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ORIGINAL PAPER

Organic–Inorganic Coatings Based on Epoxidised Castor Oil/APTES/TEOS

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Abstract Two series of organic–inorganic hybrid films were prepared from epoxidised castor oil (ECO) and the inorganic precursor 3-aminopropyltriethoxysilane (APTES), and the combination of APTES with tetraethoxysilane (TEOS) with different organic to inorganic proportions. Films were pre-cured at room temperature under inert atmosphere and subsequently submitted to thermal curing. The macro- and microscopic properties of the films, including adhesion, hardness, microstructure and thermal properties, were determined as a function of the proportion of ECO to inorganic precursors. Morphologic studies showed that the hybrid films were microscopically homogeneous. The hardness and tensile strength of the films increased with increased concentrations of inorganic precursor. All of the films exhibited good adhesion to an aluminium surface and worked as an efficient barrier against corrosion.

Keywords Coating · Organic–inorganic hybrids · APTES · Castor oil · TEOS

Introduction

New coating materials have been intensively studied to substitute the traditional metal chromium-based coatings in order to avoid the contact with toxic hexavalent chromium compounds generated in those processes, which can cause severe environmental pollution [1]. Among them, the vegetable oil coatings have been suggested, since they are green materials produced from renewable sources and present excellent adhesion to the metallic surfaces [2]. However, oil coatings alone do not present adequate hardness, affecting their coating properties. The combination of vegetable oils with hard inorganic materials improves this property as well as other characteristics, such as the mechanical resistance, among others. This is attained through the sol–gel process of inorganic precursors which polymerise into the oil systems, at mild temperature conditions, through diverse types of interaction, producing new hybrid or nanocomposite materials [3–10].

Castor oil has been considered as a special commodity for the chemical industry, since its unusual composition contains almost 90% of ricinoleic acid. Its highly hydroxylated content moiety (12-hydroxy-9-octadecenoic acid) characterises this oil as the only commercially available source of natural hydroxylated triglycerides. Its singular composition makes it interesting for the coating industry, despite its non-drying properties [11]. The hydroxyl functionality is considered to be the main property that accounts for the use of castor oil in coatings. Also, this functional group imparts high viscosity, stability and miscibility to polar solvents such as alcohols. The presence of one carbon–carbon double-bond on the fatty acids allows other modifications that can further enhance the versatility of castor oil to other applications. Among these processes, dehydration followed by conjugation, epoxidation and

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hydroxylation are the most important ones for polymerisation and, thus, for their use as the organic precursor of hybrid films.

Typical inorganic precursors containing silicon includes tetraethoxysilane (TEOS), the simplest one. However, it is also possible to prepare hybrid compositions using bifunctional or trifunctional silane $R'Si(OC_2H_5)_3$, in which the R′ groups are non-reactive during hydrolysis. Such reagents allow the carrying of some organic functionality over into the ceramic-like phase, possibly to endow this phase with some flexibility [12]. The 3-aminopropyltriethoxysilane (APTES) is a particularly interesting bifunctional silane due to its additional amine functionality. This alkoxide can form a silicon oxide three-dimensional network in which there is the possibility of bonding through the Si–OH and the NH_2 end groups. Due to this functionality, APTES has been used in organic–inorganic hybrid synthesis, contributing to the siloxane network and also working as a coupling agent to some other inorganic precursors [13].

Previous work [10] has shown that epoxidised castor oil (ECO) present better interaction with TEOS than castor oil itself. However, it is also widely known that epoxy groups react with primary amines; therefore, the addition of APTES to the ECO/TEOS system will present additional bonding sites between the organic and inorganic precursors and, consequently, the films will have distinct properties.

The objectives of the present study were to develop organic–inorganic hybrid films based on ECO/APTES and ECO/APTES/TEOS and to investigate the properties of such films after thermal curing over aluminium and Teflon.

Experimental Procedures

Materials

Glacial acetic acid and toluene used in this study were obtained from Nuclear (Diadema, São Paulo, Brazil). APTES, TEOS and dibutyltindilaurate were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and used without any further purification. Castor oil (medicinal grade) was obtained from Importadora Química Delaware Ltda (Porto Alegre, Rio Grande do Sul, Brazil).

ECO Characterisation

ECO was synthesised from castor oil using a modified procedure [14]. Hydrogen peroxide (30%, 45 mL) was added to a solution of sulphuric (1.7 mL) and glacial acetic (290 mL) acids. The mixture was maintained for 20 h at room temperature in the dark. The preformed peracetic acid solution was neutralised with sodium acetate and added dropwise over a period of 30 min to medicinal castor oil (200 g) maintained at temperatures below 25 °C and stirred continuously. As soon as the addition process ended, the reaction mixture was heated to 50 °C and stirred over four extra hours. The product was washed with deionised water and neutralised with 10% w/w aqueous sodium bicarbonate and dried over sodium sulphate. The ECO was characterised quantitatively by chemical analysis and ^{1}H-NMR spectroscopy [15].

Preparation of Films and Coating of Plates: ECO/APTES

ECO was mixed with an amount of APTES calculated to react with 10, 20, 50, 70 and 100% of the epoxy groups present in the oil (i.e. APTES: 10, 20, 50, 70 and 100%), under inert atmosphere. The mixture was vigorously stirred for 3 h at 80 °C and, thereafter, one drop of the catalyst dibutyltindilaurate and also one drop of water were added to the system, which was kept under stirring for one more hour.

The reaction mixtures were applied to aluminium plates (10 cm × 10 cm) using a 3.0-mil applicator in order to produce thin films, for adhesion, hardness and corrosion tests, or hand-poured over Teflon plates (10 cm × 10 cm) to produce thick films that could be removed from the substrate, after curing, for microscopic observation, thermal analysis and determination of the degree of swelling. Prior to curing, films were maintained under inert atmosphere at room temperature for 72 h. Films applied to Teflon were cured at 75 °C for 24 or 48 h, while those applied to aluminium were cured at 60 °C for 1 h, followed by 1 h at 130 °C, 1 h at 180 °C and 1 h at 230 °C. They were cured under different thermal and timing conditions due to the nature of the supports.

The films were named indicating the amount of APTES calculated to react with a specified percentage of epoxy groups. For instance, a film prepared from ECO and APTES calculated to react with 20% of the epoxy rings is called ECO + APTES:20%.

ECO/APTES/TEOS

ECO was mixed with an amount of APTES calculated to react with 50% of the epoxy groups present in the oil (i.e. APTES:50%), under inert atmosphere. The mixture was vigorously stirred for 3 h at 80 °C, after which the heat was turned off, TEOS was added dropwise in the mass proportions of ECO/TEOS of 100/0, 95/05, 85/15, 80/20, 75/25 or 70/30, followed by the dibutyltindilaurate catalyst and the system was kept under stirring for one more hour.

The reaction mixtures were applied to aluminium plates or hand-poured over Teflon plates, as described above, and maintained for pre-cure as well. The films on aluminium were cured the same way, whereas the Teflon plate films were cured for 24 or 48 h at 160 °C.

The films were named using the amount of APTES calculated to react with the epoxy groups following its symbol and the mass proportions of TEOS were also indicated. For instance, a film prepared from ECO and APTES calculated to react with 50% of the epoxy rings and TEOS 10% in mass proportion is called ECO + APTES:50% + 10%TEOS.

Synthesis Monitoring

Selected aliquots were extracted during the synthesis of the films for monitoring the reaction by ^{1}H NMR at 300 MHz (Varian Inova, Palo Alto, CA, USA) in $CDCl_3$ as the solvent and with tetramethylsilane (TMS) as the standard.

Infrared Spectra

Infrared spectra (FTIR-ATR) of the cured films were measured on a Shimadzu (Tokyo, Japan) FT-IR 8300 spectrometer with a horizontal attenuated total reflectance (HATR) adapter and a ZnSe crystal. Spectra were recorded in the range 4,000–400 cm^{-1} with 32 scans and a resolution of 4 cm^{-1}.

Thermogravimetric Analyses

Thermogravimetric analyses were performed using a TA Instruments (New Castle, DE, USA) model TGA 2050 analyser with a heat flow of 20 °C/min in the temperature range 25–600 °C under nitrogen and up to 1,000 °C under an oxidative atmosphere.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was carried out under nitrogen in hermetic capsules using a DuPont (Wilmington, DE, USA) model DSC 2910 instrument in the temperature range −120 to 150 °C at a heating rate of 20 °C/min.

Scanning Electron Microscopy

The morphologies of the cryogenically fractured samples were examined by scanning electron microscopic (SEM) analyses of the gold-coated surfaces using a JEOL (Tokyo, Japan) model JSM 6060 microscope. Energy-dispersive X-ray (EDX) analyses were performed on a JEOL model JSM 5800 instrument.

Determination of the Degree of Swelling

Swelling was determined by soaking a pre-weighed film sample in toluene, maintained in a thermostatic bath at 30 °C for at least 48 h and recording the weight gain. The degree of swelling was determined from Eq. 1:

$$Q = \left(\frac{m - m_0}{m_0}\right) \tag{1}$$

where m_0 is the initial mass and m is the final mass of the film.

Mechanical Properties

Measurements of stress/strain were performed with the aid of an EMIC (São Paulo, SP, Brazil) DL 10000 universal testing machine on samples with dimensions ca. 30 mm × 10 mm × 0.5 mm by applying a cross-head speed of 2 mm/min and a tension of 20 N.

Adhesion

The adhesion of a film applied to an aluminium surface was evaluated using the standard ASTM D-3359-95a cross-hatch tape adhesion test [16].

Hardness

The hardness of a film applied to an aluminium surface was evaluated using the standard ASTM D-3363-92a pencil test [17].

Salt Spray Test

The corrosion resistance standard test [18], usually referred to as “salt spray” testing, was applied to the ECO/APTES/TEOS series, using a model USC salt spray camera BASS Ltda, to evaluate the effect of the addition of inorganic precursor to the resistance of the material exposed to corrosive ambient. For this, three films of each type applied to aluminium plates were submitted to an NaCl 0.5% fog in a closed chamber. The samples were taken out from the spray test chamber after 740 h and were evaluated visually.

Results and Discussion

The starting material, castor oil (CO), was characterised by ^{1}H-NMR spectroscopy (Fig. 1) before the epoxidation reaction. The spectrum shows a multiplet associated with the $–\underline{H}C{=}C\underline{H}–$ of the unsaturated fatty acid chain at ca. 5.2–5.6 ppm, together with the overlap of resonance of the $–C\underline{H}$ group from the glycerol, while those assigned to the

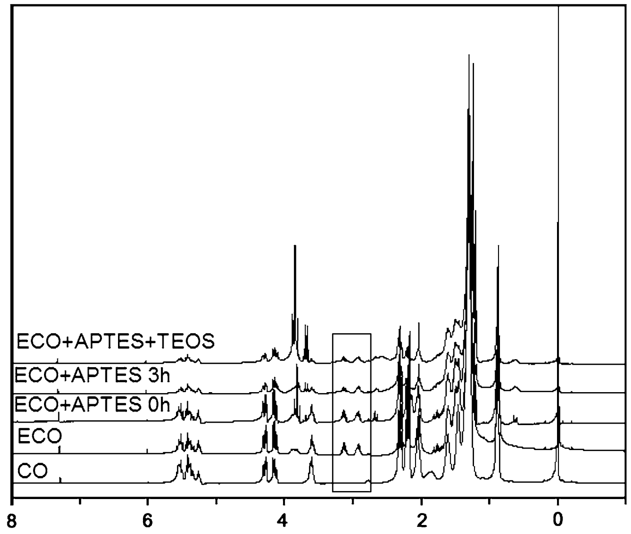

Fig. 1 ^{1}H NMR monitoring for castor oil epoxidation, ECO + APTES:50% and ECO + APTES:50% + 20%TEOS reactions

–CH_2 groups of glycerol are presented as a multiplet at the 4.0–4.3 ppm region. The resonance for –C($\underline{H}$) on carbon 12 of ricinoleic acid, which already contains a hydroxyl group, appears at 3.6 ppm, whilst the others are the resonances characteristic of the –CH_2 groups and the terminal –CH_3 of carbon backbone of ricinoleic fatty acid [7]. The ^{1}H-NMR spectrum of ECO (Fig. 1) shows the new resonances of the hydrogen bonded to the epoxidised ring carbons at the 2.8–3.2 ppm region, delimitated by the rectangle, and the partial disappearance of the vinylic hydrogens centred at 5.4 ppm. Quantitative NMR analysis of the epoxidised product showed that 40% of the –C=C– bonds have been converted into epoxy group. From the spectrum, it is also possible to identify some epoxy ring opening products due to secondary reaction (3.8 ppm).

Figure 1 also represents an attempt to follow each step of the reactions for the hybrid film formation before the gelation takes place. When APTES is added in a concentration calculated to compromise 50% of the epoxy groups of ECO, two NMR spectra were recorded. The first one—ECO + APTES (0 h)—was recorded immediately after the addition, in which some of the signals of free APTES can be identified at 3.8 ppm and 1.2 ppm for the –Si–(OC$\underline{H}_2$–C$\underline{H}_3$), respectively, as well as the signals at 2.6, 1.6 and 0.5 ppm (all of them overlapped) for H_2N–C$\underline{H}_2$–C$\underline{H}_2$–C$\underline{H}_2$–Si–, respectively. The spectrum recorded after 3 h of reaction—ECO + APTES (3 h)—showed that the multiplet at 3.8 ppm is missing due to the hydrolysis of APTES, leading to ethanol formation (whose only observable signal is at 1.2 ppm, corresponding to $\underline{H}_3$C–CH_2–OH). The C$\underline{H}_2$ groups of H_2N–C$\underline{H}_2$–C$\underline{H}_2$–C$\underline{H}_2$–Si–, which still appear in the spectrum as well as the decrease in the intensity of the epoxide signal at 2.8–3.2, suggest that the APTES is bonded to ECO through its epoxy groups. It can be inferred from the calculations concerning this spectrum that only 22% of the epoxy groups remain intact in ECO. This number is close to the 50% of APTES added in the reaction. It is normal at this time that the NMR spectrum of the reaction mixture becomes quite complex; nevertheless, it has been demonstrated to be a fine technique to follow and calculate the transformations occurring during the reaction between ECO and APTES.

With the addition of 20% of TEOS to the reaction mixture (Fig. 1, ECO + APTES + TEOS), the spectrum becomes even more complex. Hydrogen signals due to (C$\underline{H}_3$–C$\underline{H}_2$–O)$_4$Si showed up at 1.2 and 3.8 ppm, respectively. It can be proposed that the TEOS hydrolysis occurs instantaneously, since a multiplet assigned to the –CH_2 from free ethanol appears in the spectrum at 3.7 ppm. With the addition of TEOS, the final network between organic and inorganic precursors takes place.

In a previous work [19], the bond between the H_2N– of APTES with epoxy polymers was proved to occur; similar behaviour is proposed for the reaction between ECO and H_2N– of APTES of the hybrid film, as shown in Fig. 2a. Some of the possibilities for the links in the hybrid film network observed in the ^{1}H NMR spectra are tentatively indicated in Fig. 2b.

The FTIR spectra of the cured films are presented in Fig. 3. The bands of ECO are typically υ_{OH} at 3,467 cm^{-1}, $\upsilon_{\text{assim CH2}}$ at 2,927 cm^{-1}, $\upsilon_{\text{sim CH2}}$ at 2,856 cm^{-1}, $\upsilon_{\text{assim C=O}}$ at 1,737 cm^{-1}, $\delta_{\text{C-H}}$, $\upsilon_{\text{C-H}}$ at 1,456, 1,417, 1,376 cm^{1}, $\upsilon_{\text{assim/simC–O ester}}$ at 1,240/1,096 cm^{-1}, $\upsilon_{\text{assimC–O–C ester}}$ at 1,162 cm^{-1}, $\upsilon_{\text{C-H2}}$ at 726 cm^{-1} and $\upsilon_{\text{epoxy ring}}$ broad and weak band at ca. 830 cm^{-1}. With the initial addition of APTES to react with 50% of the epoxy groups of ECO to give the hybrid film ECO + APTES:50%, the spectrum shows a decrease in intensity of the epoxy ring band (~830 cm^{-1}) and, clearly, a modification of the band at 1,055 cm^{-1} due to Si–O–Si and Si–O–C formation. This band becomes larger than the band at 1,162 cm^{-1}, which is assigned to the asymmetric stretching of the C–O ester of ECO. As TEOS is added to reach the hybrid composition ECO + APTES:50% + 30%TEOS, this band increases even more as a result of a silica network. Concerning APTES, which is present in small concentrations, –NH mode bands (at 3,400–3,300 cm^{-1} and at 1,580–1,650 cm^{-1}) are probably concealed by the ECO bands of the hybrid films' spectra and due to the covalent bond formation between the epoxy groups from ECO and the NH of APTES. We believe that the presence of the OH groups of ECO is important not only for the organic/inorganic bonds (even though they alone are not enough for the hybrid formation [10]) but also for the cure reaction. However, following the IR band (at ~3,500 cm^{-1}) behaviour does not seem to be useful due to the Si–OH formation. Comparing these spectra with the ones of ECO/TEOS alone [10], it is observable that the curves are very similar, indicating that

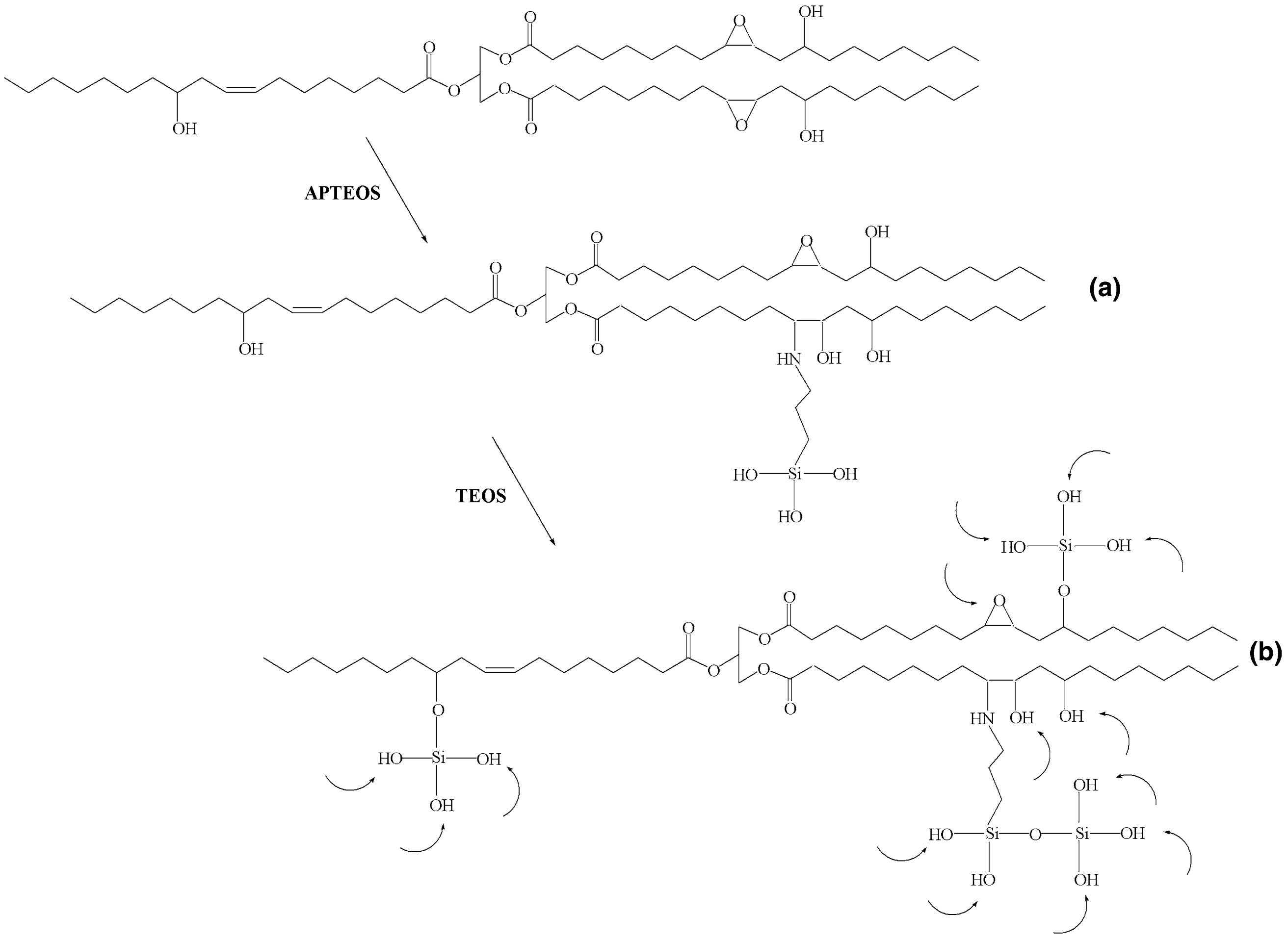

Fig. 2 Scheme of the ECO/APTES/TEOS reaction

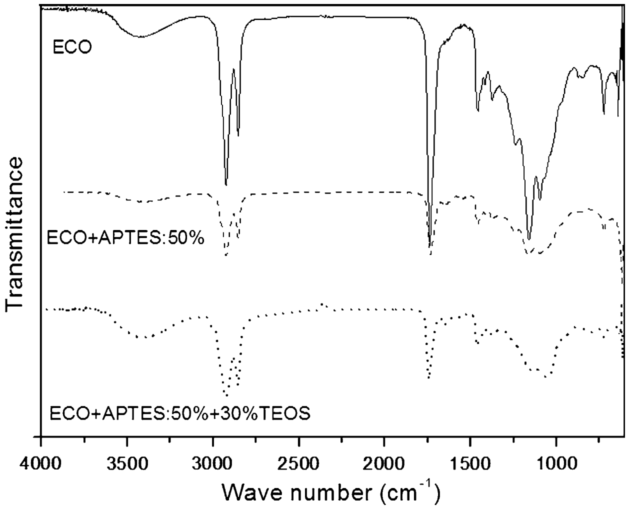

Fig. 3 FTIR spectra of ECO, ECO + APTES:50% and ECO + APTES:50% + 30%TEOS films

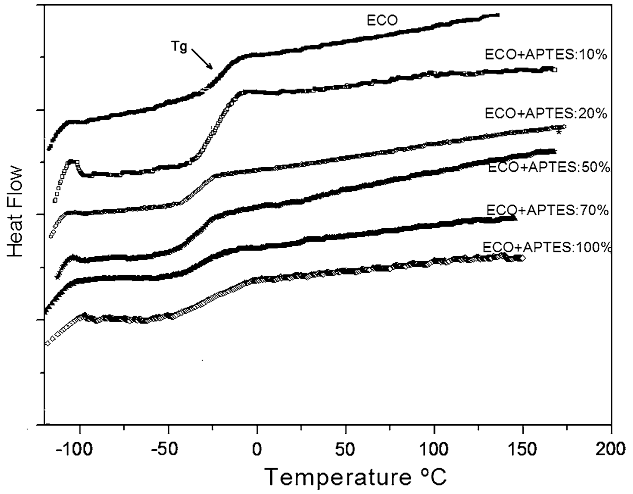

Fig. 4 DSC traces for ECO and ECO + APTES films

the IR is not sensitive enough to show the addition of APTES. The main changes are only due to the silicon network moiety.

The films so produced were yellow, as usual for thermally cured oil films, and transparent, indicating that there was no observable macroscopic phase separation.

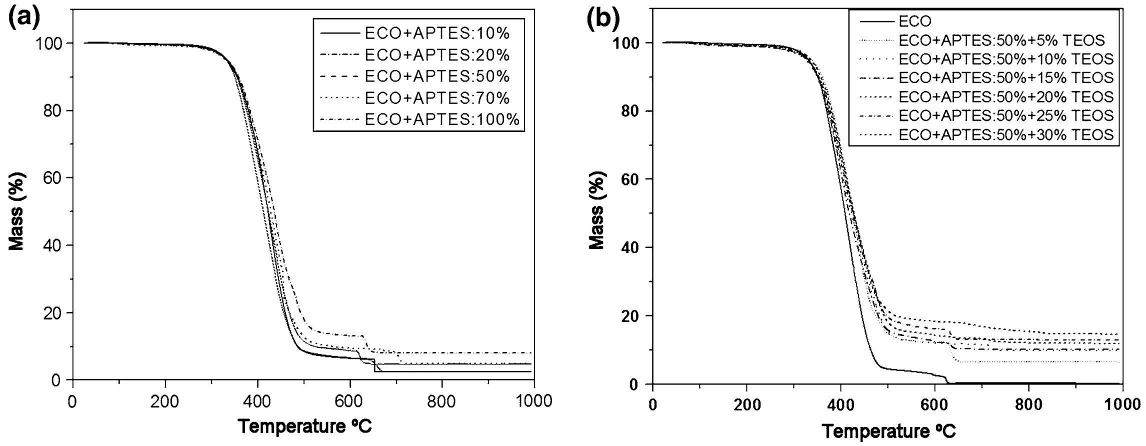

Fig. 5 Thermogravimetric curves for: **a** ECO + APTES 0–100%, **b** ECO + APTES:50% + 5–30%TEOS

DSC traces recorded between −120 and 150 °C for the ECO film as well as for those of the hybrids showed only one transition attributable to a Tg of the studied material. The traces for the ECO and ECO + APTES series are shown in Fig. 4. It appears that APTES can induce an increase in the flexibility of the chain, which can be ascribed to the propyl group attached to one of the Si arms. The Tg determined for ECO + APTES:50% + 30%TEOS is identical to that of the film without TEOS (ca. −31 °C), indicating that it is APTES which is responsible for the change in the chain flexibility.

Thermogravimetric analysis was carried out in order to estimate the stability of the hybrid films and the incorporated inorganic fraction. Figure 5a displays typical thermogravimetric curves for the ECO + APTES series, whereas Fig. 5b presents the ECO + APTES:50% + 5–30%TEOS series, together with the ECO film, in which the decrease in mass observed at ca. 600 °C corresponds to the change in gas from nitrogen to air. It can be observed that the presence of the APTES in the hybrid films did not present additional thermal stability when compared to the ECO/TEOS system previously studied.

Analysis of the thermogravimetric residues produced by the different films when heated to 900 °C (Table 1) confirmed that the amount of inorganic component effectively incorporated into the films increased with the concentration of inorganic precursor employed.

The TGA residues were usually white and the measured masses were very close to the expected values (see Table 1), signifying complete combustion of the oil and total conversion of APTES and TEOS into SiO_2. The more pronounced differences between expected and real residual masses occurred for the ECO/APTES/TEOS systems, suggesting that they were not transformed completely into pure silica as expected, but probably into amorphous silicon oxycarbide units SiC_xO_{4-x} with $0 \leq x \leq 4$ [20], which are already found in hybrid materials prepared from vegetable oil and TEOS [9].

Table 1 Theoretical and experimental percentages of silica residues produced by hybrid films subjected to TGA at 900 °C

Film composition	Expected TGA residue (%)	TGA residue (%)
ECO	0	0.07
ECO + APTES:10%	1.30	2.41
ECO + APTES:20%	2.60	2.42
ECO + APTES:50%	3.81	4.74
ECO + APTES:70%	4.85	4.97
ECO + APTES:100%	5.75	7.99
ECO + APTES:50% + 5%TEOS	4.49	6.42
ECO + APTES:50% + 10%TEOS	5.64	9.70
ECO + APTES:50% + 15%TEOS	6.79	10.11
ECO + APTES:50% + 20%TEOS	7.94	11.82
ECO + APTES:50% + 25%TEOS	9.11	12.84
ECO + APTES:50% + 30%TEOS	10.30	14.57

The morphologic characterisation of the films was obtained by SEM analyses. Micrographs of fractures of films containing ECO + APTES:10% and ECO + APTES:70% (Fig. 6a, b), as well as ECO + APTES:50% + 10%TEOS and ECO + APTES:50% + 25%TEOS (Fig. 6c, d) show that, even though white marks caused by the fracture are present in the images, it is possible to observe the microscopic homogeneity of the films with lower inorganic precursor content at the magnifications employed.

The EDX spectrum was also obtained for the hybrid films. The presence of carbon, oxygen and silicon, together with the elemental gold that was deposited on the sample surface during analysis, is revealed in the EDX in the same way as presented for ECO/TEOS [10], which (disregarding gold) could be used to determine the semi-quantitative composition of the sample. The presence of silicon

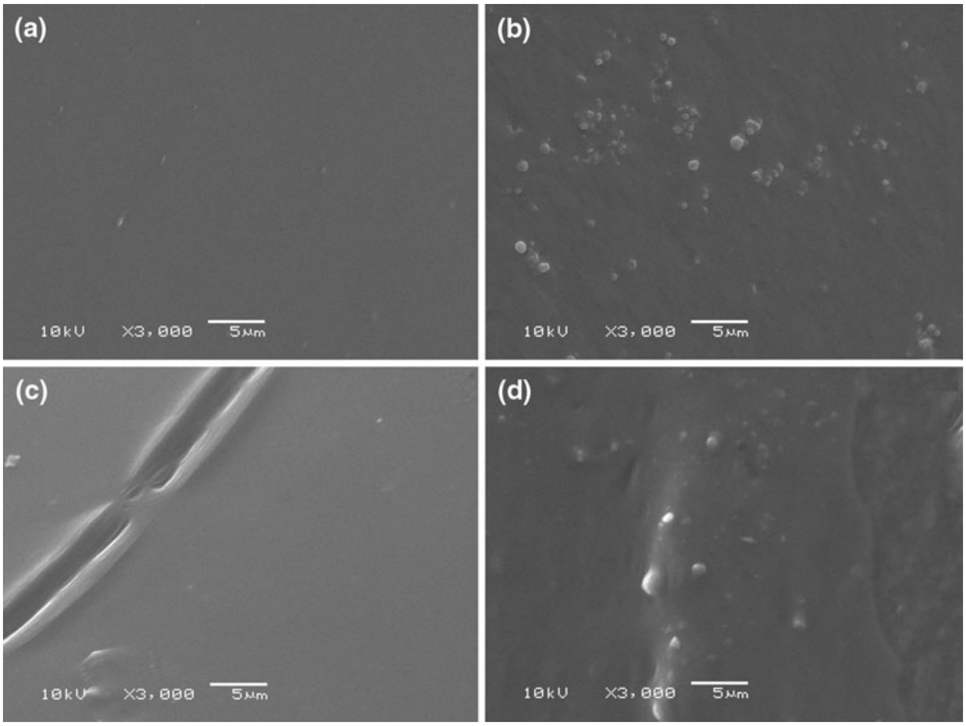

Fig. 6 Micrographs of fractures of films containing ECO + APTES:10% and ECO + APTES:70% (**a**, **b**) and ECO + APTES:50% + 10%TEOS and ECO + APTES:50% + 25%TEOS (**c**, **d**)

confirms the effective incorporation of inorganic precursor in the films.

All of the films exhibited significant swelling in toluene. The addition of inorganic precursors typically decreased the degree of swelling, indicating the formation of more closed networks, as observed also previously with the ECO/TEOS system [10]. It can be observed (Fig. 7) that, for the ECO + APTES series, the swelling degree decreases slightly, probably because of the effect of the APTES, whereas for the ECO + APTES:50% + TEOS series, the tendency curve shows a very abrupt decrease to a lower value, which remains along the hybrid series. This is expected because the concentration of inorganic precursor increases drastically with the TEOS addition, since its concentration is referred to the mass percentage, and this is a much higher value than the amount calculated to react with the oxirane rings (as it has been done for APTES) of such a big molecule as castor oil.

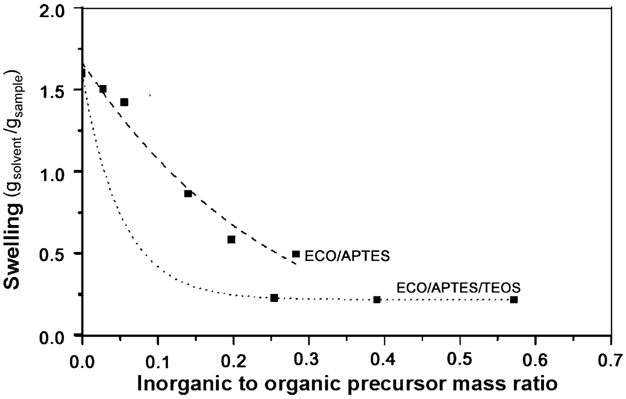

Fig. 7 Swelling index in toluene versus inorganic precursor to organic precursor mass ratio for the hybrid films series

All of the organic–inorganic films presented excellent adhesion to metal surfaces, as indicated by the value of 5B (equivalent to 100% adhesion) recorded in the cross-hatch adhesion tests, as presented in Table 2. With respect to

Table 2 Adhesion and hardness

Content of APTES/TEOS[a]	Adhesion[b]	Hardness[c]
ECO	5B	2B
ECO + APTES:10%	5B	3H
ECO + APTES:20%	5B	3H
ECO + APTES:50%	5B	HB
ECO + APTES:70%	5B	HB
ECO + APTES:100%	5B	HB
ECO + APTES:50% + 10%TEOS	5B	H
ECO + APTES:50% + 20%TEOS	5B	H
ECO + APTES:50% + 30%TEOS	5B	2H

[a] The amount of APTES employed was that calculated to react with 0, 25, 50 or 75% of the epoxy groups present in the oil; for TEOS the amount shown is the mass proportion (%) relative to ECO

[b] ASTM D-3359-09e2

[c] ASTM D-3363-05

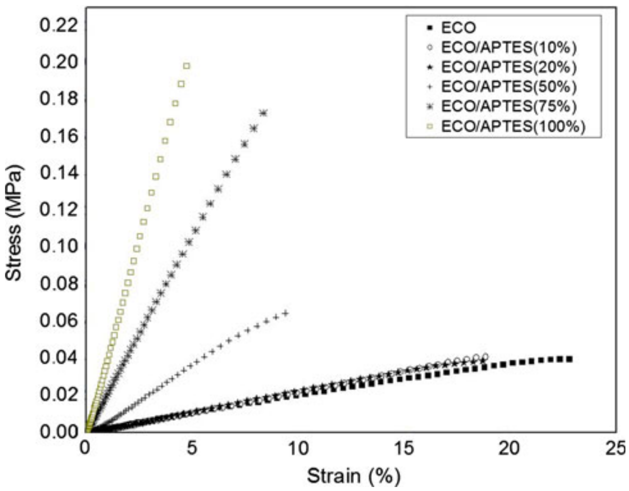

Fig. 8 Stress versus strain for ECO/APTES series

hardness, the cured ECO film presented a pencil scratch hardness of 2B (on the softness to hardness scale from 6B to 6H). Following the addition of APTES, the hardness presented by the films is always higher than the films prepared exclusively from epoxidised oil. Films containing TEOS also showed the tendency for a significant increase in hardness, although it does not scale up with the increasing amount of inorganic precursors. The APTES/TEOS inorganic precursor combination in ECO films improved the hardness of the hybrid films related to the ECO/APTES and ECO/TEOS only.

During the mechanical analysis, it was noted that the hybrid films were very breakable and resisted only small deformations. However, the very small increase in stress necessary to produce the same strain (%) follows the expected order (Fig. 8), that is, as the proportion of APTES increases, there is an increase in stress and a reduction in deformation. Similar behaviour was observed for the series containing ECO + APTES:50% + TEOS.

The hybrid films submitted to the corrosion salt spray test presented excellent protective behaviour. Figure 9 (top) presents images of uncoated aluminium plates before and after 700 h exposition to salt spray solution, whereas Fig. 9 (bottom) presents images of the aluminium plates coated with ECO and ECO/APTES50% + 20%TEOS submitted to the same test. It can be visually observed that the naked metal was severely attacked by the environment. The aluminium plates covered with ECO films presented a few unwanted corrosion points. However, the ones of the ECO/APTES50%/TEOS series are completely protected in the whole, as can be observed in Fig. 9, suggesting that the ECO/APTES/TEOS hybrid films can be used as a barrier for protection against corrosion.

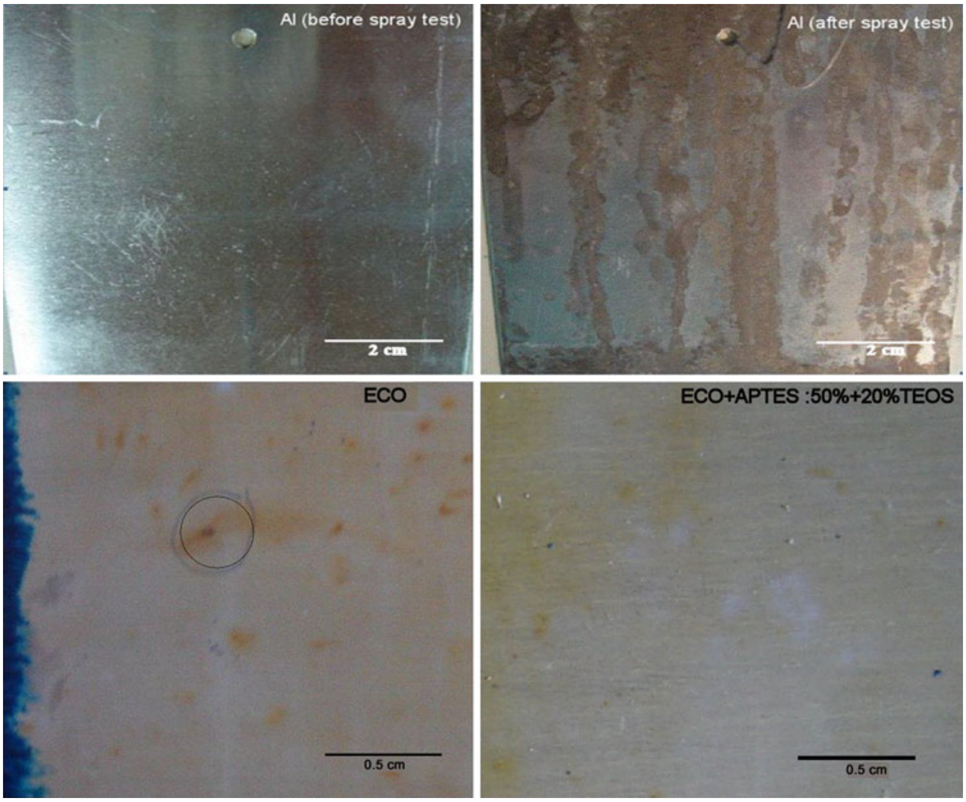

Fig. 9 Image of aluminium plates before and after (*upper images*) submission to corrosive environment and of aluminium plates coated by ECO and ECO + APTES:50% + 20%TEOS (*lower images*) after 700 h of salt spray test

Conclusion

The series of hybrid films containing epoxidised castor oil (ECO) and 3-aminopropyltriethoxysilane (APTES) and APTES + tetraethoxysilane (TEOS) were successfully made using sol–gel methodology, fully characterised and tested for metal coating protection.

The films are all microscopically homogeneous and their properties, such as adhesion and hardness, are enhanced by the APTES content, as well as the addition of the second inorganic precursor, TEOS. The addition of APTES before the TEOS allowed the increase in TEOS concentration of up to 30% relative to the mass of the inorganic precursor.

Corrosion tests by means of the salt spray test showed an excellent performance even after 700 h exposure, demonstrating that these coatings are promising as surface treatment systems, which provide improved protection for aluminium alloys by forming an impenetrable barrier to water and corrosive agents such as chloride and oxygen.

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