Cationic polymerization of glycidyl ethers and furans: improved electron beam and UV cured epoxy networks

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Curing composites using electron-beam radiation (EB) offers significant advantages over traditional thermal curing but is limited by poor mechanical characteristics of the resulting polymers and their composites. Commercially, EB has advantages over thermal processing, for a number of reasons. Among these are rapid curing times, reduced energy requirements, curing at lower temperature, reduced shrinkage and residual stresses, the ability to co-cure dissimilar materials, and long shelf life as well as reduced volatile organic compounds (VOC) emissions. These characteristics allow for the manufacture of complex composite structures using low cost tooling and staged operations. However, composites made from such polymer systems suffer from low compressive strength, poor interlaminar shear strength, and low fracture toughness when compared to incumbent thermally cured systems. Thus, while possessing great processing benefits, EB cured polymers' poor mechanical performance prevents them from being adopted. The objective of this work is to develop a fundamental understanding of the physical and chemical processes underlying EB and ultra-violet (UV) polymerization of epoxy systems that will enable the design of improved systems. Specific goals include (i) obtaining a detailed understanding of the influence of process parameters, particularly water concentration and discontinuous application of EB dose on polymerization behavior, (ii) developing an understanding of relationships among cure process variables with network structure/morphology and properties, and (iii) designing new systems with improved properties based in part on the understanding developed in i and ii. EB and UV curing processes were monitored in-situ using near infrared (NIR) fiber optic spectroscopy. Based on such data, a detailed kinetic model was developed that elucidates the influence of water on EB induced polymerization of glycidyl ethers. Moreover, the influence of initial water concentration on final polymer behavioral characteristics were assessed quantifying the potentially deleterious effects of not controlling humidity during EB processing. Previous studies of epoxy cure behavior have been conducted under continuous irradiation. The processing of parts via EB generally occurs in a step-wise fashion. The transient behavior upon stopping irradiation, "dark reaction," was examined and revealed that while pronounced initial reductions in reaction rates occur, active centers responsible for polymerization persist for many thousands of hours. Therefore for practical purposes this is a living polymerization. It was found that traditional deactivation models do not capture the observed behavior suggesting that the combination of diffusion limitations and chain transfer reactions need to be considered as a possible explanation. A novel class of comonomers for improving the fracture toughness of EB and UV cured epoxy systems was discovered and studied. These monomers are based on the five-member furan ring that was shown to ring open and copolymerize with glycidyl ethers. By using tetrahydrofuran, a string of four methylene units is inserted in the network providing chain extension and greatly increased fracture toughness. Multifunctional monomers based on this chemistry were developed that increase the fracture toughness of the base epoxy resin five fold while maintaining the glass transition temperature. This is a remarkable achievement because it is an enabling technology that solves the major deficiency of EB and UV cured epoxies.