

SEQUENTIAL PHOTO-THERMAL CURING OF (METH)ACRYLATE-EPOXY THIOL FORMULATIONS

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In this work, a novel dual-curing procedure has been developed. It is a combination of a first radical UV-initiated thiol-(meth)acrylate reaction, followed by a second thermal thiol-epoxy step catalysed by a base. Since (meth)acrylates can lead to homopolymerization by radical mechanism, the amount of thiol have to be optimized to reach cross-linked materials with T_g s above room temperature and good mechanical performance. It should be considered, that if the amount of thiol is too low, epoxy homopolymerization can take place. The use of glycidyl methacrylate in combination with trifunctional meth(acrylates) allow this system to gel in the 1st stage and avoid possible dripping or exudation of free monomers in the storage of the intermediate materials. We selected trimethylolpropane tris(3-mercaptopropionate) as the thiol, 2,2-dimethoxy-2-phenylacetophenone as UV initiator and 1-methylimidazole as the base catalyst.

The curing evolution was studied by DSC and FTIR. All the materials obtained were characterized by thermogravimetry, thermomechanical analysis and tensile tests.

By DSC we could see that when the mol % of thiol in the mixture was lower than 54%, epoxy homopolymerization occurred. We also proved that in the UV-stage acrylates homopolymerized in a lower extent than methacrylates and therefore the amount of thiol in the optimized formulation should be higher. The data of methacrylate final materials revealed higher homopolymerization in the UV-stage, thus, $T_{tan\delta}$'s were considerably higher and the storage modulus (E') at rubbery stage greater than acrylate thermosets due to their higher crosslinking density. Since the epoxy homopolymerization also increases crosslinking density, the lower amount of thiol in the formulation the higher $T_{tan\delta}$ and $E'_{rubbery}$. Methacrylate materials showed higher tensile modulus and stress at break than acrylates. When the concentration of thiol increased in the sample, epoxy homopolymerization was reduced and subsequently, both mechanical properties decreased. Acrylate materials presented higher strain at break and ductility in comparison to methacrylate specimens because of the lower homopolymerization of acrylates. In both type of materials strain at break increased with the proportion of thiol.

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