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AN EPOXY RESIN TELLS ITS LIFE STORY
Thermal analysis as a constant companion from development to disposal

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Abstract

With the aid of thermal analysis, epoxy (EP) resins have been characterized from the curing of the components all the way to disposal. The methods employed for the investigations were DSC, TMA, DMA, TG and TG-QMS. The experimental results obtained will be used here to demonstrate the typical possibilities offered by these methods for characterization of an epoxy resin from 'cradle to grave'.

Keywords: curing kinetics, DMA, electronic scrap, epoxy resin, TG-MS, thermal expansion

Introduction

Epoxy (EP) resins are among the thermosets displaying a series of interesting characteristics, which can be adjusted within broad boundaries [1]. They are used as high-grade synthetic resins, for example in the electronics, aeronautics and astronautics industries. Through modification of the hardener systems and appropriate glass or carbon fibers for reinforcement, their properties can be adapted to the particular application. They are distinguished by good bond strength on the most varied materials, a comparatively low thermal expansion, through great toughness and elasticity, good chemical resistance and excellent electrical, mechanical and thermal properties. Of course, epoxy systems also have certain disadvantages, e.g. the high price or, at the latest, when it is time to dispose of them. The following will show that thermal analysis methods are available as quick and efficient procedures for the characterization of the EP resins over their complete life cycle from the curing of the components all the way to disposal.

Experimental

Observations during the birth of an EP resin (Curing of the components and kinetic analysis)

After the resin components (e.g. bisphenol A) have been more or less homogeneously mixed with the hardener (e.g. 4,4-diaminodiphenylmethane), a chemical reaction is set into motion, during which the EP resin is formed by polyaddition.

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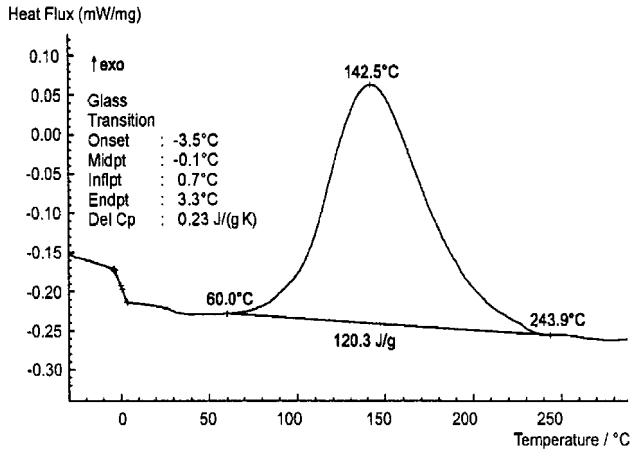

Fig. 1 DSC curve with T_g and exothermal curing reaction

This exothermal curing, during which energy is released, can be readily investigated with the aid of DSC measurements.

Figure 1 shows the heat flow curve of a typical EP resin system in the temperature range –30 to 290°C. The uncured resin was heated at 10 K min^{-1} in sealed aluminum crucibles. The glass transition of the sample was detected at 0°C (midpoint), i.e. the transition from the amorphous-solid state in a viscous-fluid phase. The exothermal curing reaction begins at 60°C, displays its maximum peak at 143°C and is completed at 244°C. The heat of reaction is 120 J g^{-1}. Normally, industrial curing is carried out isothermally at the highest temperature possible without damaging the component. With the aid of kinetic analysis according to the principle of multivariate nonlinear regression [2], it is possible to draw conclusions about the curing time and degree of conversion at defined temperatures through dynamic DSC measurements executed at a minimum of three significantly different heating rates.

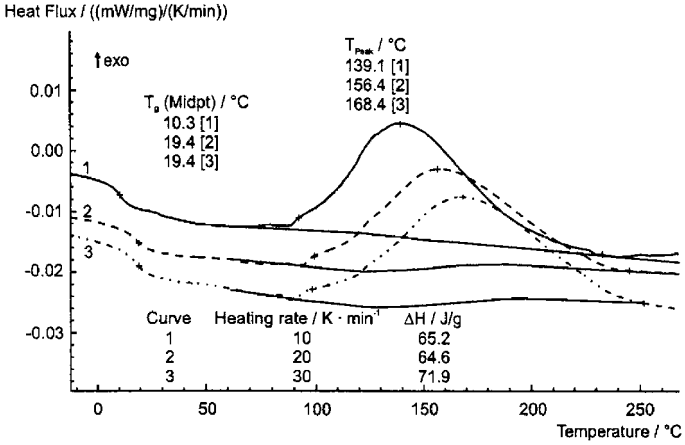

Fig. 2 Curing at different heating rates

Figure 2 shows the DSC results for an epoxy resin with inorganic filler measured at heating rates of 10, 20 and 30 K min^{-1}. Through kinetic analysis of the experimental data and assuming a three-step consecutive reaction as shown below, a high quality of fit is achieved (correlation coefficient 0.9985) for all three curves.

$$A \xrightarrow{F_1} B \xrightarrow{F_1} C \xrightarrow{F_n} D$$

F_1: 1st-order reaction
F_n: *n*th-order reaction

Kinetic parameters:			
	$A \rightarrow B$	$\log(A/s^{-1})$	23.51
		E/(kJ mol^{-1})	175.59
		order of reaction	1
		portion of reaction	1.1%
	$B \rightarrow C$	$\log(A/s^{-1})$	7.14
		E/(kJ mol^{-1})	67.98
		order of reaction	1
		portion of reaction	14.3%
	$C \rightarrow D$	$\log(A/s^{-1})$	3.88
		E/(kJ mol^{-1})	48.78
		order of reaction	1.5
		portion of reaction	84.6%

The good fit is clearly shown in Fig. 3. From the kinetic data, statements can now be made about the degree of conversion at a certain temperature or after a certain period of time. Thus, it can be seen from Fig. 4a that for 120°C this EP is not completely cured after 26 min. (The product D is reaching only 87% out of 100%.) At 150°C the crosslinking is finished, because the end product D has reached practically 100% (Fig. 5) after 26 min.

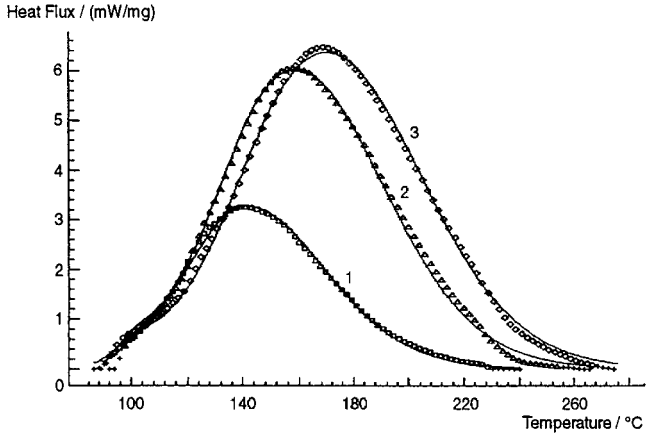

Fig. 3 Kinetic fit of experimental data (□, Δ, ◊)

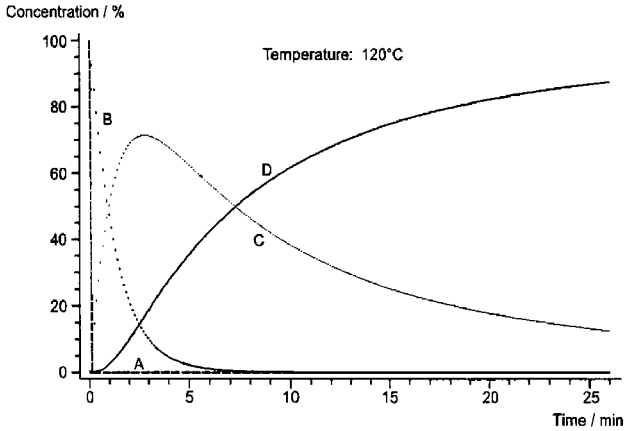

Fig. 4a Reactants as a function of time at 120°C (0–26 min)

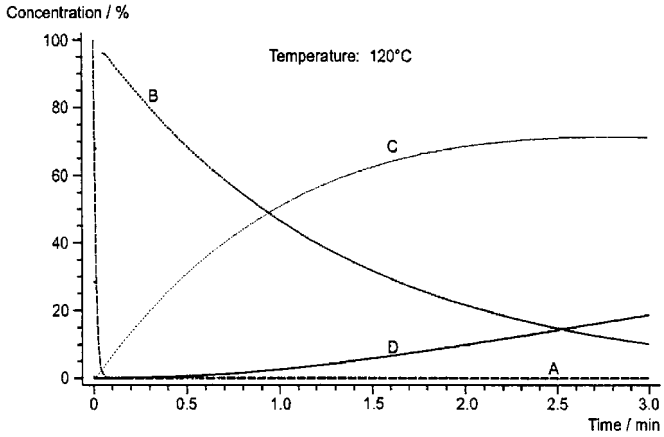

Fig. 4b Reactants at the start of reaction at 120°C (0–3 min)

Thermal expansion (Stability even at high temperatures)

The life of the EP resin is of course appropriated – one of the main applications being to protect other materials chemically or mechanically. The thermal expansion behavior of EP should be known through the desired intensive combination with other materials. In the stricter sense this means that the thermal expansion of the EP should lie in the range of the embedded components (e.g. Si wafer), in order to prevent mechanical stress or separation of the resin when the temperature changes. This statement also holds for the curing process. The expansion can, for example, also be influenced by relevant fillers. This becomes clear in the TMA example shown in Fig. 6, which depicts the strong anisotropic behavior of a glass-fiber-reinforced printed circuit board. Measured in the direction of the board thickness (cross-ply), a

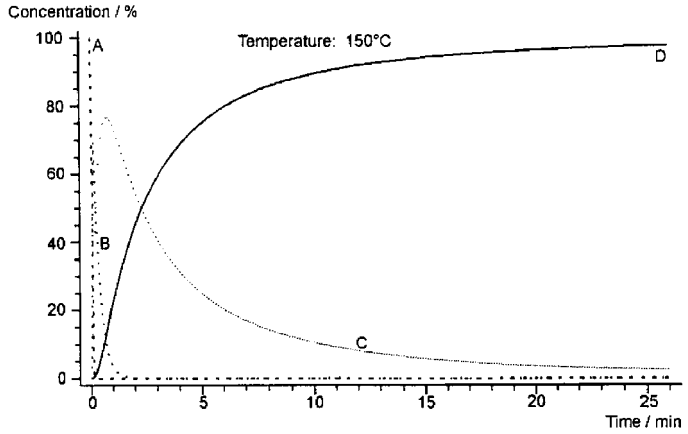

Fig. 5 Reactants as a function of time at 150°C

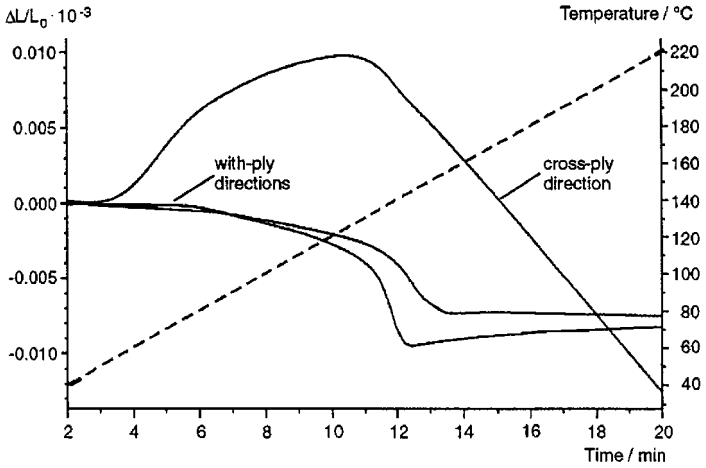

Fig. 6 TMA (expansion), glass-fiber-reinforced EP

large expansion is observed up to the glass transition at 120°C. Due to the influence of the glass fibers, the expansion is very slight in the two longitudinal (with-ply) directions.

Dynamic-mechanical analysis (Flexibility and elasticity are necessities of life)

Not only thermal expansion, but elasticity and flexibility are also important in the life of an EP resin. DMA is a popular and proven method for measuring the viscoelastic properties as a function of temperature, load and frequency [3].

A carbon-fiber-reinforced EP composite with applications in the aerospace industry was selected as an example and measured in the three-point bending mode at 1 Hz. It is for just such applications, in which a great deal of money and possibly human lives are at stake, that it is of course of immense importance to use extremely

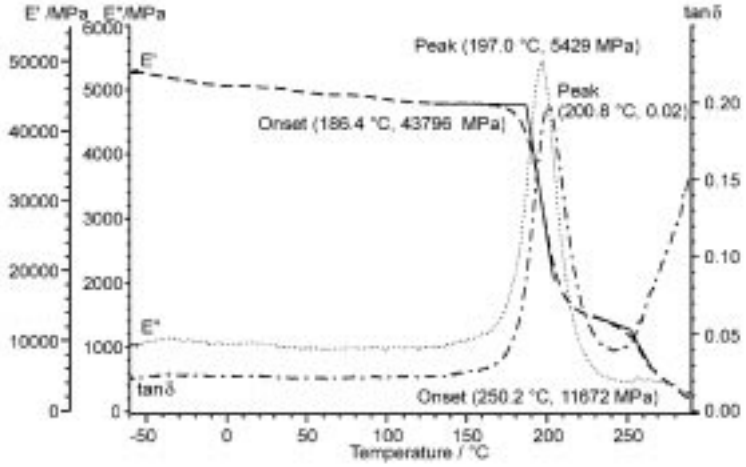

Fig. 7 DMA curves – carbon-fiber-reinforced EP

reliable and resistant components. Figure 7 shows the drop in stiffness (expressed through the storage modulus, *E′*) from approx. 44000 MPa at approx. 186°C to approx. 14000 MPa at 220°C. This glass transition can also be evaluated as a damping peak of the loss modulus, *E″*, at 197°C or of the loss factor, tanδ, at 201°C. At 250°C, delamination starts, which yields a second decrease in stiffness (*E′* onset).

Thermogravimetry (The partner through life is also checked thoroughly)

As a rule, electronic components such as semiconductors are manufactured and processed prior to encapsulation in the EP resin. Thus, a Si wafer undergoes a number of etching and passivation and bonding processes, etc. before reaching its final

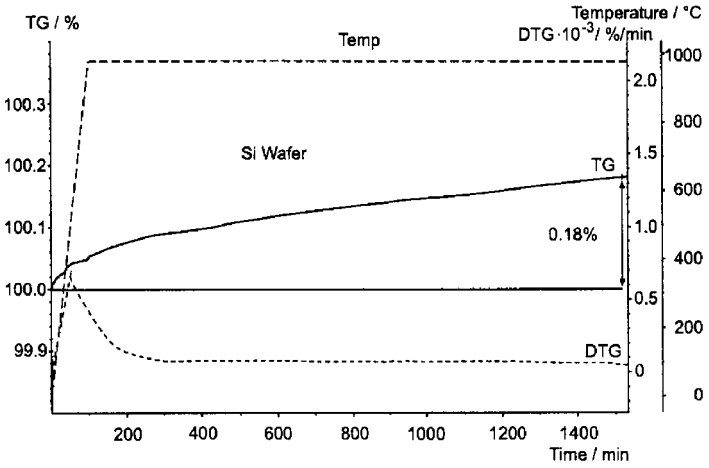

Fig. 8 Oxidation of a Si wafer

operability. These types of passivations (usually surface oxidation of the silicon to SiO_2) can be investigated by means of thermal analysis. With the aid of high-precision thermobalances, such oxidation processes can be measured as a function of temperature and time at different O_2 partial pressures. The thickness of the oxide layer can be calculated from the mass increase and the sample geometry. Figure 8 shows the oxidation of a Si wafer during a 23 h exposure to N_2/O_2. It can be clearly seen that after 7 h the oxidation behavior of the surface changes from exponential to a practically linear function of time, which is clearly demonstrated through the DTG curve.

TG/DSC coupled with mass spectrometry (New partner – new tasks, at the end of life is disposal)

Silicon is a much-studied semiconductor material, whose properties, and thus, the limits during application are well known.

For special applications, compound semiconductors are very promising materials. Among the variety of these substances (e.g. GaAs, CdTe etc. representing the so-called III-V or II-VI semiconductors) the I-III-VI2 semiconductors with a chalcopyrite structure [4] also show interesting electronic and electro-optic characteristics due to the direct energy band gap. Here, however, the problems in production and crystal growth increase, since now, in addition to the electrically active impurities, the stoichiometry plays a major role. With a capable thermobalance coupled with a quadrupole mass spectrometer [5], it is possible to prove, for example, that the synthesized $CuGaSe_2$ was contaminated with I_2 and that there was still excess selenium in the batch. Because selenium usually exists in the amorphous state, the conventional characterization by X-ray diffraction analysis is not possible. Figure 9 is a 3D plot of the TG-MS results for this $CuGaSe_2$ sample. A TG step, during which the I_2 (impurity) and excess selenium (Se_3) are released, is detected between 300 and 500°C. Perhaps, in the not-too-distant future, the task of the EP resin could also be

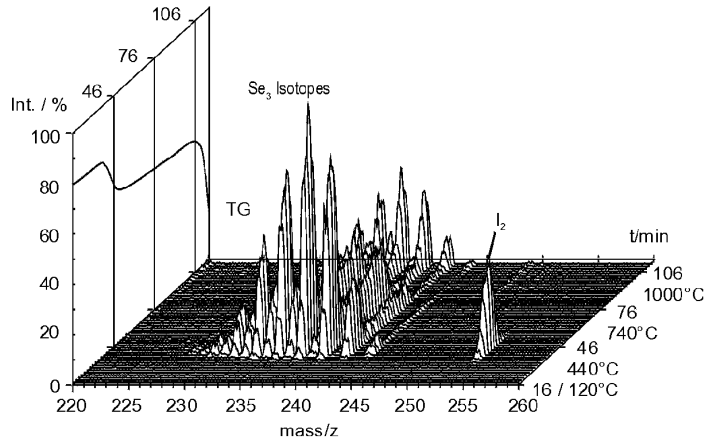

Fig. 9 3D TG-MS plot of $CuGaSe_2$

to protect, both physically and chemically, such semiconductors at elevated temperatures as well.

The end of the life of an electronic component usually concludes the life of the EP resin bodyguard as well, i.e. in this case it accumulates as electronic scrap. In highy industrialized countries, great efforts are being made to recycle this in part 'valuable', in part problematic scrap, or to dispose of it only in such a way that is toxicologically quite safe. The most common method is the thermal disposal (incineration, pyrolysis) of the material [6], which is sometime preceded by treatment with mineral acids, leaching solutions or solvents. These 'pretreatments' can unmistakably change the behavior of the EP matrix during pyrolysis. Figures 10 and 11 depict different decomposition behavior in electronic scrap, treated in one case with a

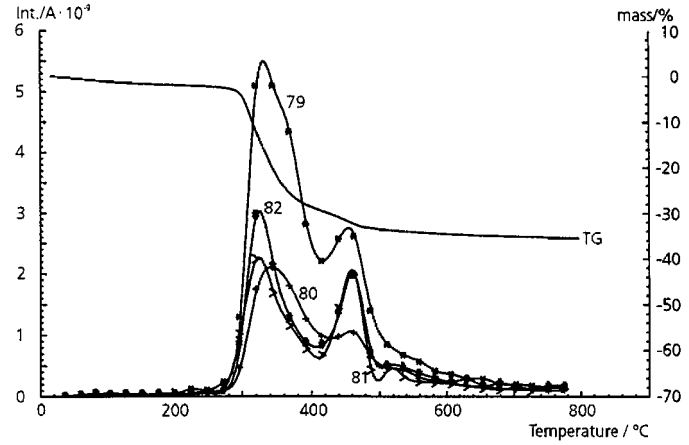

Fig. 10 TG-QMS of untreated milled electronic scrap

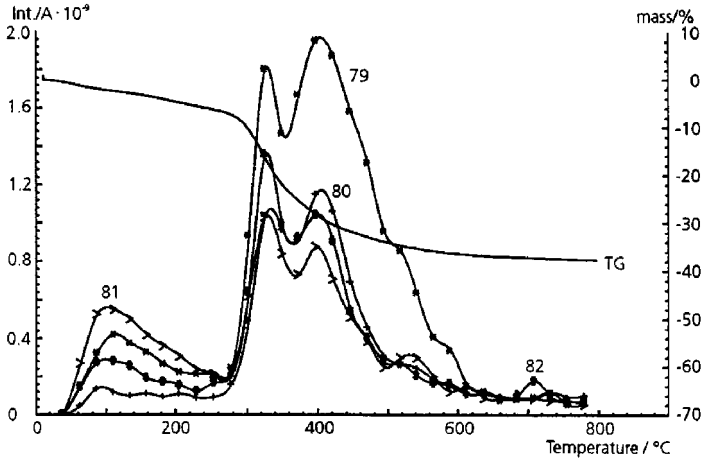

Fig. 11 TG-QMS results for electronic scrap treated with acids and milled

HCl/HNO_3 mixture and in the other case with no pretreatment. It is clearly recognizable that in the pretreated sample, the Br (mass numbers 79, 81 amu), which is present in the printed circuit board as a fireproofing agent, is released at a lower temperature in the form of HBr (mass numbers 80, 82 amu).

Conclusions

Thermal analysis offers a wealth of test methods for the characterization of such high-quality synthetic thermosets as epoxy resins. It is possible to investigate the curing of the components, the thermal behavior of the cured resin – with and without fillers, the thermal and thermomechanical stability, as well as the decomposition products resulting during disposal.

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