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Application of Romero García method to the degradation process of DGEBA/ETDA filled with ultra fine metallic copper

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Summary

The thermal properties of an epoxy resin (diglycidyl ether Bisphenol A, DGEBA) cured with a primary amine (ethylenediamine, ETDA) and filled with 10, 20 and 30 wt.% of ultra fine copper particles were analyzed. The thermal results were evaluated by means of the Romero-Garcia method, which allowed to obtain the resin degradation kinetic parameters, as well as the possible decomposition mechanism. From the obtained results is possible to infer that higger copper content strongly affects the degradation process of the epoxy resin, which causes a drop off on the composites thermal stability. This behavior could be attributed to water presence, being this effect less pronounced for the resin with 10wt.% copper and unfilled resin. Regarding to decomposition mechanism, three way transport showed the best correlation for all samples.

Introduction

For many purposes it can be considered that epoxy resins show disadvantages such as high viscosities, elevated cost and an excessive rigidity. Those reasons made necessary the modifications of the resin trough solvent, filler and plasticizer addition.

Fillers added to adhesive epoxy resins are almost exclusively inorganic. They include oxides and silicates. Small amount of powdered metals are used to increase the thermal or electrical conductivity.

Inclusion of conductive particles in epoxy resins has become a field of growing interest because these materials are very useful for fabrication of adhesives capable of joining metallic parts without interfering the current flow. Most common fillers are silver, copper and in some special cases gold. The amount of filler will depend on the particle shape and size.

Copper-epoxy adhesion is key to the reliability of many types of electrical interconnects. Copper-based conductive adhesion is of industrial interest, and there have been many research efforts whose goal has been to determine what factors lead to maximum adhesion. In most instances, this has led to many different approaches using various adhesion promoters and resulted in questions about whether mechanical or chemical interactions control interfacial adhesion [2].

Nakamura et al. [3], studied the particle size effect on the mechanical behavior of cured epoxy resins filled with silica. Hong & Wang [4] analyzed the copper oxide effect on thermo-oxidative degradation on a bromide epoxy resin cured with dicyandiamide using Thermogravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

Mechanical properties of epoxy/amine systems filled with Zinc (Zn) and aluminum (Al) particles at 10, 20 and 30 wt%, with epoxy/amine molar ratios of 1:1, 1:1.5 and 2:1 were evaluated by Brito and Sánchez [1].

Sánchez et al. [5] studied the thermodegradative behavior of an epoxy resin filled with Al and aluminum oxide particles. They used the Avrami isothermal method and two dynamic methods: Coats-Redfern and Horowitz-Metzger at different heating rates (5, 10 and 20 ºC/min). The filler content varied from 10 to 40 wt% and the epoxy amine ratio was 1:1.5. They observed that when the heating ratio was increased, the material tended to be more stable. In addition, filler content did not affect the thermal stability of composites even when they found that Al propitiates the degradation process in higher proportion than Al_2O_3. On the other hand, they concluded that the predominant mechanism was nucleation for all studied samples.

Therefore, in the present study thermal properties of an epoxy resin (diglycidyl ether Bisphenol A, DGEBA) cured with a primary amine (ethylenediamine, ETDA) and filled with 10, 20 and 30 wt% of ultra fine copper particles (250 mesh) were analyzed. The thermal results were evaluated by means of the Romero-Garcia [6] (R-G) method, which allowed to obtain the resin degradation kinetic parameters, as well as the possible decomposition mechanism.

The classical models used in the kinetic analysis of this kind of reactions study the simultaneous influence of temperature and conversion. However, the effect of temperature can mask the conversion or vice versa. The Romero-García method [6] tries to separate both effects; therefore experimental data at different heating rates is needed.

The Romero-García equations are:

At constant temperature

$$G(\alpha)=\frac{RT_1^2A}{E(T_1-T_0)}*\left(1-\frac{2RT_1}{E}\right)*\exp\left(-\frac{E}{RT_1}\right)*t \qquad \textbf{(1)}$$

At constant conversion

$$\ln\frac{\beta}{RT^2}=\ln\frac{A}{EG(\alpha)}-\frac{E}{RT} \qquad \textbf{(2)}$$

where α is the reacted fraction at the time t, E is the activation energy (J/mol), A is the pre-exponential factor, R is the gas constant and T is the temperature (K), T_o is the initial temperature of the reaction (K), β is the heating rate and T_1 is the temperature at which the study is carried out at constant temperature (K). The reaction mechanism is represented by different equations [7] expressed as functions of conversion, depending upon the controlling mechanism; therefore, there is a $G(\alpha)$ function for each one of these mechanisms (Table 1).

Experimental

An epoxy resin (diglycidyl ether Bisphenol A, DGEBA) with an average molecular weight of 473 g/mol and Brookfield viscosity of 9150cp was selected.

Toluene was used as solvent and a primary amine (Ethylene Diamine, ETDA) was used as the curing agent. The epoxy/amine ratio employed was 1:1.5. Ultra fine particles of metallic copper acted as fillers. These particles were dried in an oven at 110ºC for 1 hour in order to eliminate the presence of water.

Table 1: Kinetic-equations used for the construction of the simulated decomposition reactions [7].

Mechanism	Symbol	G(α)
Random nucleation and nuclei growth (Ec. Avrami-Erofev)		
Bidimensional nuclei growth	A2	$(-\ln(1-\alpha))^{1/2}$
Three-dimensional nuclei growth	A3	$(-\ln(1-\alpha))^{1/3}$
Random nucleation and nuclei growth		
First order random nucleation	F1	$-\ln(1-\alpha)$
Second order	F2	$(-\ln(1-\alpha))^{-1/2}$
Third order	F3	$(-\ln(1-\alpha))^{-1/3}$
Diffusion		
One-way transport	D1	$\alpha^2/2$
Two-way transport (Holt-Cutler-Wadsworth equation)	D2	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-way transport (Jander equation)	D3	$3/2(1-(1-\alpha)^{1/3})^2$
Three-way transport (Ginstling-Brounshtein equation)	D4	$3/2((1-2\alpha/3)-(1-\alpha)^{2/3})$
Three-way transport (Zhuravlev-Lesokhin-Tempelman equation)	D5	$3/2((1-\alpha)^{-1/3}-1)^2$
Limiting surface reaction between both phases		
One dimension	R1	α
Two dimensions	R2	$2(1-(1-\alpha)^{1/2})$
Three dimensions	R3	$3(1-(1-\alpha)^{1/3})$

The epoxy resin curing process was carried out as follows: The resin was placed in a glass reactor. Then, the filler was added under continuous agitation for 15 minutes in order to homogenize the blend. After this, a toluene/ETDA solution at 10% toluene was slowly dropped into the reactor. Once the addition was ended, temperature was controlled by a thermocouple that was submerged in the material so its increase could be measured and stop the agitation. The resulting material was poured into molds. Same procedure was used for the DGEBA/amine blend without filler.

For thermal tests, 8-10mg of powdered samples (unfilled and filled cured materials) were placed on the thermal analyzer (TA Instrument, 2959), under a nitrogen atmosphere, from 25 to 600ºC at heating rates of 5, 10, 15 and 20 ºC/min. This procedure allowed obtaining the degradation kinetic parameters as well as the possible decomposition mechanism. Morphology studies of cryogenically fracture samples were carried out using a scanning electron microscope (SEM) Hitachi, S-2400. A Phillips CM10 transmission electron microscope (TEM) was used to analyze the microstructure of the composites. The samples were prepared by ultramicrotomy and observed without any further treatment.

Results and Discussion

Figure 1 shows the thermograms of the unfilled and 10wt.% copper filled resin heated at 5ºC/min. The curves are similar to those obtained for the other materials, which indicated the possibility to infer that the degradation pattern of the epoxy/amine system was similar for all the composites. Degradation occurred between 300 and 400 ºC even when little mass loss was observed around 100 ºC. This loss was attributed to moisture, toluene remnant (boiling point 111ºC) and amine evaporation (boiling point 117ºC). In spite of the fact that solid decomposition processes are complex because elementary steps such as bond ruptures, gas products diffusion, rupture and creation of crystalline networks, etc. are involved, the characteristics of the thermograms obtained evidenced a one step of degradation process.

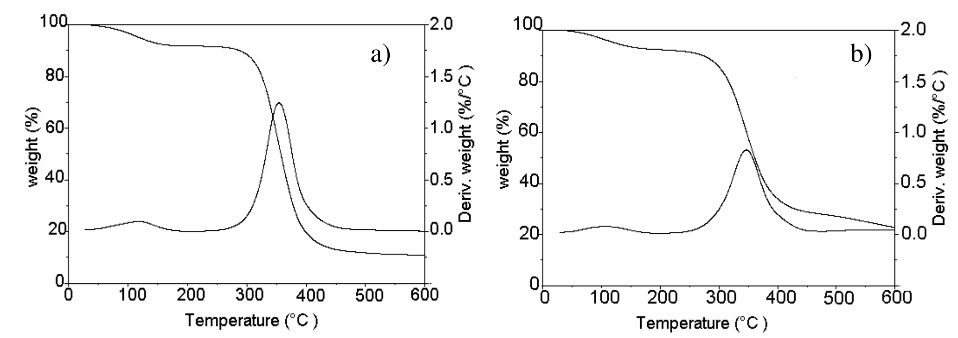

Figure 1: Termograms of epoxy/amine system: a) unfilled and b) with 10wt.% copper.

In Table 2, thermal parameters of composites degradation, which were extracted from the thermograms, are presented. Initial decomposition temperatures (Ti) as well as maximum peak temperatures (Tmax) were observed between 300-350 and 380-420 ºC intervals, respectively. These values tended to increase when the heating rate was raised and a slightly decrease when filler content was increased.

Final degradation temperatures (Tf) were around 400ºC and showed similar behavior than Ti and Tmax. The tendency observed when filler content was increased indicated that metal particles are affecting the epoxy resin degradation.

It was observed for cured epoxies samples without and with 10 wt.% copper (Table 2) that the residue weight (Rw) percentages are significantly higher than the corresponding theoretical contents indicating that at higher filler content a stronger degradative effect on the resin was exerted. This could also indicate a metal catalytic effect on the resin. Additionally, it was observed for materials with 20 and 30% of filler content, that residue weight varied with heating rate when compared to 10% and unfilled ones. This can be attributed to several facts, such as filler dispersion reached during mixing that becomes harder at higher filler contents, because materials viscosity increases as a consequence of a curing rate raise so epoxy-metal hardening occurs in accelerated way. Another reason could be that at higher concentrations, filler particles, that are very fine, tend to agglomerate, so dispersion can not be homogeneous (Figure 2).

For the kinetic parameters determination, Romero-García [6] method was used. This method was designed to consider conversion and temperature effects separately and requires performing tests at different heating rates. In order to illustrate this, Figure 3 shows an analysis of the decomposition kinetic model of the unfilled resin at constant temperature and conversion, respectively. The two models shown are just two of the many analyses that must be made to apply this method.

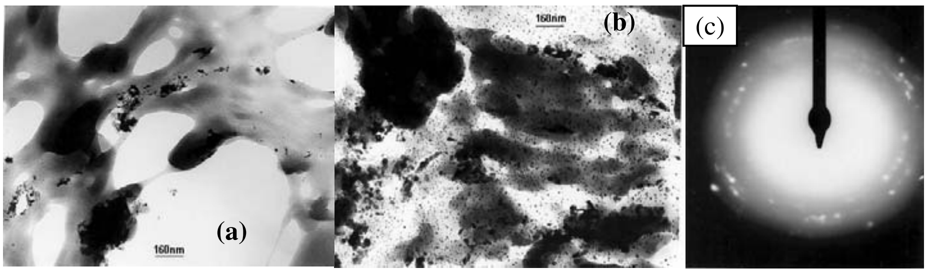

Figure 2: TEM micrographs of the composite with 10 (a) and 30 (b) wt.% and diffraction pattern of the filler (c).

Table 2: Thermal date of the degradation systems epoxy/amine/Cu.

Filler (%)	Heat Rate(°C/min)	T_i (°C) ±1	T_f (°C) ±1	T_{max} (°C) ±1	Rw (%)
0	5	321	387	355	10.9
	10	338	404	370	7.2
	15	344	409	376	6.8
	20	349	416	381	6.0
10	5	308	384	346	23.0
	10	314	392	356	24.1
	15	331	403	367	20.3
	20	338	408	372	17.9
20	5	313	387	350	20.0
	10	323	397	359	22.0
	15	326	407	368	23.1
	20	331	407	369	22.7
30	5	310	383	346	26.2
	10	321	395	357	27.1
	15	320	401	363	30.6
	20	326	406	369	30.2

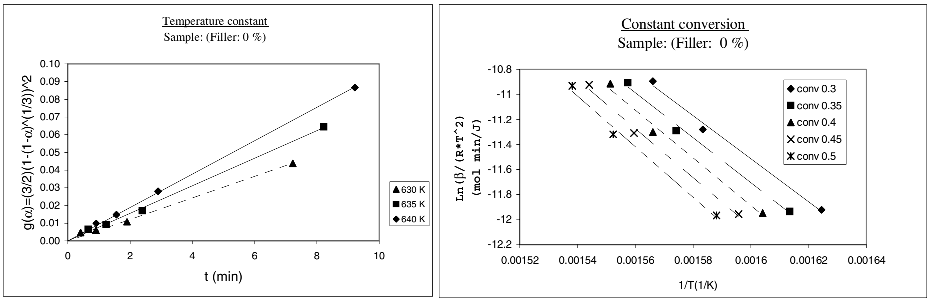

Figure 3: Analysis at temperature constant represented according to the D model for patron epoxy-amine and conversion constant.

It was noticed that activation energy values at constant conversion varied with the conversion stages (Table 3). Depending on the filler content this parameter showed different behaviors even though the values obtained were similar to those reported for epoxy-amine systems (32-60 *k*J/mol) [8,9].
Unfilled resin and materials filled with 10wt% copper showed an increase in the activation energy with both temperature and conversion (Table 3). Instead, at higher filler contents even when values were higher than the previous discussed, they tended to decrease either with temperature or conversion, which implied that the copper content strongly affects the degradation process of the epoxy resin.

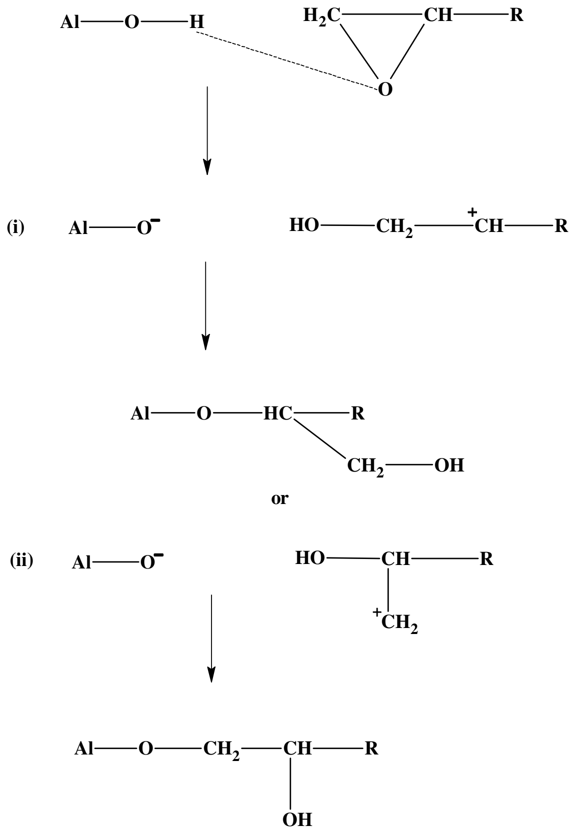

Figure 4: Possible mechanisms between epoxy groups and hydrated metal oxide surface[11].

It is important to point out that metals available for industrial applications usually are covered with a thin hydroxide layer that if it is removed, immediately forms again [10], this can be confirmed by diffraction pattern. (Figure 2c). This layer affects metal-resin adhesion by improving it[8] because resin polar groups propitiate strong electromagnetic bonding attractions between epoxy molecules and metal hydroxide. These epoxy groups can react with the hydrated metal oxide surface to produce an ether type chemical bond across the interface. Some possible mechanisms that involve Al are shown in Figure 4 [11]. Copper also, in air presence, forms a hydroxide layer on its surface. Based on this fact, it is possible to affirm that there is a good adhesion between the epoxy resin and metal. Brito et al [12] observed by electronic microscopy that for systems with aluminum particle size similar to used in this investigation there was certain miscibility between metal and epoxy resin. Moreover, copper high surface energy (500-700mJ/m^2) [13] assists this miscibility.

On the other hand, based on Figure 4 mechanism, in the course of degradation, hydroxyl groups present in composites can be eliminated as water, be eliminated as water, forming olefin type bonds. In this case, water as decomposition product, affects metal-epoxy interactions, being this effect more pronounced at higher filler contents. Kerr et al. [14] and Delollis et al [15] point out that the resin is slightly permeable to water, so is virtually impossible to prevent water from reaching metal-epoxy interfacial region. The water layers formed on the interface deteriorate the adhesion strength by reducing the interfacial region force of the metal-epoxy system. These water molecules are very strong hydrogen bonding agents; they can readily break the bonds between the metal and the epoxy resin to form new hydrogen bonds with the metal hydrated oxide surface.

Relating activation energy values (Table 3) with residue weight (Rw) percentages (Table 2) it can be observed a higher residue amount for unfilled resin and 10 % copper composite. For these materials activation energies were initially low but tended to increase with conversion and temperature, which indicated reactions between the two components that did not allow resin decomposition reactions occur. Instead, for

Table 3: Samples activation energy values at constant conversion and temperature.

Constant conversion				Constant temperature		
Filler (%)	Conversion (%)	Ea (*k*J/mol)		Filler(%)	Temperature (K)	Ea (*k*J/mol)
0	30	34		0	630	34
	35	36			635	38
	40	38			640	40
	45	39		10	625	36
	50	40			630	42
10	30	37			635	49
	35	40		20	620	50
	40	44			625	45
	45	49			630	40
	50	53		30	610	55
20	30	50			620	48
	35	46			625	38
	40	45				
	45	42				
	50	40				
30	30	55				
	35	51				
	40	48				
	45	43				
	50	37				

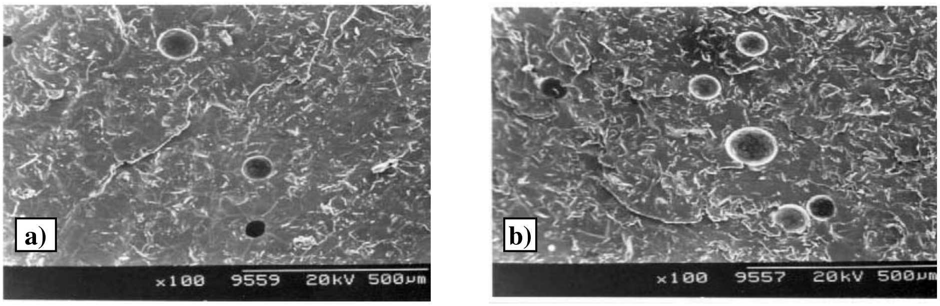

Figure 5: Micrographs of epoxy-amine with cupper. a) 20wt.%; b) 30wt.%.

higher copper content even when Ea values were higher initially, they tended to decrease with temperature as well as conversion and residue percentages corresponded to added filler.

This phenomenon was observed by Gledhill et al [16], who demonstrated that when a water layer was present, the adhesion values changed from positive to negatives. This change plays an important role on the interfacial strength loss and as a consequence, the stability decreases. The behavior observed could be attributed to water presence being this effect less pronounced for 10wt.% and unfilled samples in which water and copper content were lower so resin-water-metal contact surface was lowest. For higher copper amounts, there are more filler-polymer interactions, but there is also higher water content which originated air voids that acted as stress points as can be observed in micrograph of Figure 5. Water locates on the metal polymer interface, debilitating the interactions and as a consequence Ea decreases as long as the decomposition process occurs. This implies a drop off on the composites thermal stability, effect

Table 4: Values of the correlation coefficient (r^2), intercept (I), and slope (S) obtained using mechanistic equation of table 1. for 20 wt% copper filled resin.

	Temperature (K)								
	620			625			630		
Mechanisms	S	I	r^2	S	I	r^2	S	I	r^2
D1	0.01490	0.04160	0.98940	0.01810	0.04910	0.98990	0.02020	0.06230	0.98010
D2	0.00890	0.02180	0.99150	0.01120	0.02530	0.99210	0.01300	0.03210	0.98410
D3	0.00240	0.00500	0.9935	0.00310	0.00570	0.99410	0.00380	0.00720	0.98790
D4	0.00210	0.00490	0.99220	0.00270	0.00570	0.99280	0.00310	0.00720	0.98550
D5	0.00350	0.00530	0.99650	0.00500	0.00500	0.99610	0.00650	0.00570	0.99130
F1	0.03510	0.23740	0.98130	0.03990	0.26350	0.98420	0.04260	0.30020	0.97420
A1	0.00880	0.05940	0.98130	0.01000	0.06590	0.98420	0.01700	0.07510	0.97420
A2	0.01760	0.11870	0.98130	0.01990	0.13180	0.98420	0.02130	0.15010	0.97420
A3	0.01170	0.07910	0.98130	0.01330	0.08780	0.98420	0.01420	0.10010	0.97420
A4	0.02630	0.17810	0.98130	0.02990	0.19760	0.98420	0.03200	0.22520	0.97420
A5	0.02340	0.15830	0.98130	0.02660	0.15570	0.98420	0.02840	0.20010	0.97420
R1	0.02430	0.21490	0.97350	0.02570	0.23800	0.97570	0.02560	0.26820	0.96120
R2	0.01460	0.11300	0.97760	0.01600	0.12540	0.98020	0.01650	0.14220	0.96810
R3	0.01030	0.07660	0.97880	0.01150	0.08500	0.98160	0.01200	0.09660	0.97020

more pronounced in materials with bigger copper content, for this reason Ea values obtained decrease at constant temperature and conversion.

Regarding to the decomposition mechanism, three-way transport seemed to be predominant for all materials, being D3, D4 and D5 who showed better correlations. As example, Table 4 shows the models for 20 wt% copper filled resin, with intercept values tending to zero and correlation factor close to one. From these results and values showed on Table 2, it is possible to conclude that there is a decomposition mechanism for all the materials varying on different stages (D3, D4, D5).

Conclusions

The copper content strongly affected the degradation process of the epoxy resin. The water presence played an important role in the resistance loss on the interface, which implied a decrease in composites thermal stability, specifically at copper concentrations starting from 20wt%. The decomposition mechanism was three dimensional diffusion, being D3, D4 and D5 who showed better correlations.

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