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The Influence of Cross-link Coordination on the Mechanical Properties of Polymers – A Monte Carlo Study

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Abstract:

Reversible cross-linking is a powerful strategy employed by nature to specifically tailor the mechanical performance of load-bearing polymeric structures. These crosslinks are found in a variety of biological systems such as bone, silk or mussel threads. They provide an efficient toughening mechanism due to hidden length unraveling and repeated rupture and reformation of cross-links during the course of deformation. In this dissertation, the main objective is to investigate the influence of cross-link coordination on the mechanical properties of polymeric structures. Three different structures are investigated: a single linear chain, fiber bundles and a stiff random network. The aim is to contrast the deformation behavior of polymers cross-linked with two-fold coordinated cross-links only (the "classical" system) with the behavior of system where three-fold coordination of cross-links is energetically most favorable. The inspiration for the current study stems from various natural and technological systems that show cross-links of different coordination. Prominent examples from nature are Zn-histidine and Fe-DOPA complexes found in marine mussels.

Monte Carlo simulations in the NVT (Helmholtz) ensemble are employed to study the quasi-static properties of the investigated system. Displacement controlled computational loading experiments were performed for linear polymer and aligned fiber bundles to investigate the mechanical properties and deformation behavior of the system. The REBO (Reactive Empirical Bond Order) potential is used to control the energetics of the cross-link coordination. In a stiff random network, the percolation transition and cluster size distribution near the percolation threshold are thoroughly investigated using MC simulations.

The results indicate that the coordination of cross-links is an important parameter to specifically tailored the properties (physical, mechanical and structural) of the polymeric structure. In linear chain and fiber bundles, the deformation behavior (overall shape of the load-displacement curve) in general and basic mechanical properties (stiffness, toughness and strength) in particular depends crucially on the coordination of cross-links. In a stiff random network, the coordination of cross-links can affect the cluster size distribution below and near the percolation threshold.