

Predicting thermal degradation mechanisms in polymer composites

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Kinetic modeling and structural analyses are used to determine degradation pathways in metal-filled epoxy materials.

Polymer composites that contain metal particles are a fascinating class of materials, particularly because of their valuable and wide-reaching applications. These composites can be either electrically/thermally insulating or conducting materials, both of which are equally useful.^{1–5} Insulating composites are applicable as thermal greases, thermal interface materials, and electric cable insulations. Conductive composites can be used in thermoelectrical and thermomechanical applications, such as for solar devices. Nevertheless, there are still several important issues with these materials that remain to be addressed. One necessary task is developing process control for their eventual efficiency optimization. This task requires profound insights into the materials. As well as their structures, the temperature-dependent processes that occur within the materials need to be considered.

Kinetic analysis of thermally activated condensed phase processes can be used to determine activation parameters (i.e., activation energies and pre-exponential factors). As such, the transition states, and ultimately, the process mechanisms, can be understood. Kinetic parameters are physically meaningful as they control the process under consideration. These parameters can also be used to predict the thermal stability/life of materials outside of the experimental range.⁶ Thermally activated condensed phase processes, however, are known to be particularly complex. Indeed, even apparently simple reactions can consist of multiple steps.

We have therefore recently proposed a new and advanced kinetic approach for modeling condensed phase processes.⁷ We can apply this same methodology to obtain reliable mechanistic information on the thermal degradation of polymer/metal composites. The polymer matrix that we use in our experiments is diglycidyl ether of bisphenol-A, which is associated with a hardener (triethylene tetramine). The filler of our composites is a commercial powder of metallic tin (β -Sn) from Panreac. This powder has a purity of about

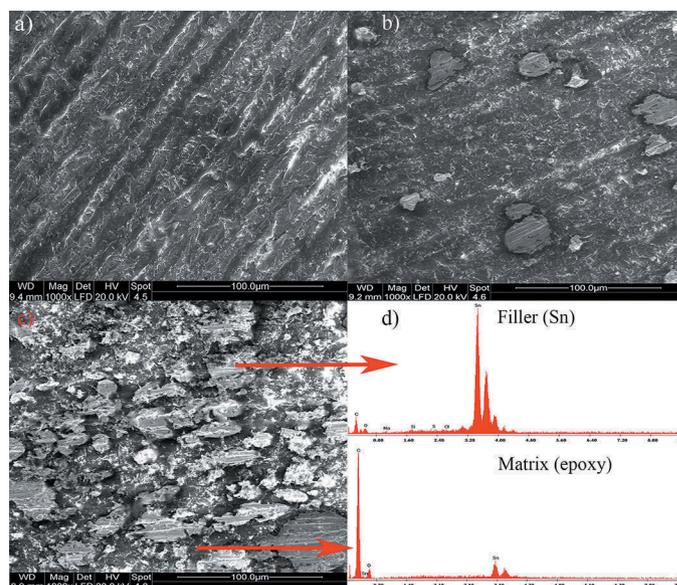


Figure 1. Scanning electron microscope images of (a) pure epoxy, (b) insulating epoxy/tin composite (epoxy/Sn-I), and (c) conducting epoxy/tin composite (epoxy/Sn-C). (d) The energy dispersive x-ray diffraction spectra from the filler (tin) and matrix (epoxy) of the epoxy/Sn-C sample.

97%, a density of 7.29g/cm^3 , an average grain size of $15\pm 10\mu\text{m}$, and an electrical conductivity on the order of 10^4S/cm . We follow the same procedure to prepare all our composite samples, which has previously been described.^{3,4}

After our epoxy/Sn composite samples have been fabricated, we perform a detailed structural characterization of them. For this purpose, we choose a pair of insulating and conducting composites (epoxy/Sn-I and epoxy/Sn-C, respectively). We then use scanning electron microscopy (SEM) and x-ray diffraction (XRD) to analyze the dispersion of the metallic particles inside the composites, the polymer–metal interfaces,

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as well as the number and types (crystallinity and amorphicity) of internal phases that are present. Cross-sectional SEM images of the epoxy and epoxy/Sn composites (e.g., those shown in Figure 1) reveal the interior morphologies and the effect of introducing Sn into the epoxy matrix. Our SEM and XRD results suggest that the composites are fairly homogeneous and that the interactions between the epoxy and Sn probably have a physical nature.

Once our structural analyses show that the fabricated composites are suitable for further characterization, they can progress to the thermoanalytical stage of our method. We use thermogravimetric analysis (TGA) to collect the thermoanalytical data for the composites. We make the TGA measurements in a non-isothermal experiment mode, at different heating rates. We are thus able to conduct a thermal degradation kinetic study of the composites from 30–600°C under nitrogen flow. The apparent thermal behaviors of the epoxy and epoxy/Sn composites are shown in Figure 2. We find that the thermal degradation responses of the epoxy/Sn-I and epoxy/Sn-C composites can be explained reasonably through the variation of specific heat, as well as the changing catalytic activity of Sn with temperature in the epoxy.

We also conduct kinetic modeling on the thermoanalytical data from the epoxy/Sn composites to obtain an in-depth understanding of the samples' thermal behaviors. We use the basic condensed phase kinetic equation to model the thermally stimulated process. This equation can be used to determine the reaction rate from the gas constant, the pre-exponential factor (describes the collision frequency of particles that are involved in the formation of the activated complex), the activation energy barrier of the reaction, and the degree of

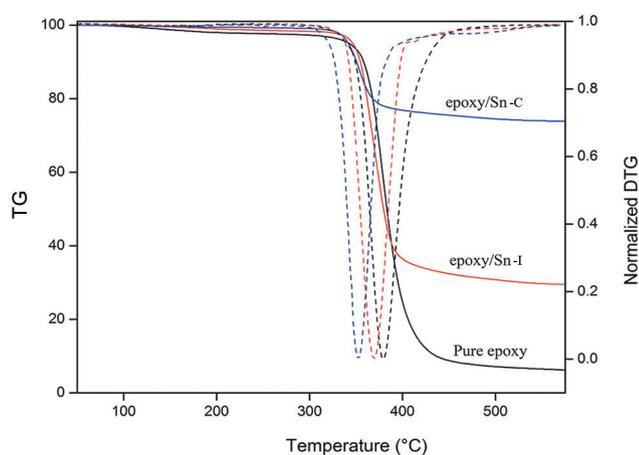


Figure 2. Thermal behavior of pure epoxy and epoxy/Sn composites. Thermogravimetric (TG) and derivative of TG (DTG) curves (solid and dashed lines, respectively) for pure epoxy (black), epoxy/Sn-C (blue), and epoxy/Sn-I (red) are shown.

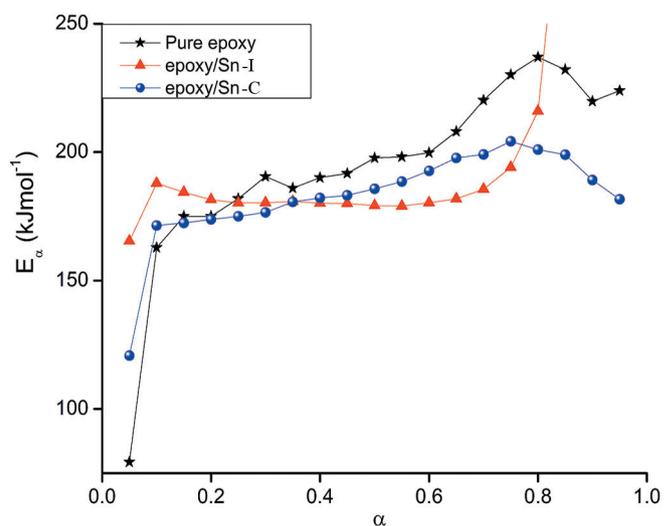


Figure 3. Variation in activation energy (E) with the degree of reaction advancement (α), calculated using kinetic analysis. Results are shown for pure epoxy and epoxy/Sn composites.

conversion (describes the reaction mechanism). The activation energies of epoxy and epoxy/Sn composites can be determined by several different kinetic methods. The results from our generalized method are shown in Figure 3. In the next step of our approach, we use the advanced reaction determination methodology⁷ to evaluate the reaction models of the epoxy and epoxy/Sn composites. For this, we use a fundamental mechanistic function. We thus generate theoretical reaction rate curves by taking the determined kinetic parameters⁵ into account. Our theoretical results are in good agreement with our experimental data. In our final step, we combine our structural characterization and kinetic analysis results to predict the thermal degradation mechanisms of the epoxy/Sn composites. We are thus able to compare these results to the reaction mechanisms of epoxy/zinc and epoxy/aluminum composites.^{3,4}

In conclusion, we use a kinetic modeling approach—combined with structural analyses—to predict the thermal degradation mechanisms that operate within metal-filled epoxy composites. We are continuing to use this approach to study a variety of different materials. We are currently testing composites of urea-formaldehyde cellulose filled with tin, zinc, and aluminum. The ultimate goal of our research is to develop economical, environmentally friendly, and multipurpose polymer composites that have excellent thermal, electrical, mechanical, and optical properties for several applications.



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