

CONTROLLING SELF-HEALING IN SOFT EPOXY NETWORKS VIA SUPRAMOLECULAR ASSOCIATION AND NETWORK DEFECTS

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ABSTRACT

In recent years, supramolecular hydrogen bonding polymers aroused a considerable interest. Such polymers form a new class of materials, and some of their singular properties are very appealing: low viscosities at high temperatures, slow dynamics at low temperatures and, more recently shown, self-healing abilities.

Today, two main issues slow down their development as materials at a large industrial scale. First, there is still room for improvement of synthesis. Secondly, in comparison to conventional crosslinked networks, these materials have low storage moduli and high viscous losses. Some alternatives can be envisaged to overcome these difficulties. For example, hybrid networks containing both covalent and supramolecular crosslinks could exhibit better mechanical properties and still have self-healing attributes.

We recently reported a facile two-steps synthesis of such hybrid networks from epoxy and fatty acids [1].

In a first step, a mixture of dimers and trimers of fatty acids is end-capped with an hydrogen bonding group, UDETA. The ratio of tri and di-acids is chosen in order to have a high average functionality ($n \sim 2.53$), so that chemically-crosslinked networks are obtained. The second synthetic step is a polyaddition of a stoichiometric amount of epoxy dimers with the remaining fatty acids. It yields soft elastomers, with glass transitions around 15°C.

The two-steps procedure allows for a good control of the composition of the network: the supramolecular content can be varied at will.

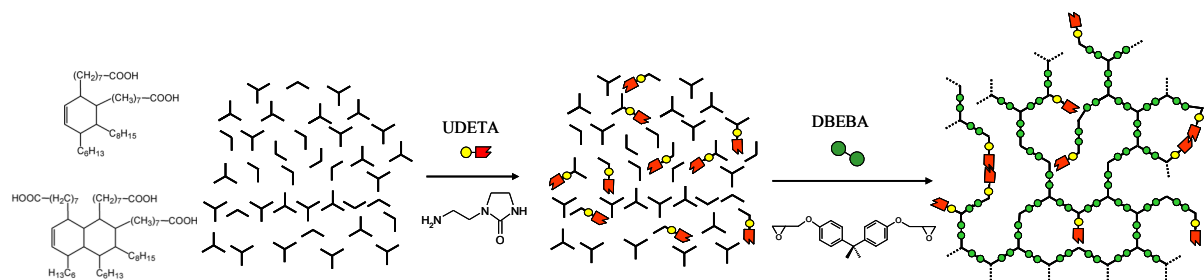


Figure 1: The two-steps reaction procedure.

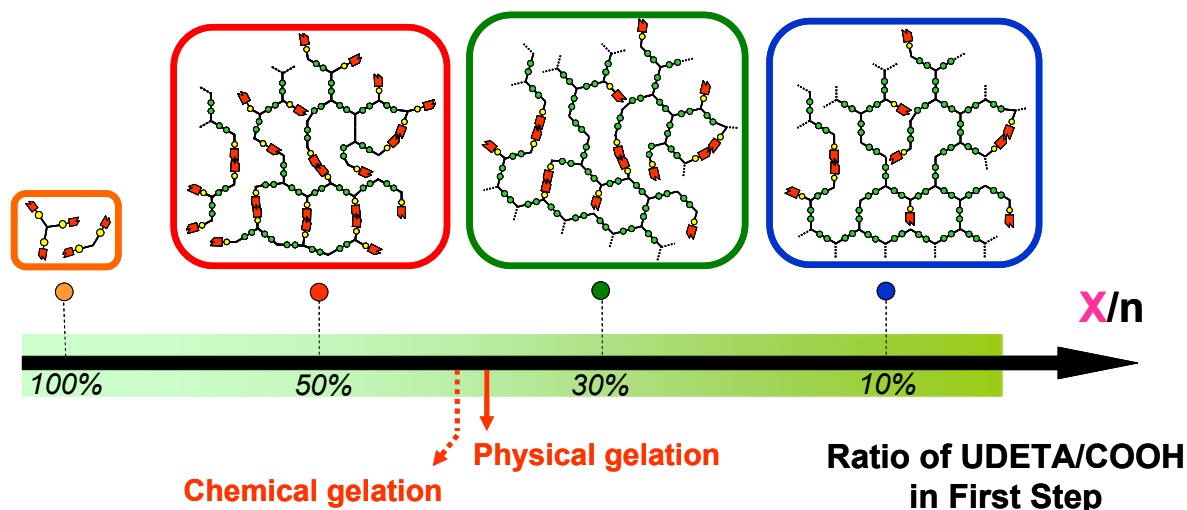


Figure 2: Varying the supramolecular content yields different topologies.

The elastomers obtained exhibit self-healing abilities: broken samples can be mended for a few minutes at room temperature and recover part of their mechanical performances. The self-healing efficiency increases with the supramolecular content in the network and tensile tests show that samples can recover up to 80% of their elastic properties.

By changing the composition of the systems, both network topologies and supramolecular contents can be varied. Thus, these systems constitute a very convenient model to study the relation between network structure and self-healing abilities.

The particularity of our synthesis route is that it introduces supramolecular groups but at the same time produces defects in the network, such as dangling chains or sol fraction. It is known that interdiffusion of defects and sol molecules also results in self-healing properties [2]. In this study, we discuss the respective roles of network defects' interdiffusion and supramolecular association in our networks.

To that purpose, we synthesized different hybrid networks with different contents of associating groups UDETA. Similar networks were also synthesized, by replacing UDETA with a non-associating group, dodecylamine. These networks should have the same structure and defect composition, but do not form supramolecular crosslinks.

The networks were characterized by dynamical mechanical analysis and rheology. The self-healing properties were measured using a tack-like experimental setup [3].

REFERENCES

- [1] D. Montarnal, F. Tournilhac, M. Hidalgo, L. Leibler, Epoxy-Based Networks Combining Chemical and Supramolecular Hydrogen-Bonding Crosslinks, *Journal of Polymer Science, Part A: Polymer Chemistry*, **48**, 2010, pp 1133-1141.
- [2] M. Yamaguchi, S. Ono, M. Terano, Self-repairing property of polymer network with dangling chains, *Material Letters*, **61**, 2007, pp 1396-1399.
- [3] F. Maes, L. Corté et al., to be published.