

Real Time In-Situ Spectroscopic Characterization and Modeling of Radiation Induced Cationic Polymerization of Glycidyl Ethers

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Radiation curable polymeric materials for composites offer a wide range of advantages over traditional thermally cured systems, including, low energy consumption and reduced manufacturing costs. However, such materials suffer from relatively poor mechanical properties. Moreover, the curing behavior of such systems as defined by the relationship between chemical kinetics and key processing variables is not fully understood. In order to design improved epoxy based electron beam (EB) curable systems, and in order to develop appropriate process models, a detailed knowledge of the kinetics of epoxy cationic polymerization induced by UV or EB irradiation is required. In this work, we present our development of a technique based on near infrared (FIR) spectroscopy for performing real-time *in-situ* kinetic analysis of radiation induced cationic polymerization of epoxy systems including phenyl glycidyl ether (PGE) and diglycidyl ether of bisphenol A (DGEBA). To our knowledge this is the first time such data have been collected for EB induced polymerization. The experimental technique developed in this work proved to be a reliable and reproducible way to characterize the chemical reactions investigated.

A model was developed to describe the intrinsic chemical kinetics and the diffusion limitations for crosslinkable systems and to relate the cure behavior to processing variables. PGE was used as a model compound to assess the intrinsic kinetics of the cationic polymerization reaction. The model was extended to the crosslinking reaction of DGEBA by using a free volume approach to account for diffusion limitations that are typical of the curing of multi-functional resins.

The model predictions show very good agreement with experimental data for the range of conditions investigated. The intrinsic kinetic model and parameters developed for the PGE polymerization **can** be used to accurately predict the behavior of DGEBA systems at low conversions. Furthermore, the cationic active centers originating from the photo-initiator were found to be long lived in relation to typical times for polymerization. Thus in principle living polymerization can be achieved. For the DGEBA systems, the glass transition temperature at a given conversion was found to be independent on radiation intensity and photo-initiator concentration. In all cases, moisture content was found to affect the cure kinetics.

For the EB induced polymerizations, it was found that the same kinetic models developed for the **UV** curing process can be used to accurately represent experimental data. Furthermore it was observed that, with the exception of the initiation rate constant, ZTV and EB induced polymerizations can be described using the same values of the kinetic parameters.

Relationships were developed to relate kinetic parameters to processing conditions, This provides predictive capability for the dependence of chemical conversion on time, temperature, composition and radiation intensity and represents an important step towards the design of improved epoxy networks.