

MORPHOLOGICAL AND THERMAL DEGRADATION BEHAVIORS OF DGEBA/ETDA FILLED WITH ULTRAFINE METALLIC COPPER

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In the present study morphological and thermal behavior 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. For thermal tests, powdered samples were placed on the thermal analyzer, under a nitrogen atmosphere, from 25 to 600°C at heating rates of 5, 10, 15 and 20 °C/min. This procedure allowed obtaining the degradation kinetic parameters, Romero-García [1] method was used. 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.

Thermal parameters of composites degradation were extracted from the thermograms. Initial decomposition temperatures (T_i) as well as maximum peak temperatures (T_{max}) were observed between 300-350 and 380-420 °C intervals, respectively. These values tended to increase when the heating rate was raised and a slightly decrease when filler content was increased. It was observed for cured epoxies samples without and with 10 wt.% copper that the residue weight (Rw) percentages (10.9-6.0 and 23.0-17.9, respectively) 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 (20.0-22.7 and 26.2-30.2, respectively) 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 1). Unfilled resin and materials filled with 10wt% copper showed an increase in the activation energy with both temperature and conversion (Table 1). 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. Relating activation energy values (Table 1) with residue weight (Rw) percentages 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 higher copper content even when E_a values were higher initially, they tended to decrease with temperature as well as conversion and residue percentages corresponded to added filler.

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 2. Water locates on the metal polymer interface, debilitating the interactions and as a consequence E_a decreases as long as the decomposition process occurs. This implies a drop off on the composites thermal stability, effect more pronounced in materials with bigger copper content, for this reason E_a values obtained decrease at constant temperature and conversion.

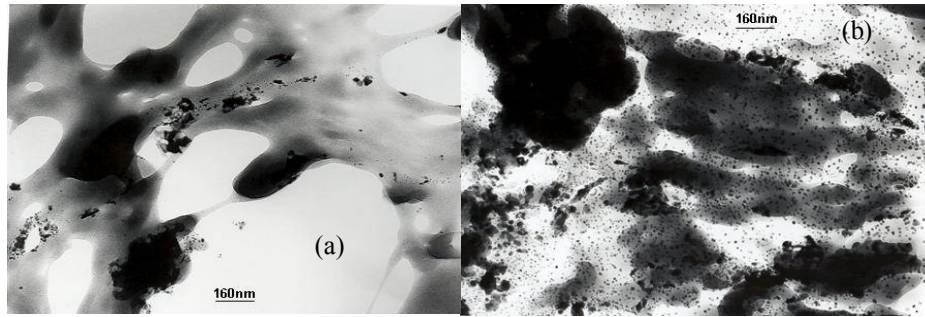


Figure 1: TEM micrographs of the composite with 10 (a) and 30 (b) wt.% .

Constant conversion			Constant temperature		
Filler (%)	Conversion (%)	Ea (kJ/mol)	Filler (%)	Temperature (K)	Ea (kJ/mol)
0	30	34.19	0	630	34.19
	35	35.68		635	37.89
	40	37.89		640	40.08
	45	38.93	10	625	36.18
	50	40.08		630	42.03
10	30	36.58	20	635	49.20
	35	40.16		620	49.88
	40	44.24	30	625	44.52
	45	48.93		630	40.00
	50	53.28		610	55.30
20	30	49.90	30	620	47.64
	35	46.41		625	37.50
	40	44.52	30	610	55.30
	45	42.35		620	47.64
	50	40.43		625	37.50
30	30	55.00			
	35	50.84			
	40	47.64			
	45	43.42			
	50	37.33			

Table 1: Samples activation energy values at constant conversion and temperature.

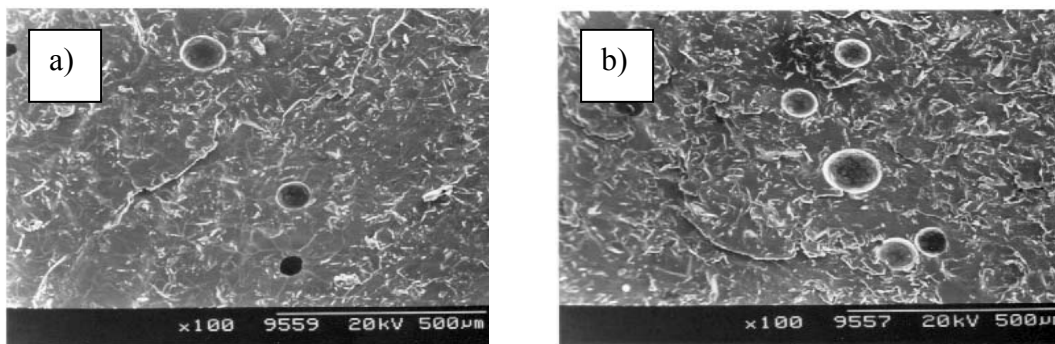


Figure 2: Micrographs of epoxy-amine with copper. a) 20wt.%; b) 30wt.%.