DEVELOPMENT OF PHOTOCURABLE GRAPHENE COMPOSITES DERIVED FROM EPOXY/THIOL-ENE PHOTOPOLYMERIZATIONS WITH SHAPE-MEMORY PROPERTIES

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The development of smart materials with actuation properties is attracting increasing interest due to their potential uses in high technology and in medical applications. Shape-memory polymers are smart materials that change their form when subjected to a variation in temperature. To display shape-memory properties, the polymers must be constituted by a hard phase and a soft phase. In this work, polyether-polythioether/graphene composites with shape-memory properties were prepared by photopolymerizing an epoxy/thiol-ene photocurable formulation that comprised an epoxy resin, the diglydidyl ether of bisphenol A [DGEBA], and a thiol system that included the N1, N1, N6, N6, tetraallyl hexane 1,6-diamine [ALA4] as curing agent, a tetrafunctional thiol like the pentaerythritol tetrakis (3-mercaptopropionate) [PTKMP] and dimethoxyphenyl acetophenone [DMPA] as radical photoinitiator. To modulate the inherent shape-memory properties of the polyether-polythioether co-network, parameters like the concentration of thiol-ene system as well as the concentration of graphene, were varied. The intention of adding graphene to the formulation was to improve, on one hand, the mechanical properties of the composites and on the other hand, the thermal conductivity. The kinetics of photopolymerization of the epoxy/thiol-ene/graphene formulations were determined. The thiol-ene concentration was varied from 20-40 mol % and the concentration of graphene was varied from 5-15 % w/w. It was found that despite the presence of the graphene nanoparticles that could scatter the UV light, all photocurable systems displayed high reactivity. The formulation with 40 mol % of the thiol-ene concentration and 15 % of graphene displayed the higher photopolymerization rate and conversion, achieving 90 % in two minutes.

The shape-memory properties were analyzed by means of dynamic mechanical analysis (DMA). Parameters like shape fixity (R_f) shape recovery (R_r) and velocity of shape recovery were determined. The presence of the soft-phase (polythioethers), the hard-phase (polyethers) as well as the nanoparticles of graphene resulted in a complex behavior of the composites. Values of R_f that ranged from 85-99% as well as values 90-98 % of R_r were observed. The composite with the higher concentrations of both the thiol-ene system and of graphene displayed the highest velocity of shape recovery (1.97 s).