MATERIALS AND METHODS

Resins were formulated with two photoinitiators, one active in the visible region of the spectrum (Irgacure 784 (a titanocene derivative from Ciba Specialty Chemicals)) at 0.1 wt% and one active in the near ultraviolet (Irgacure 819 (a phenylphosphine oxide derivative from Ciba)) at 0.25 wt%, unless otherwise stated. The specimens were fully cured under irradiation for four minutes from a visible light dental curing lamp at room temperature. The visible photoinitiator photolyses rapidly and photobleaches significantly during the curing stage, thus the ultraviolet photoinitiator was included in the formulation to ensure residual photoinitiator capable of introducing radicals in each specimen upon irradiation. Each resin consisted of a stoichiometric ratio of pentaerythritol tetra(3-mercaptopropionate) (PETMP) and triethylene glycol divinylether (TEGDVE) as well as varying concentrations of 2-methyl-7-methylene-1,5-dithiacyclooctane (MDTO). A stoichiometric ratio of 1,6-hexanedithiol (HDT) and TEGDVE was used as a reactive, non-crosslinking diluent for the PETMP/TEGDVE.

Specimens for strain and strain/recovery experiments had approximate dimensions of 12 mm long × 3.3 mm wide × 0.9 mm thick. These specimens were mounted in a Perkin Elmer DMA7. For the constant force strain tests, a constant tensile force of 300 mN (~10^5 Pa) was applied from t = 0 and continued throughout the experiment. From t = 2 min to t = 62 min, the specimens were irradiated in the near UV-visible region (320-500 nm, 30 mW.cm^-2). For the
strain/recovery tests, the tensile force was alternated between 300 mN for 3 minutes and 0 mN for 5 minutes in each experiment. The specimens were not irradiated for the duration of the experiments in part A. In part B, the specimens were irradiated (320-500 nm, 30 mW.cm\(^{-2}\)) during loading and were not irradiated during unloading.

Temperature rise experiments were performed by embedding micro-thermocouples in specimens equivalent to those tested in the strain experiments which were irradiated for 15 minutes under equivalent experimental conditions as those used in the strain experiments.

Specimens for stress relaxation experiments had approximate dimensions of 60 mm long × 7 mm wide × 0.9 mm thick. These specimens were mounted in a MTS Synergie 100 mechanical tester fitted with a 10 N load cell and the initial gap between the grips was set to 40 mm. For the ‘constant strain’ experiments, a strain rate of 0.0064 min\(^{-1}\) was applied until a strain of 0.032 was achieved, then maintained for the remainder of the experiment. Specimens were then irradiated (320-500 nm, 20 mW.cm\(^{-2}\)) for 15 minutes, starting 30 seconds after the strain of 0.032 was achieved. For the ‘constant initial stress’ experiments, a strain rate of 0.0064 min\(^{-1}\) was applied until a stress of 0.15 MPa was achieved then the strain was maintained for the remainder of the experiment. The specimen was then irradiated (320-500 nm, 20 mW.cm\(^{-2}\)) for 15 minutes, starting 60 seconds after the stress of 0.15 MPa was achieved.
Stress gradients through specimens were introduced by irradiating rectangular, optically dense specimens on one side only that were under tension. These specimens were almost equivalent to those used in the stress relaxation experiments; however, they contained 0.1 wt% Irgacure 784 and 2.5 wt% Irgacure 819 before polymerization to yield a significant optical gradient through the specimen thickness. They were irradiated at 365 nm, 20 mW.cm\(^{-2}\) for 15 seconds while under a strain of 0.0375.