Residual stresses developed during curing of epoxy thermosets in thick section casting is a serious technical problem leading to cracks and other defects during the cure process. Residual stresses in cast thermosets can be managed by flexibilization and or toughening of the thermoset. Incorporation of disparate building blocks in an epoxy resin, composed of so-called soft-segment and hard-segments has been utilized to prepare such flexibilized thermosets that are resistant to residual stress related defects. Formulation selection can result in polymers that exhibit material behavior tunable from elastomeric behavior to a plastic-plastic behavior with high glass transition temperatures, which arises from a range of morphologies achieved during cure induced phase separations. The multi-phase morphology also results in higher glass transition temperatures and novel cure profiles. Modification of the soft-segment components in the resin has been used to tune the mechanical behavior of the thermosets.