

The rheological fingerprint of vitrimers

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Vitrimers are a specific class of epoxy-based materials that combine the superior mechanical properties of thermosets with the ease of processing of thermoplastics. They were recently developed in the group of L. Leibler (ESPCI, Paris).¹⁻³ Bond-exchange reactions were included in epoxy networks based on diglycidyl ether of bisphenol A and fatty acids by the addition of a catalyst for the reversible transesterification reaction between alcohol and ester groups. Strong easy processable networks, termed “vitrimers”, were obtained, which can be readily prepared by mixing standard chemicals. We performed extensive experimental investigations using rheometry and differential scanning calorimetry of the curing and viscoelasticity of these vitrimers over wide ranges of possible formulations with different content of mono-, di- and tri-carboxyl fatty acids at fixed catalyst concentration thereby controlling the number of links in the network.

We studied the linear viscoelasticity of the cured vitrimers over wide ranges of frequencies and temperatures. The vitrimers obeyed the time-temperature superposition principle well and master curves were obtained covering the complete dynamic range above the glass transition. The terminal relaxation regime could often not be reached in oscillatory tests and the frequency axis was extended by performing long-time creep experiments. We observe strong, systematic variations of the relaxation time and moduli of the samples with formulation and we systematically observe a peculiar double relaxation, i.e. next to the high frequency plateau modulus, we observe a secondary plateau at lower frequencies. The high frequency plateau moduli of the vitrimers obey the classical rubber theory while the terminal relaxation time is roughly independent of formulation (at fixed catalyst content). The double relaxation behavior remains however elusive but could be related to the “vitramer transition” as reported in Ref. 1.

¹Montarnalet al., *Science* **2011**, 334, 965

²Capelot et al., *ACS MacroLett.* **2012**, 1, 789

³Capelot et al., *JACS* **2012**, 134, 7664