

Preparation and Characterization of Hybrid Materials of Epoxy Resin Type Bisphenol A With Silicon and Titanium Oxides by Sol Gel Process

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Abstract. Hybrid materials were synthesized from epoxy resins as a result bisphenol type A-silicon oxide and epoxy resin bisphenol type A-titanium oxide were obtained. The synthesis was done by sol-gel process using tetraethyl orthosilicate (TEOS) and titanium isopropoxide (ITi) as inorganic precursors. The molar ratio of bisphenol A to the inorganic precursors was the studied variable. The materials were characterized by thermal analysis, infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDAX). The hybrid nature of the materials was demonstrated through thermal analysis and infrared spectroscopy. In both systems, as the amount of alkoxide increased, the bands described above were more defined. This behavior indicates the interactions between the resin and the alkoxides. Hybrids with TEOS showed a smoother and homogeneous surface in its entirety, without irregularities. Hybrids with titanium isopropoxide had low roughness. Both TEOS and ITi hybrids showed a decrease on the atomic weight percentage of carbon due to a slight reduction of the organic part on the surface.

Key words: Synthesis, epoxy resin, sol-gel process, hybrid materials.

Resumen. Fueron sintetizados materiales híbridos a partir de resinas epóxicas del tipo bisfenol A con óxido de silicio y óxido de titanio, respectivamente. Para la síntesis de los materiales se utilizó el proceso sol-gel usando tetraetilortosilicato (OSTE) e isopropóxido de titanio como precursores inorgánicos. Se estudió la relación molar de bisfenol A con los diferentes precursores inorgánicos. Los materiales fueron caracterizados por análisis térmico, espectroscopía de infrarrojo (IR), microscopía electrónica de barrido (MEB) y energía dispersiva de rayos X (EDX). La síntesis de materiales híbridos fue demostrada mediante análisis térmico y espectroscopía de infrarrojo. En ambos sistemas al incrementar la cantidad del alcóxido la intensidad de las bandas descritas anteriormente se presentaron más definidas. Este comportamiento indica la interacción entre la resina y los alcóxidos. Híbridos con OSTE mostraron una superficie lisa y homogénea sin irregularidades. Híbridos con isopropóxido de titanio de igual forma mostraron una superficie homogénea pero con baja rugosidad. Ambos sistemas híbridos mostraron una disminución del porcentaje de peso atómico de carbono, debido a una disminución de la parte orgánica en la superficie.

Palabras clave: Síntesis, resina epóxica, proceso sol-gel, materiales híbridos.

Introduction

An epoxy is a copolymer formed from two different chemicals referred as the “resin” and the “hardener”. The resin consists of monomers or short chains. A chain is composed by polymers with an epoxide group at the end. Usually the epoxy resins are produced from a reaction between epichlorohydrin and bisphenol-A [1]. Epoxy resins are dysfunctional or multifunctional in terms of the epoxy group. They may be based on aliphatic or aromatic structures; however, they are sometimes mixed with aliphatic material. Resins based on aliphatic material are often the basis of adhesive or coating systems where flexibility is improved [2]. Most epoxy resins are based on three chemical structures: TGMDA (tetraglycidyl methylene dianiline), DGEBA (Diglycidyl ether of bisphenol A), and novolac fenol-formaldehyde [3]. The main difference between these molecules is that the TGMDA and the novolac cure a density of cross-linking greater than the epoxy Bisphenol A, which has higher values of Young’s modulus and glass transition temperature (T_g), but lower values of deformation at fracture. The epoxy resin that is synthesized in this research is DGEBA-resin which is based on the epoxy bisphenol A resin, the Figure 1 shows the structure of the latter [4]. The DGEBA-resin has a highest breaking deformation and lowest water absorption.

In terms of ceramic materials, this resin is highly resistant to abrasion, corrosion and UV action and has been used in coatings formulation. On the other hand, a ceramer is defined as a material with a combination of final properties between ceramics and polymers [5]. The concept has been developed using organic coatings with sol-gel precursors.

The hallmark of a ceramer, regarding a mixture of inorganic and organic materials, is that in a ceramer there is a bond that actually binds the inorganic to the organic component. Although the birth of hybrid materials remains unknown, it is clear that the mixture of organic and inorganic components was carried out since ancient world. At that time, the production of bright and colorful paints was the driving force to consistently try novel mixtures. Dyes, inorganic pigments and other inorganic and organic components were mixed to elaborate paints that were used thousands of years ago [6]. Aside from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials. The sol-gel process was developed in the 1930s using silicon alkoxides as precursors from which silica was produced. In fact this process is similar to an organic polymerization starting from molecular precursors, resulting in a bulk material. Contrary to many other procedures used in

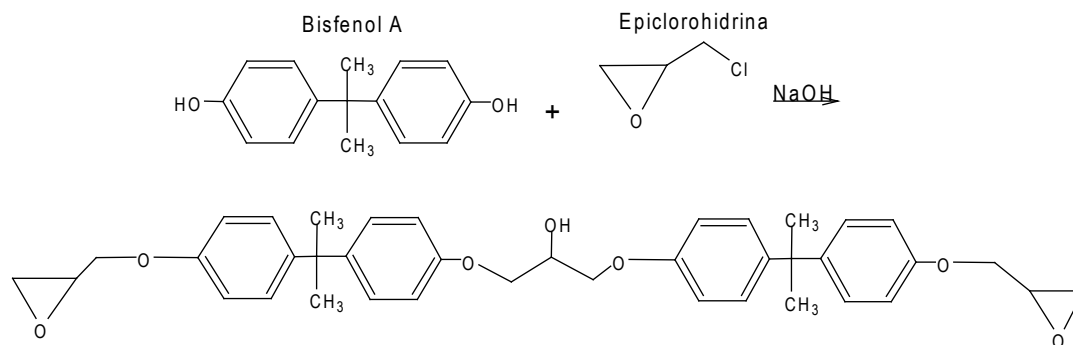


Figure 1. Epoxy resins reaction.

the production of inorganic materials, this was one of the first processes where ambient conditions were applied to produce ceramics. The control over the elaboration of multicomponent systems by a mild reaction method also led to industrial interest in the sol-gel process. Inorganic-organic hybrids can be applied in many branches of materials chemistry because they are simple to process and are amenable to design on the molecular scale. Currently there are four major topics of interest in the synthesis of inorganic-organic materials: (a) their molecular engineering, (b) their nanometer and micrometer-sized organization, (c) the transition from functional to multifunctional hybrids, and (d) their combination with bioactive components. This work shows the results of the synthesis and characterization of DGEBA-resin and the hybrid, produced from this resin with tetraethyl orthosilicate or titanium isopropoxide used as curing agent 1-6 diamino-hexane obtained by the sol-gel process.

Results and Discussion

Thermogravimetric analysis (TGA)

The Figure 2 shows TGA thermograms from the epoxy resins and hybrid materials with silicon oxide. The decomposition range of the resin is 80 °C-370 °C. Furthermore in the range of 230 °C-370 °C, there is a deflection due to the final decomposition.

TGA thermograms in the Figure 2a shows that for hybrids with TEOS, the hybrid materials decomposition occurred from 130 °C to 560 °C. The major weight loss occurred between 350 °C-560 °C, is mainly due to the rupture of chemical bonds in the hybrid material.

Figure 2b shows TGA thermograms of the hybrids with ITi. The hybrid materials decomposition occurred from 100 °C to 600 °C. The major weight loss occurred between 230 °C-600 °C, as in the hybrids with TEOS. The weight loss is due to the rupture of chemical bonds in the hybrid material. The factor that shows the existence of an hybrid material being synthesized, is the increase on alkoxides amount due to the weight loss percentage decrease when compared to the resin with hybrid materials.

Differential thermal analysis (DTA)

Figure 3 shows the results of the hybrids with epoxy resins under differential thermal analysis. In the temperature range from 233 °C to 330 °C, the resin showed a molecular restructuring.

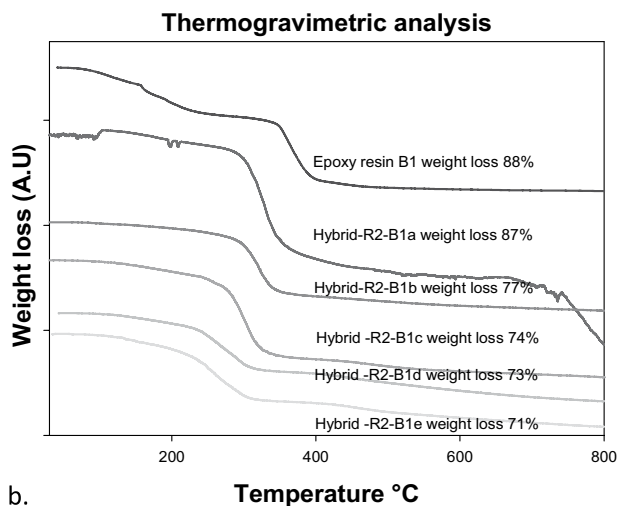
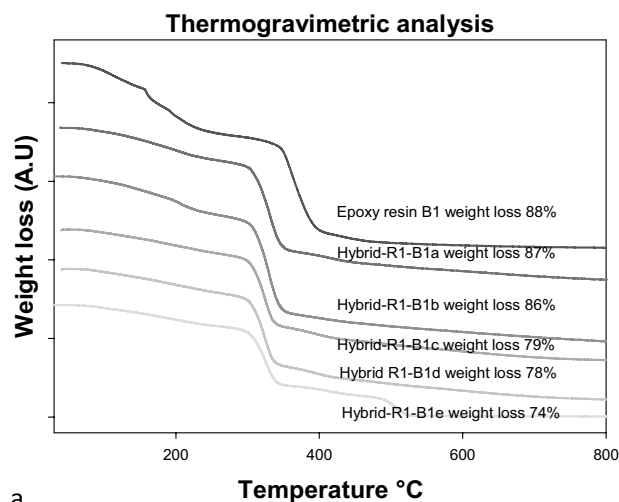


Figure 2. Thermogravimetric analysis of hybrid epoxy resins. a. Hybrids with TEOS and b. Hybrids with titanium isopropoxide (ITI).

At 358 °C the resin also showed endothermic events due to the beginning of its decomposition, which conveys two endothermic events at 470 °C and 500 °C.

Since the beginning of the DTA analysis, the hybrids with TEOS showed a molecular restructuring (Figure 3a). The hybrids decomposition started at 320 °C. At 544 °C or higher temperatures hybrid materials showed a rearrangement.

Hybrids with titanium isopropoxide showed a behavior similar to hybrids with TEOS. As in the previous situation, the analysis showed molecular restructuring around 366 °C. When the concentration of alkoxide increased, the decomposition was at 320 °C for hybrids and 233 °C for resins. At 500 °C or higher temperatures hybrid materials with ITi showed molecular restructuring at the same as hybrids with TEOS.

Infrared spectroscopy (FTIR)

The principal bonds for epoxy resin were identified through FTIR. According to the results shown in the Table 1, the resin synthesized in this work corresponds to DGEBA-resin.

Therefore the Table 1 presents the principal FTIR vibrations for the epoxy resin and is divided by section according to the chemical structure of the epoxy resin [7,8].

Figure 4 shows the results for infrared spectroscopy of hybrids with TEOS. Three characteristic peaks revealed the

Table 1. Identification of infrared bands for epoxy resins and hybrids materials.

Vibration type	Group	cm ⁻¹
Amine		
A.- stretching	C-H	2910 y 2850
B.- bending	N-H	1620
C.- bending	CH ₂	1458
D.- stretching	C-N	1063
Aromatic		
E.- elongation	C-H	3060,3030 y 3000
F.- elongation	C-H metilo	2950, 2835
G.- Overtone region	C-C	2000 and 1650
H.- ring stretching	C-C	1590480
I.- asymmetric stretching	C-O-C	1245
J.- symmetric stretching	C-O-C	1030
K.- out of plane bending, ring bending	C-H C-C	800-740 680
Alkane of the amine		
L.- elongation	C-H de CH ₂	2926 y 2853
M.- bending Oscillation	CH de CH ₂	1465
	CH ₂	620
Alcohol		
N.- stretching	OH	3330
O.- stretching	C-H	2907
P.- bending	C-H	1460 and 1361
Q.- stretching	C-O	1101

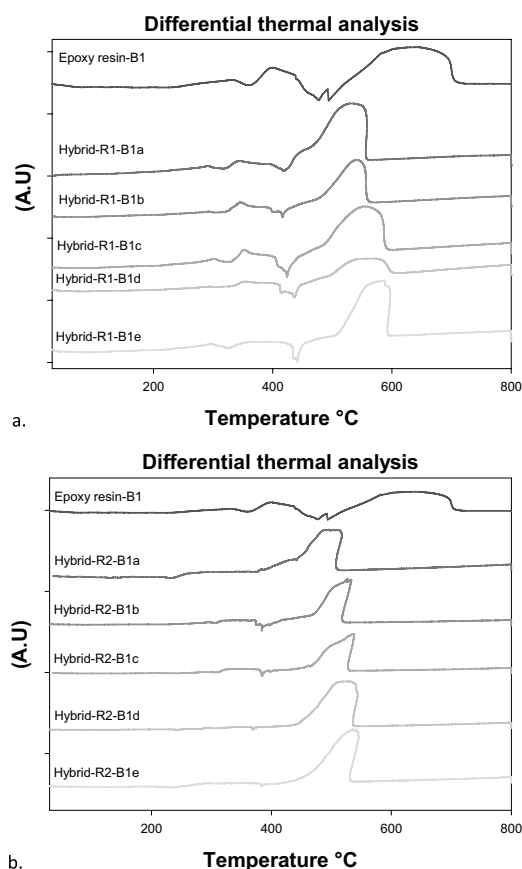


Figure 3. Differential thermal analysis of hybrid epoxy resins. a. Hybrids with TEOS and b. Hybrids with titanium isopropoxide (ITI).

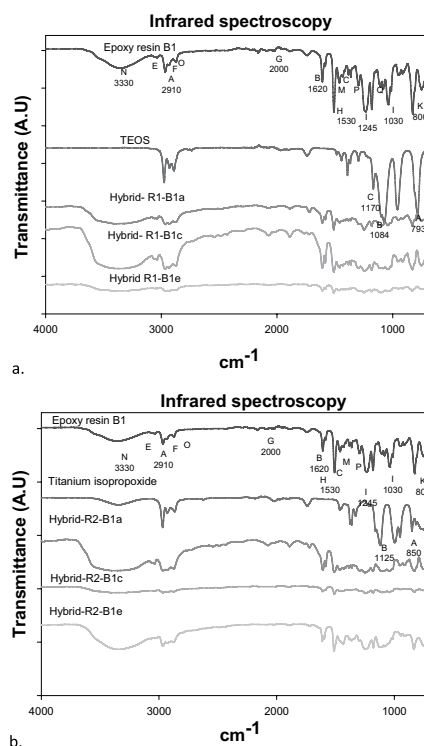


Figure 4. Infrared spectroscopy of epoxy resin and hybrids a. Hybrids with TEOS and b. Hybrids with titanium isopropoxide (ITI).

synthesis of the hybrid materials at 793, 1084 and 1170 cm^{-1} ; corresponding to the vibrations of Si-O, Si-O-Si and Si-C, respectively [9,10].

Hybrids with ITi (Figure 4b) showed additionally bands at 850 and 1125 cm^{-1} , which correspond to vibrations Ti-O-Ti and Ti-O-C, respectively. The bands revealed the synthesis of hybrid materials, in this system as well as in the system with TEO [11].

Scanning electron microscopy (SEM)

Figure 5 shows micrographs for the epoxy resin and hybrids. The epoxy resin showed an homogeneously surface. Compar-

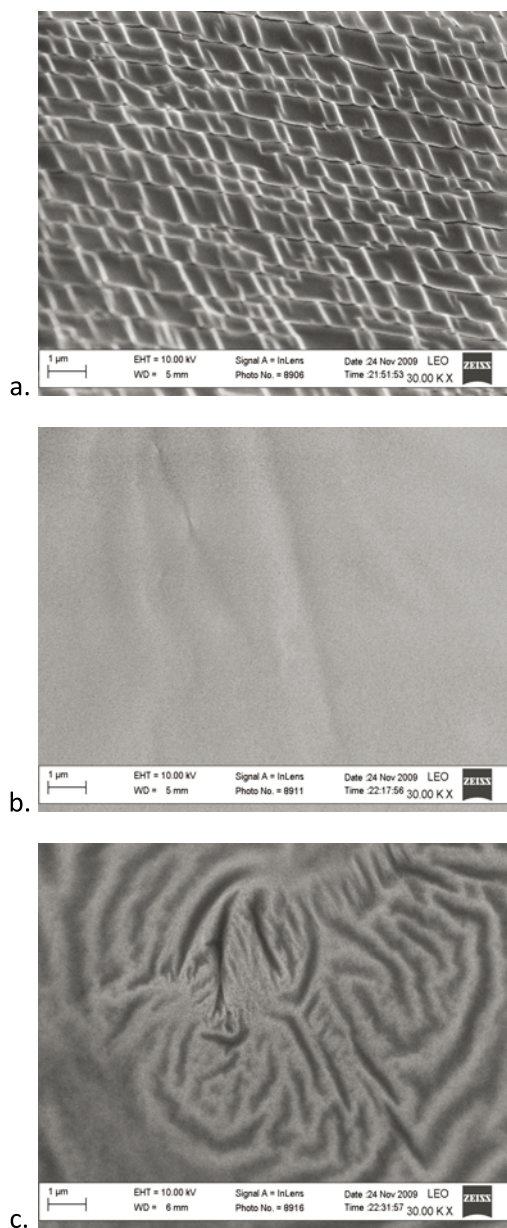


Figure 5. SEM micrographs obtained at 30 000 KX: a. Epoxy resin b. Hybrid with TEOS (R1-B1e) and c. Hybrid with titanium isopropoxide (R2-B1e).

Table 2. Quantification by EDX of the samples surface.

Epoxy resin			Hybrid with titanium oxide		
Element	% Wt*	% At**	Element	% Wt*	% At**
C	76.83	87.46	C	75.51	84.77
O	12.18	10.41	N	1.30	1.25
Au	6.67	0.46	O	11.98	10.09
Cl	4.32	1.67	Cl	7.39	2.81
			Hybrid with silicon oxide		
			Ti	3.81	1.07
C	79.49				
N	1.09	1.02			
O	11.20	9.17			
Cl	7.89	2.92			
Si	0.33	0.15			

(*) Percentage of the total weight of the sample.

(**) Percentage in relation to the atomic weight of the sample.

ing the two hybrid systems; these shows that hybrid with TEOS had a homogeneous smoother surface and the hybrid with titanium isopropoxide had a slightly rough surface.

Energy Dispersive X-ray analysis

Table 2 shows the EDX analysis of the epoxy resin and hybrids of two systems. The local distribution of elements was determined by EDX, considering the weight percentage (% wt) and the atomic weight percentage (% At). The resin and hybrids R1-B1e for the system with TEOS and R2-B1e for the system with titanium isopropoxide were the materials analyzed.

The carbon was the most significant element in the materials tested due to its organic nature. In the resins, the carbon showed an atomic weight percentage of 87.46 %. For the hybrids in both systems (silicon oxide and titanium oxide), the atomic weight percentage of carbon decreased. The decreasing suggests a reduction of the organic part of the hybrid materials. The weight percentage of oxygen is in the same order for both, the resin and the hybrids, principally due to water absorption and by EDAX we only obtained evidence of elements present in the systems.

Conclusions

Hybrids materials were synthesized from epoxy resins with silicon oxide and titanium oxide by sol-gel process. It was determined that the crosslinked network of the prepolymer interacts directly with the oxides obtained. In both systems the decomposition temperature was higher. When compared hybrids with the epoxy resin, the hybrids showed molecular restructuring. Therefore it was confirmed that the molecular restructuring is the result of the reaction between inorganic precursors and the epoxy resin. The molecular restructuring

Table 3. Set of experiments for the synthesis of epoxy resins-silicon oxide.

Sample	Epichlorohydrin Molar concentration	Bisphenol A Molar concentration	Bisphenol A/TEOS Molar ratio
Epoxy resins B1	0.162	0.022	0
R1-B1a	0.162	0.022	0.0048
R1-B1b	0.162	0.022	0.0096
R1-B1c	0.162	0.022	0.0144
R1-B1d	0.162	0.022	0.0192
R1-B1e	0.162	0.022	0.0240

Table 4. Set of experiments for the synthesis of epoxy resins-titanium oxide.

Sample	Epichlorohydrin Molar concentration	Bisphenol A Molar concentration	Bisphenol A/TEOS Molar ratio
Epoxy resins B1	0.162	0.022	0
R2-B1a	0.162	0.022	0.0035
R2-B1b	0.162	0.022	0.0070
R2-B1c	0.162	0.022	0.0105
R2-B1d	0.162	0.022	0.0141
R2-B1e	0.162	0.022	0.0176

indicates the synergy between organic and inorganic materials used in the synthesis.

Experimental part

Materials

The epichlorohydrin 99%, bisphenol A 97%, sodium hydroxide, TEOS 98%, titanium isopropoxide 97%, 1-6 hexanodiamine were supplied by Alfa Aesar Chemicals.

Synthesis of epoxy resin bisphenol A type

Methodology. Epoxy resin was synthesized with epichlorohydrin and bisphenol A, as precursors. The resulting resin and hybrid materials were studied using different characterization techniques.

Thermal gravimetric analysis (TGA) was implemented with a SHIMADZU TGA 50 at heating rate of 10 °C per min in air atmosphere. Infrared spectroscopy was carried out using a Perkin-Elmer spectrophotometer 16 PC, with at least 20 sweeps under 4 cm⁻¹ of resolution. For the morphology, SEM Zeiss SUPRA 40 was used. The local distribution of elements was determined by EDX using the X-ray (EDX) energy dis-

persive analysis PERKIN ELMER PHI 5600 ESCA System for elemental analysis.

Procedure. Pre-established amount of bisphenol A and epichlorohydrin were mixed (Table 3 and Table 4). 0.5 ml of 0.1N NaOH was added and the reaction was stirred at 500 rpm and 80 °C for 5 min. The solution was placed in a 100 ml glass reactor; the product of this reaction was the prepolymer. Subsequently 1 ml of 1-6 hexanodiamine was added as curing agent and the reaction was maintained in agitation at 80°C for 6 hours. At the end, the obtained gel was cooled at room temperature and subjected to a drying process inside an oven at 60 °C for 24 hours.

Hybrid materials synthesis

Methodology. For the synthesis of hybrid materials, a set of experiments were performed. One of them was the DGEBA epoxy resins containing silicon oxide and titanium oxide by sol-gel process. The other was varying the bisphenol A /TEOS and bisphenol A/titanium isopropoxide molar ratio. The materials were characterized under the same techniques and conditions than the resin.

Procedure. Each one of the inorganic precursors (TEOS or titanium isopropoxide) was mixed in ethanol at 500 rpm at room temperature for 5 min. The solutions were added to the prepolymer. Then 1 mL of 1-6 hexanodiamine was added as a curing agent and the reaction was maintained in agitation at 80 °C for 6 h. Finally, the obtained gel was cooled to room temperature and subjected to a drying process in an oven at 60 °C for 24 h. The experimental conditions in the synthesis for both materials are listed in Table 3 and Table 4 for hybrids with silicon oxide and hybrids with titanium oxide respectively.

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