Ceramer Coatings from Castor Oil or Epoxidized Castor Oil and Tetraethoxysilane

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ABSTRACT: New inorganic–organic hybrids were synthesized through the reaction of castor oil (CO) or epoxidized castor oil (ECO) with tetraethoxysilane (TEOS). The mass proportions of ECO/TEOS varied from 90:10 to 60:40, and films of the material were thermally cured. An IR spectroscopy analysis was performed, and macro- and microscopic properties such as adhesion, hardness, swelling in toluene, microstructure (scanning electron microscopy), and T_g were investigated as a function of the proportion of their inorganic–organic precursor. Morphologic studies showed that the hybrid films were homogeneous when lower proportions of the inorganic precursors were used. Hardness and tensile strength increased with TEOS concentration, whereas swelling in toluene decreased with TEOS concentration. Good adhesion was observed throughout the hybrid series.

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KEY WORDS: Castor oil, coating, epoxidized castor oil, film, organic–inorganic hybrid, sol-gel, TEOS.

Castor oil (CO) is a versatile vegetable oil because of its unique composition, in which the main component is 12-hydroxy-9-*cis*-octadecenoic acid, the so-called ricinoleic acid, which represents 90% of its FA content. The rich chemistry of raw CO is attributed to its structure (one double C=C and one –OH group per FA chain), which makes it a good starting material for a wide range of applications such as lubricants, coatings, nylon, and organic intermediates for several industries (1). CO can also be converted to a number of derivatives, especially to increase the coating ability (2). In general, one of the most important modifications in vegetable oils is epoxidation (3). Figure 1 shows CO and epoxidized castor oil (ECO) structures. In this derivative, the oxirane groups can be reacted with a variety of compounds or can be used as latent polyols for either improving the drying properties (4) or accelerating the curing process (5). Specifically in the case of CO, its natural hydroxyl functionality can be used straight for cross-linking reactions and, through a dehydration process in which the hydroxyl group can be removed to afford another double bond to the FA chain, by improving its film properties (4). These properties could be further improved by adding inorganic characteristics such as hardness and strength through combination with inorganic precursors.

In the last 20 years, organic–inorganic hybrid materials have been prepared with the goal of combining properties of inorganic and organic materials (6–8). This is preferentially achieved through the sol-gel process, which facilitates the combination of ceramic-like materials with polymers at room temperature. For this reason, the chemical in this process has been designated as Chimie Douce by some authors (9,10). For hybrids based on silica, the reactions involve the hydrolysis and condensation of alkoxide precursors, as shown in Figure 2. The organic components of the hybrid materials are incorporated into the cross-linked sol-gel network, and the resulting hybrid materials are often termed ceramers (11), which comes from a combination of the words *cera*mic and poly*mer*.

For vegetable oil-based ceramers, the literature describes the synthesis of hybrids from linseed (12–15) and sunflower oils (12–14,16) (typical "drying oils"), soybean (17) and blown soybean oils (18), and epoxidized soybean (5) and linseed (5) oils using different sol-gel precursors. Their properties (surface adhesion, flexibility, hardness, and impact resistance) were determinate and varied with the amount of sol-gel precursor, especially their flexibility and rupture tension.

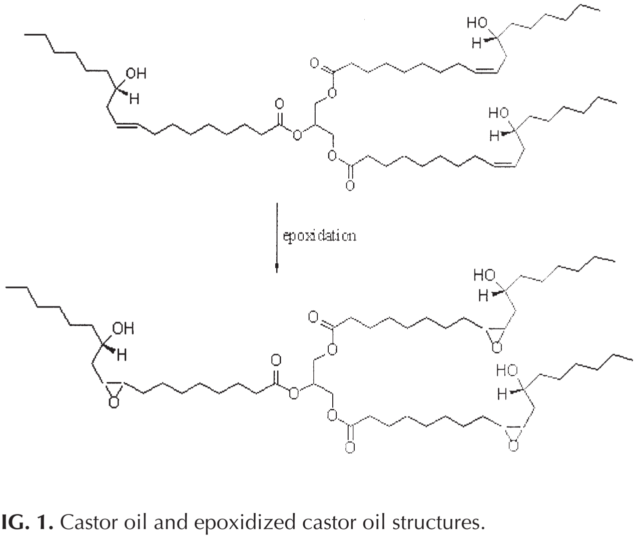

FIG. 1. Castor oil and epoxidized castor oil structures.

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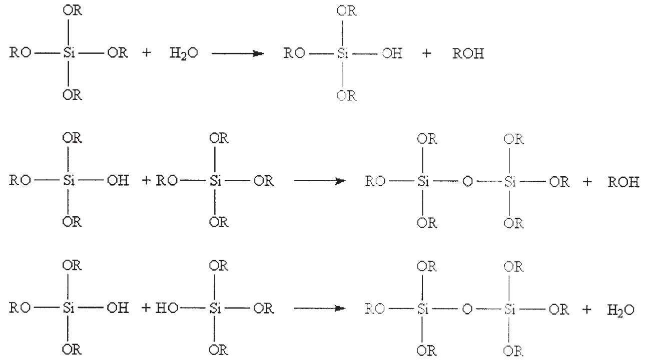

FIG. 2. Schematic representation of the hydrolysis and condensation of an alkoxysilane sol-gel process.

Epoxidized or hydroxylated oils are more reactive than natural vegetable oils and should react more promptly with the sol-gel precursor. In this work, hybrid materials from CO or ECO, both naturally containing OH groups, and the hydrolysis product of tetraethoxysilane (TEOS) were prepared and characterized.

EXPERIMENTAL PROCEDURES

Materials. The formic acid and toluene used in this study were obtained from Nuclear (Diadema, São Paulo, Brazil). TEOS and ethyl alcohol were obtained from Aldrich Chemical (Milwaukee, WI). They were used without any further purification. CO was obtained from Importadora Química Delaware Ltda. (Porto Alegre, Rio Grande do Sul, Brazil). ECO was prepared from CO by following a general process (19) and was quantitatively characterized by chemical analysis (19) and ^{1}H NMR spectroscopy (20), showing 97% conversion.

Film preparation. CO or ECO was acidified to approximately 1.5 pH with formic acid. TEOS was added in the mass proportions of oil/TEOS of 90:10, 80:20, 70:30, and in some cases, 60:40. Water and ethanol were added to the systems in stoichiometric molar proportions of water/TEOS of 2:1 and alcohol/TEOS of 4:1. The hydrolysis of TEOS was carried out *in situ*. The resulting sols were applied to aluminum plates of about 10 × 10 cm, using a 30-mils applicator to produce thin films. The rest of the solution was poured onto Teflon plates (about 10 × 10 cm), producing thick films that were removed from the substrate after curing for swelling determinations, thermal analyses, and microscopic observations.

The films were allowed to stand at room temperature for at least 48 h. Those applied to Teflon were cured at 150°C for 48 h, whereas the ones applied to aluminum were cured in a sequence of 2 h at 60°C, followed by 1 h at 160°C, 1 h at 180°C, and 1 h at 230°C.

Film characterization. (i) Scanning electron microscopy (SEM) analysis. The morphology of the cryogenically fractured samples was examined by SEM (JEOL JSM 5800) on gold-coated surfaces. Energy-dispersive spectrometry (EDS) analyses were also performed in a few selected samples.

(ii) Degree of swelling determination. The degree of swelling was determined by soaking the film samples in toluene and water in a thermostatic bath at 30°C for at least 48 h. The initial (m_o) and final mass (m) were determined and the degree of swelling was calculated according to Equation 1:

$$Q=\left(\frac{m-m_o}{m_o}\right)\cdot 100 \qquad [1]$$

(iii) Measurement of mechanical properties. Stress–strain measurements were performed in an EMIC DL 10000 testing machine (EMIC, São Paulo, Brazil) in samples with dimensions of approximately 40 × 10 × 0.5 mm, with a 2 mm/min rate and tension of 20 N.

(iv) Thermal analysis. The thermogravimetric analyses (TGA) were performed in a TGA2950 thermogravimetric analyzer, model 2050 (TA Instruments) with a heat flow of 20°C/min in the temperature range of 25 to 600°C under nitrogen and up to 1,000°C under an oxidative atmosphere. DSC analysis was carried out in DSC equipment (modulated DSC 2920; TA Instruments) in the temperature range of −100 to 200°C, at a heating rate of 10ºC/min under nitrogen, in hermetic capsules.

(v) Adhesion. The ASTM Standard Test Method was used to evaluate the films' adhesion for Measuring Adhesion by the Tape Test (21) (ASTM D 3359-95a), in the cross-cut mode, in films applied to aluminum surfaces.

Film hardness. Film hardness was evaluated by the ASTM Standard Test Method for Film Hardness by the pencil test (22) (ASTM D 3363-92a) on films applied to aluminum surfaces.

IR spectroscopy. All spectra of the hybrid films, cured at 150°C, were collected on FTIR equipment (Nicolet Magna; 550 horizontal attenuation total reflection), using a ZnSe crystal. They were performed in the 4000–650 cm^{-1} range, with 32 scans and a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Films prepared from ECO were macroscopically homogeneous in a relatively large range of compositions. The films were yellow and also transparent in those compositions in which the epoxidized oil predominated. With CO, however, homogeneous films could be obtained only for small amounts of TEOS (up to 10%); otherwise, CO/TEOS resulted in heterogeneous films that generated two materials when soaked in water, the oil film and silica colloids.

Morphological characterization of the films was carried out by SEM analysis. Figure 3a shows a micrograph of a fracture of pure CO film. For the CO/TEOS films, even in the CO90/TEOS10 films phase separation occurred, in many cases showing silica aggregations in the microcrack regions. This was better observed in SEM in the backscattering mode, as shown in Figure 3b (arrows). For the ECO/TEOS series, the films containing an excess of oil were as homogeneous as the CO films. Figure 3c shows an SEM image of a hybrid prepared from the epoxidized oil and TEOS (ECO80/TEOS20). For larger amounts of TEOS (for instance, 40%) phase separation

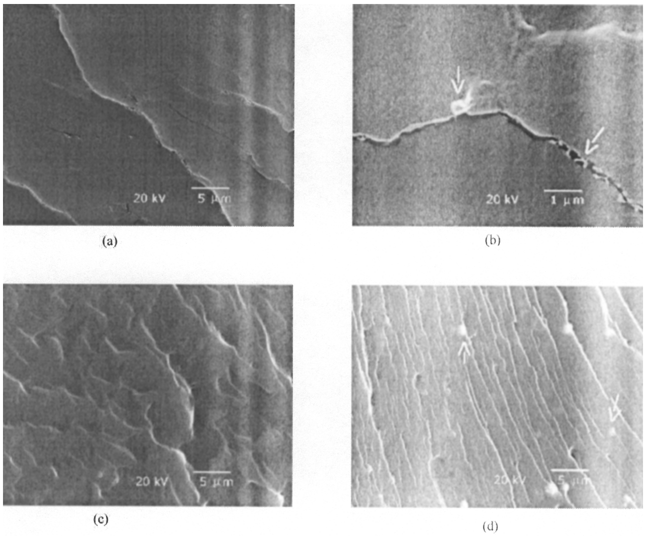

FIG. 3. (a) Scanning electron microscopy (SEM) image of castor oil (CO). (b) SEM image (backscattering mode) of CO90/TEOS10. (c) SEM image of ECO80/TEOS20. (d) SEM image of ECO60/TEOS40. TEOS, tetraethoxysilane; ECO, epoxidized castor oil.

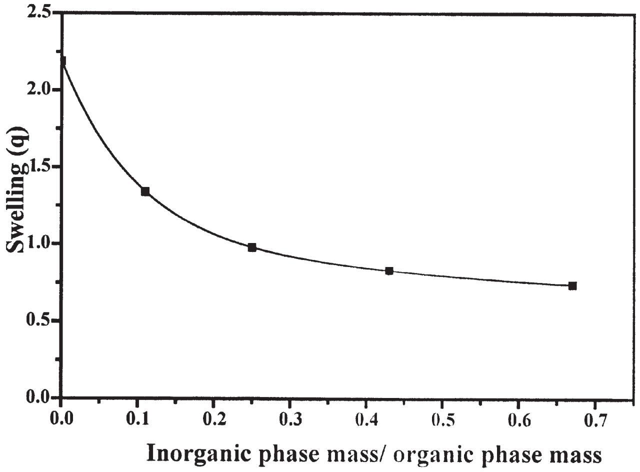

FIG. 5. Degree of swelling in toluene of the ECO hybrids as a function of the proportion of the phases (weight ratio between the inorganic and polymeric phases). For abbreviation see Figure 3.

occurred; this can be observed in the SEM images (arrows). Figure 3d is an SEM image of films prepared from ECO60/TEOS40.

We observed that the series prepared with ECO could accept much more of the inorganic component in its composition without showing phase separation than the one prepared from CO. However, even in those films in which phase separation occurred, the presence of silicon could be observed in the continuous phase, as can be seen in the EDS analysis of the continuous phase of the film CO70/TEOS30 (Fig. 4).

None of the tested materials swelled in water. However, significant swelling was observed in toluene, and this varied with the proportion of inorganic phase, as shown in Figure 5. One can see that an increase in the proportion of inorganic precursor produced films with a smaller degree of swelling, indicating that the presence of the hydrolysis product of the inorganic precursor produced more closed networks.

For the mechanical analysis performed on the hybrid films, we observed that the ECO/TEOS films were very breakable and were resistant only to small deformations, which presented some practical problems such as sample fixing and rapid rupture. Figure 6 shows the stress–strain curves. Qualitatively, it was possible to see a great increase in stress and a diminishment of deformation as the proportion of inorganic phase increased.

The TGA was carried out to estimate the stability of the hybrid and the silicate fraction incorporated. Figure 7 shows typical TGA curves for a hybrid series prepared with ECO. One can observe that the thermal stability of the hybrid films was similar to the pure epoxidized oil films. The amounts of TEOS effectively incorporated into the systems were confirmed by

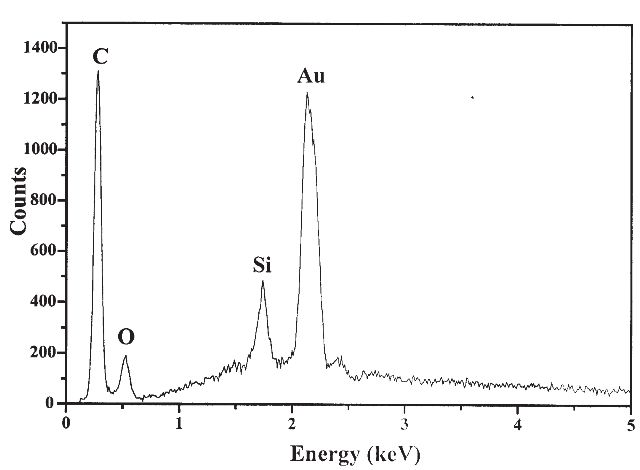

FIG. 4. Energy-dispersive spectra of CO70/TEOS30 in the continuous phase. For abbreviations see Figure 3.

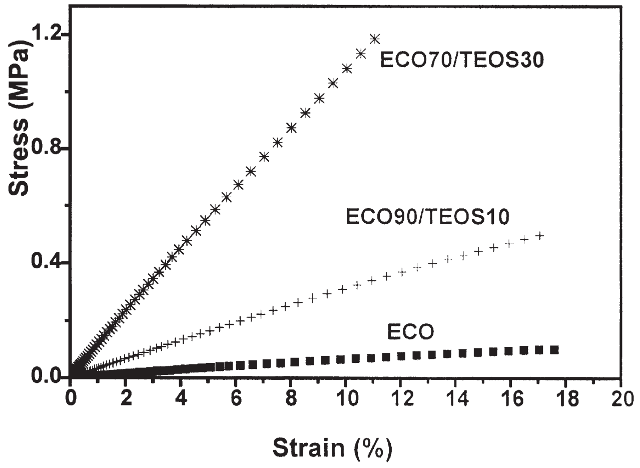

FIG. 6. Stress–strain curves for the hybrids obtained from ECO with proportions of ECO/TEOS of 100:0, 90:10, and 70:30. For abbreviations see Figure 3.

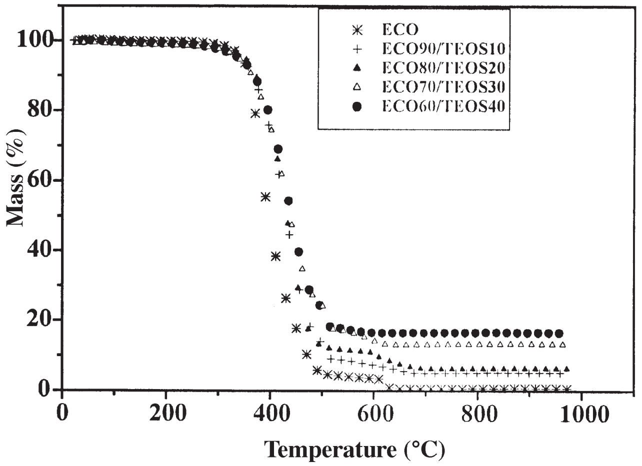

FIG. 7. Thermogravimetric curves of a series prepared with ECO with proportions of ECO/TEOS of 100:0, 90:10, 80:20, 70:30, and 60:40. For abbreviations see Figure 3.

analysis of the TGA residue at 900°C, considering total conversion of TEOS to silica. The values were close to those expected, except for films with higher amounts of TEOS (e.g., ECO60/TEOS40), in which they were lower than those expected. This may be due to loss during the process as well as nonhomogeneity of this particular sample.

The DSC traces were analyzed for the characteristic T_g of the new films. In general, there was a tendency for the T_g to increase slightly with the amount of TEOS, starting at −22.7°C for the ECO film and increasing up to −16.3°C for the cured ECO70/TEOS30 film, and to −15.4°C for the ECO60/TEOS40 film. This indicates that the mobility of the chemical chains decreased slightly with the addition of the silica precursor, as expected.

The crosshatch adhesion in films deposited on aluminum substrates increased from 2B (for ECO cured alone) to 4B (for the hybrid films), which is very good adhesion (5,15) (at least 95%) for an oil-based hybrid film, independent on the amount of added TEOS.

Only the cured ECO was soft, with a pencil scratch hardness of 2B. The addition of TEOS slightly improved the pencil hardness to B.

The CO and hybrid films obtained from different ECO/TEOS molar ratios were submitted to IR spectroscopy analysis. Table 1 shows the characteristic IR absorption bands observed in the films as well as some values of interest from the literature.

Figure 8 shows comparative spectra from the results obtained for ECO films and a typical spectrum for an ECO/TEOS film. In the pure ECO spectrum, it is possible to observe the typical bands at 3467, 2927, 2855, and 1737 cm^{-1} attributable to –OH, CH_2, and –O–C=O, respectively, and from 1450 to 700 cm^{-1} the bands attributable to C–C stretching, C–H bending, and C–H deformation (1446, 1380, and 725 cm^{-1}), and also the asymmetric and symmetric stretching absorptions of –O–C=O ester and –C–OH (1240–1096 cm^{-1}). The absorptions observed in the region between 3500 and 3300 cm^{-1} suggest that only a few–OH groups remained after the curing process. On the hybrid spectra, it was also possible to observe a weak and broad band at the same wave region, indicating that the OH groups of TEOS were almost totally combined.

For the ECO/TEOS systems, the bands of silica became more pronounced although dislocated. The region between 1200 and 1050 cm^{-1} appeared modified, possibly owing to the extensive Si–O–C– formation. The weak band at 3400–3500 cm^{-1} attributable to –OH groups observed in the spectra of ECO and ECO/TEOS films and the band at 800 cm^{-1} attributable to Si–O–C and Si–O–Si also support this assignment. The

TABLE 1
Characteristic IR Absorption Bands of the Films[a]

Band designation	CO[b]	ECO	ECO60/TEOS40	TEOS[c]
ν_{SiOH} free				4400 *vw*
ν_{OH}	3467 *w, br*	3467 *w, br*	3479 *w, br*	
$\nu_{Si\text{–}OH}$, $\nu_{SiO\text{–}H}$ terminal				3400 *w*
$\nu_{assim\ CH_2}$	2927 *s*	2927 *s*	2928 *s*	
$\nu_{sim\ CH_2}$	2856 *s*	2855 *s*	2856 *s*	
$\nu_{assim\ C=O\ ester}$	1732 *vs*	1737 *vs*	1740 *vs*	
$\delta_{C\text{–}H}$, $\nu_{C\text{–}C}$	1457, 1416, 1376 *m*	1456, 1417, 1376 *m*	1456, 1415, 1376 *m*	
$\nu_{assim\ C\text{–}O}$	1236 *s, sh*	1240 s, *sh*		
$\nu_{assim\ Si\text{–}O\text{–}}$ (TO mode)				1220 *s*
$\nu_{assim\ C\text{–}O\text{–}C\ ester}$	1162 *vs*	1163 *vs*	1168 *vs*	
$\nu_{assim\ Si\text{–}O\text{–}}$ (LO mode)				1080 *s*
$\nu_{sim\ C\text{–}O\ ester}$	1097 *vs, sh*	1096 *vs, sh*	1062 *vs*	1030 *s*
$\nu_{Si\text{–}OH\ and\ SiO\text{–}H}$ terminal			960 *sh*	960 *w*
$\nu_{sim\ Si\text{–}O\text{–}Si}$ ring			800 *w*	800 *w*
$\nu_{C\text{–}H_2}$	726 *m*	725 *m*	725 *w*	

[a] CO, castor oil; ECO, epoxidized castor oil; TEOS, tetraethoxysilane; TO mode, transverse optical lattice vibration; LO mode, longitudinal optical lattice vibration.
[b] From Reference 23.
[c] From References 24 and 25.

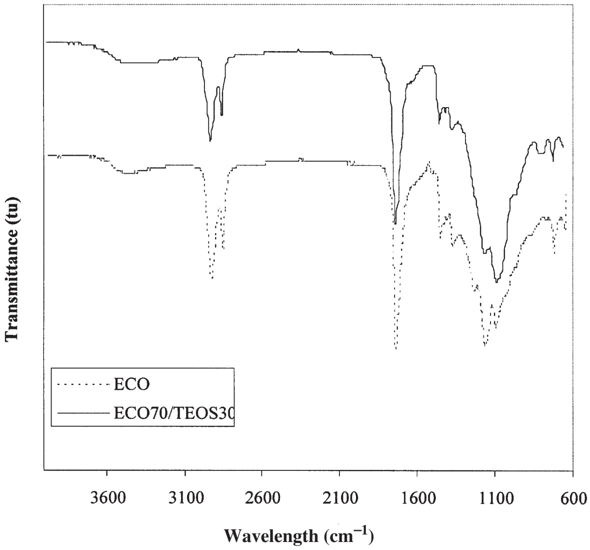

FIG. 8. IR spectra of cured films of ECO and ECO70/TEOS30. For abbreviations see Figure 3.

most intense band at 1162 cm^{-1} in the spectra of the hybrids resembled the spectrum of the silica Si–O dislocated due to increased chemical interaction on the formation of a Si–O–C network (25). The results of this strong organic–inorganic interaction in the ECO/TEOS hybrid films agree with the homogeneous microstructures observed in a large interval of TEOS concentrations. All the results obtained to the present provide strong evidence that the combination of ECO with the products of the *in situ*-hydrolyzed TEOS formed hybrid materials with great potential for use as coating materials.

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