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Radiation Curing by Cross-Linking Polymerization of Multifunctional Monomers: a Comparison Between Free Radical and Cationic Mechanisms

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Radiation-curing by polymerization of multifunctional monomers is a well-established technology in the field of coatings and adhesives as well as in the graphic arts. UV-visible light and high energy radiation are alternative activation processes exhibiting their specific scope, advantages, and limitations depending on the application. The situation is quite different when the industrial goal is to cure thick and large parts of composites reinforced by fillers or by fibrous materials that induce opacity with respect to UV visible light. High energy radiation processing has been identified since decades a promising method for performing out-of-autoclave curing, with several advantages in terms of processing time, energy consumption, environmental footprint and sanitary concerns. The challenging objective of developing the EB/X-ray curing technology for high performance composite materials drives the needs of the advanced knowledge and understanding of reactivity - structure - properties inter-relations. Our paper will focus on the nanostructural features of radiation-cured networks.

The radiation-induced polymerization of multi-acrylate monomer compositions is known to proceed heterogeneously at various dimension scales, depending of monomer composition. In radiation-cured materials based on a single type of monomer, the network were shown to display heterogeneities of cross-link densities resulting from a complex interplay between mechanistic and kinetic factors along the solidification process. Compared to free-radical chain polymerization, radiation-initiated cationic polymerization exhibits peculiarities at the different steps of the chain process (complex initiation and propagation mechanisms, pseudo-living character ...). The influence of these features on the reactivity and on the microstructure of multifunctional aromatic epoxy monomers and of their acrylate analogs has been examined using various types of radiation (UV, visible, EB, X-ray). Complementary spectroscopic and analytical methods were implemented in order to correlate the changes of network physical properties with the progress of polymerization.

AFM analysis of the networks in the topographic, phase contrast and indentation modes provides quite informative data with indications on the actual dimensions of the soft and rigid domains, and of their evolution, as the curing level is driven to higher values.

Solid-state proton T2 NMR relaxation experiments were also performed on radiation-cured materials with valuable quantitative information on the local mobility in the nanoheterogeneous samples as well as on the associated fraction of material, as polymerization proceeds.

On the basis of these observations and measurements, a consistent scenario for the build-up of radiation-cured networks is proposed for both types of polymerization mechanisms. The influence of this general behavior is discussed in the perspective of elaborating materials with demanding use properties.

Country/Organization invited to participate

France

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