

Application of Time-Resolved Pulse Radiolysis Technique in the Investigation of the Mechanism of Epoxy Resins Cationic Polymerization

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Objective- E-beam induced cationic polymerization of epoxy resins is of great interest to industry because it offers many advantages over thermal curing methods. Despite good thermal properties, epoxy-based composites prepared using e-beam curable resins exhibit low compression strength, poor interlaminar shear strength, and low fracture toughness. We have initiated a comprehensive study to investigate the mechanism of cationic polymerization of epoxy resins in an attempt to identify the factors that are responsible for these shortcomings associated with e-beam curable resins. The objectives of this investigation is to use pulse radiolysis technique as a tool to identify the reactive intermediates involved in the polymerization process. We have employed pulse radiolysis in conjunction with optical detection and Electron Paramagnetic Resonance (EPR) spectroscopy to elucidate spectral features and the identity of reactive intermediates involved in the cationic polymerization of epoxy resins.

Results- E-beam induced cationic polymerization of epoxy resins using CD-1012 as the photoinitiator is believed to proceed via protonation of the epoxy oxygen by the super acid HSbF_6 (as a viable path) which is formed on decomposition of CD-1012. We have employed bromophenol blue, an acid indicator, in a methanol solution of CD-1012 to monitor the formation of super acid (upon radiolysis of CD-1012) using absorption spectroscopy. Upon formation, the superacid will induce a change in the absorption spectrum of bromophenol blue that can be easily detected. Our data indicate that HSbF_6 is produced on γ -radiolysis of CD-1012 in methanol. Although an increase in total dose is accompanied by an increase in the acidity of the media, an increase in the dose rate (from 1 Krad/min to 20 Krad/min) causes a decrease in acidity. Pulse radiolysis/optical detection and pulse radiolysis/EPR techniques were both employed to obtain information on the spectral features and lifetime of reactive intermediates (transients) produced by e-beam excitation of PGE/CD-1012 and Tactix123/CD-1012 solutions. A 10 ns pulse of a linear accelerator was used as the excitation source to produce the transients observed in PGE/CD-1012 and Tactix123/CD-1012 solutions. Our transient absorption and decay data indicate that radical cations of both PGE and Tactix123 are involved in the polymerization process. Furthermore, we observe the formation of other carbon-centered radicals that are generated by the interaction of initially formed radical species (from CD-1012 by cleavage of the carbon-iodine bond) with both monomers. Spectral characteristics of these transients and their lifetimes will be discussed in more detail during this presentation.

Significance of the study- E-beam curing is a multibillion-dollar industry with enormous potential for new and improved materials for application to automobiles, airplanes, spacecrafts, and sporting goods. A thorough understanding of the polymerization mechanism coupled with the fundamental knowledge gained from such studies can lead to synthesis of new high performance materials with improved thermal and mechanical properties.

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