

Stress-relaxing thermosets with easily regulated bond exchange kinetics

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Introduction

We have carried out stress-relaxation experiments on poly(acrylate) and poly(thiol-ene) based thermosets prepared from in-house synthesized epoxy-acid adducts with acrylate (for the former) and ene functionalities (for the latter). The adducts contain disulphide bonds at their center which allow their cured thermosets to undergo disulphide metathesis when heated above a certain temperature [1]. The possibility of concurrent transesterification, albeit at a significantly lower rate, between ester and hydroxyl moieties present in the components is not discarded (See Figure 1) [2].

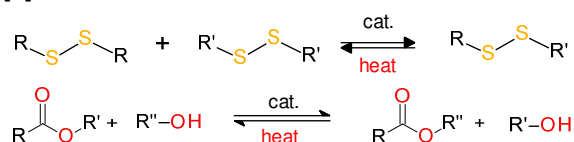


Figure 1. Disulfide metathesis (top) and transesterification reactions (bottom).

As a result of any or both of these exchange reactions, these materials, when strained, can relax stresses at elevated temperatures, without compromising their mechanical properties.

Materials

Two adducts were synthesized and named DAG and DGM, whose molecular structure is given in Figure 2. They are the prevalent reaction products of 4,4'-dithiobutyric acid and either allyl glycidyl ether, abbreviated as AGE (for the former), or

glycidyl methacrylate, abbreviated as GM (for the latter).

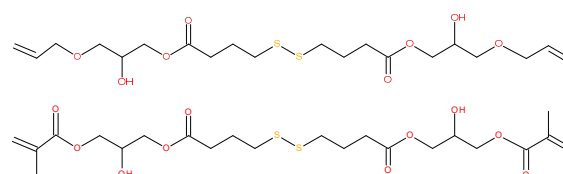


Figure 2. Disulfide containing adducts DAG (top) and DGM (bottom).

For the curing of DAG, a trifunctional thiol, tris(2-(3-mercaptopropionyloxy)ethyl isocyanurate), was used as curing agent. As control and also to partially arrest the stress relaxation capability, 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TATATO), without disulfide bonds, was used as another allylic component along with DAG. For the curing of DGM, hydroxyethyl methacrylate (HEMA) and hydroxyethyl acrylate (HEA) were used as reactive diluents for optimum thermoset properties. DGM:HEMA:HEA weight fractions were 0.5:0.25:0.25. A disulfide-free allylic adduct was also synthesized using azelaic acid instead of 4,4'-dithiobutyric acid to prepare control samples (denoted as AzAcGM) for thermosets based on DGM. Tributyl phosphine (TBP) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were used as metathesis catalysts [3]. Both were at 0.5% (w/w) on total solids. 2% (w/w) of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was used as photoinitiator for both thiol-ene and methacrylate photopolymerization reactions.

Methods

The synthesis of epoxy-acid adducts began with melting of either acid at 100°C, followed by the addition of the epoxide component (AGE or GM) and 0.1% (w/w) of triethyl amine as catalyst. It was necessary to add a radical scavenger, 2,2,6,6-Tetramethylpiperidine 1-oxyl, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) at 0.5% (w/w) for the DTBA-GM reaction to avoid homopolymerization of GM. For either adduct, the mixture was held under agitation for 2h at 100°C after which it was left to cool down to ambient temperature. FTIR spectra confirmed complete epoxy conversion after 24h. We used DMA for storage modulus and tan delta measurements and to monitor stress relaxation (in 3-point bending mode), FTIR to monitor C=C bond conversion during photocuring reactions and to monitor epoxy and carboxylic acid groups during adduct synthesis.

Results and Discussion

In Figure 3, we present normalized stress responses of poly(acrylate) (based on DGM) samples subjected to 1% strain in 3-point bending configuration at 180°C.

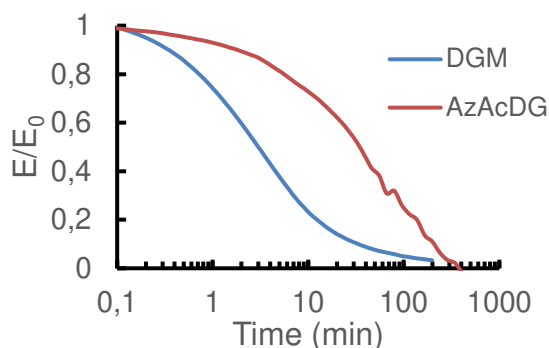


Figure 3. Normalized relaxation modulus in log time. Experiment was carried out at 180°C.

It is hypothesized that the non-sulphur containing thermoset (i.e. AzAcDG) relaxes at a significantly lower rate since the only available relaxation mechanism to this thermoset is transesterification. The DGM thermoset fully relaxes in approximately 3h.

For the optimized version of the DGM thermoset (modified with HEMA and HEA), relaxation was successfully initiated at 120°C. About 45% of relaxation was complete by 3h (Figure 4).

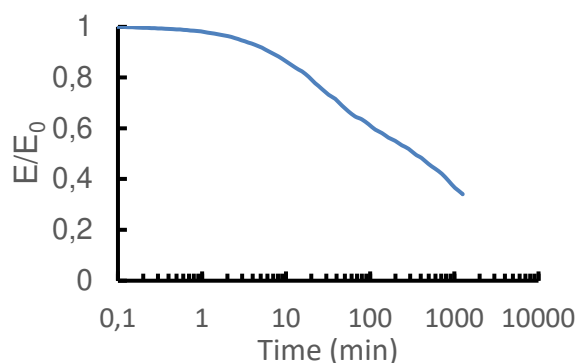


Figure 4. Normalized relaxation modulus at 120°C of optimized DGM (with DGM:HEMA:HEA weight fractions 0.5:0.25:0.25).

Thiol-ene (based on DAG) thermosets can also relax stresses efficiently. Kinetics of stress relaxation can be regulated by their TATATO content (Figure 5).

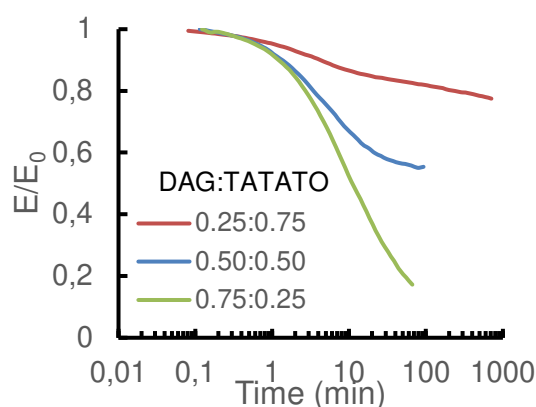


Figure 5. Normalized stress relaxation response of DAG based thermosets at 120°C.

As an application of stress relaxation, cured samples will be tested for malleability and reparability. It is also possible to formulate hybrid systems, such as thiol-ene-epoxy by adding an epoxide component to our DAG based formulations. This would facilitate sequential curing and versatility in processing. Thanks to their desirable viscosity and fast curing kinetics, the formulations are potentially suitable for photocure-based 3D printing.

References

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3. Lei, Z.Q., et al. (2014). Chem. Mat. 26, 2038-2046.