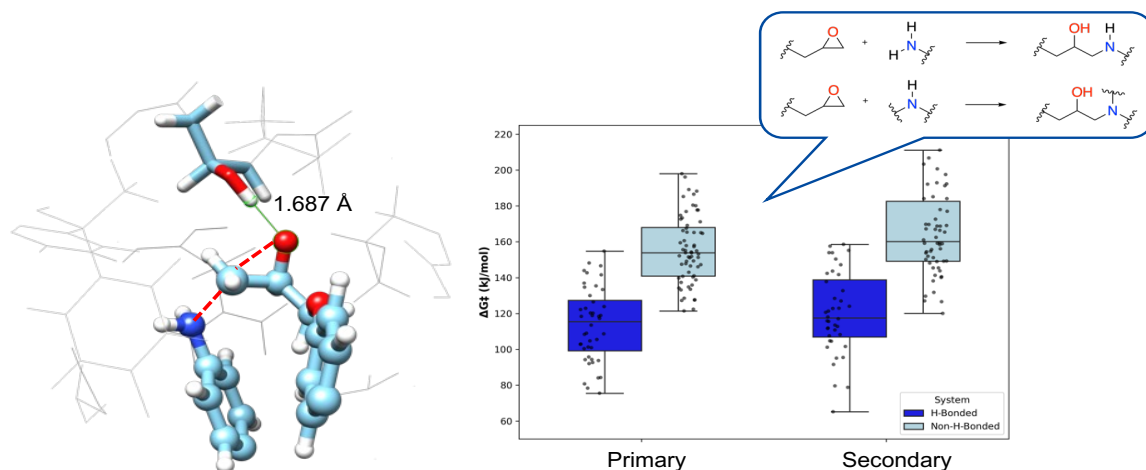


What is the impact of covalent-network formation on the curing kinetics of thermosets?

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In this work, we used a combination of reactive molecular dynamics and QM/MM modelling to fully understand the impact of the local network structure on the kinetics of the curing reaction of thermosets on the atomistic scale. Thermosets are covalently cross-linked glassy network materials, which are widely applied in e.g. airplane construction, as flooring materials or in the renewable energy sector. The attractive mechanochemical properties of thermosetting polymers are strongly coupled to the chemical formation of a covalent network, which happens in the so-called curing reaction of the material. During curing, typically a liquid mixture is converted into a glassy polymeric material in a highly exothermic process. However, the curing kinetics of the individual chemical reaction is strongly dependent on the local environment of the reactive sites, which we expect to strongly depend on the degree of cross-linking. Using a DGEBA/DDS based epoxy example system, we investigated the differences in the curing kinetics starting from isolated gas-phase systems to micro-solvated systems using different continuum approaches. We find that the curing reaction is strongly depended on the reaction geometry and can be facilitated by hydrogen bonding interactions on both the amine and the epoxy sites. However, while such simplified models do qualitatively reflect experimentally observed reaction energetics, they cannot elucidate the effect of the evolving network structure on the reaction mechanism during curing. Therefore, we increase the model complexity by sequentially coupling reactive molecular dynamics simulations [1] to QM/MM transition state (TS) analyses, which allows us to investigate mechanisms and energetic barriers during in silico curing of epoxy thermosets. Our findings underline the importance of hydrogen bonding, which generally lowers the activation energy, though its effect strongly depends on bond type and reactive site. When hydrogen bonds are present on both reactive sites (N and O), the activation energy is significantly reduced, approaching experimental values (70 kJ/mol vs. 50 kJ/mol). Hydroxyl (OH) bonding at the epoxy oxygen (O) and sulfonyl (SO) bonding with amine (N-H) led to the lowest activation barriers, highlighting their critical role in reaction kinetics. Finally, our methodology will allow us to investigate the curing kinetics as a function of the curing degree and observe the influence of the emerging network structure on the curing reaction.