 1, as mass percentage of silicon. It can be observed that the films prepared from HSOF198 and HSO–BF₃ were the ones that incorporated the highest proportion of the inorganic precursor.

Figure 4 is a typical SEM analysis of a film prepared from the fully hydroxylated soybean oil and TEOS (HSOF198/TEOS), and shows the SEM image of a fracture of the film as well as the energy-dispersive spectra for the indicated region. The EDX spectrum shows the presence of carbon, oxygen and silicon, and also the element gold that was deposited on the sample surface for the film analysis. The elements proportion is used for determination of the semiquantitative composition of the sample (except the gold that is present in the sample's surface but that is not considered for the calculation of the sample composition), as can be seen in Table 1. The presence of silicon can be observed, confirming the effective incorporation of the inorganic precursor to the system.

It can be concluded that it is possible to prepare macroscopically homogeneous HSO(90%)/TEOS(10%) films. Based on our results, their properties vary with the type of HSO employed. They seem to be more strongly influenced by the amount of OH groups than by the available functionality (epoxide, primary and

Fig. 3 SEM images of the films prepared from the inorganic precursor TEOS and different hydroxylated soybean oils: **a** HSOF75 soybean oil partially hydroxylated with formic acid/hydrogen peroxide; **b** HSOmeso epoxidized soybean oil hydroxylated with meso-erythritol/sulfuric acid; **c** HSO–BF₃ epoxidized soybean oil hydroxylated in situ with BF₃·Et₂O; and **d** HSOEG epoxidized soybean oil hydroxylated with ethylene glycol/sulfuric acid

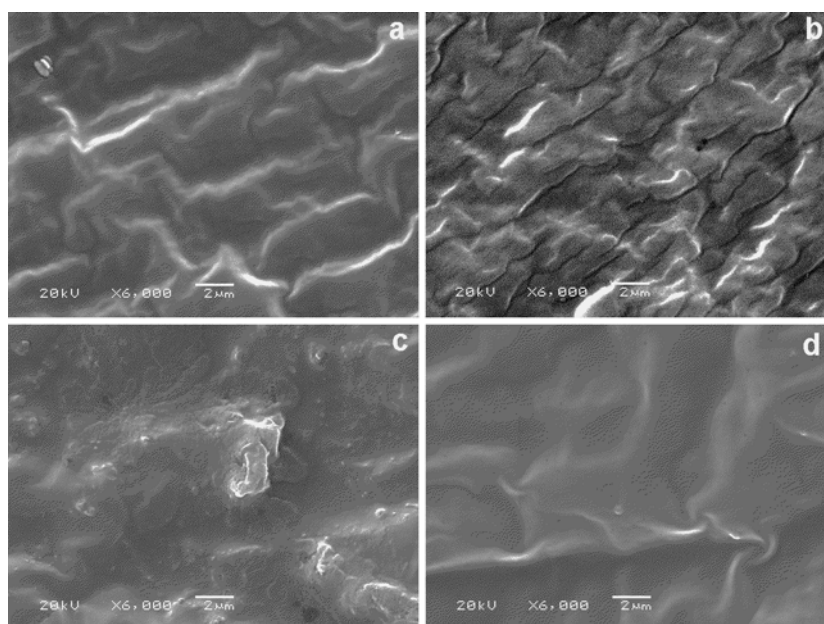
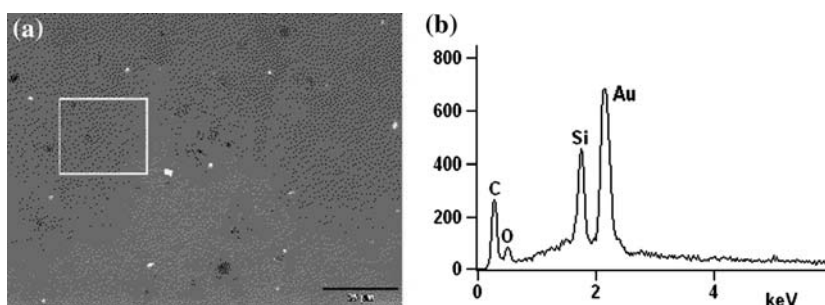


Fig. 4 Scanning electron microscopy analysis of a film prepared from a fully hydroxylated soybean oil (HSOF198) and TEOS: **a** SEM image of a fracture of the film and **b** energy-dispersive spectra for the indicated region



secondary OH groups). The best hybrid system was the HSOF198/TEOS, which has a lower swelling coefficient, very good adhesion on aluminium surface and good hardness. These properties can be attributed to an effective incorporation of silicon.

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