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Atomistic simulation and modeling of the interface between cellulose nanocrystal elementary fibrils

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ABSTRACT

Cellulose nanocrystals (CNCs) are ubiquitous in some of nature's toughest biological nanocomposites such as wood and bacterial cell walls [1] and exhibit outstanding mechanical properties rivaling those of synthetic materials such as Kevlar [2]. Although the impressive elastic properties of CNCs and mechanical properties of macroscale cellulosic materials have been well characterized, a molecular level understanding of how cellulose-based materials achieve high fracture toughness with relatively weak secondary interactions remains to be explained. Earlier study [3] focused on understanding the molecular interactions within individual CNCs and revealed key information on the types of molecular mechanisms at work in these systems, as well as size effects that govern the optimal size of CNCs from a fracture perspective. To further understand this molecular level of how CNCs develop high resistance to failure, here we present new analyses based on atomistic, steered molecular dynamics (SMD) simulations and theoretical considerations to calculate the fracture energy of interfaces between CNCs. In this work, CNCs of "elementary size" (36 individual cellulose chains arranged hexagonally [4]) are considered as they are commonly found and extracted from biological systems. This study focuses on understanding the (200)–(200) and (110)–(110) interfaces between elementary fibrils as the (200) and (110) surfaces are exposed in this particular arrangement of cellulose chains. In order to better understand the interfaces between CNC elementary fibrils, simulations were performed using SMD techniques to forcibly separate the crystals both perpendicular (i.e., pulling apart) and parallel (i.e., shearing) to the interfaces. Pull-apart simulations show that the (110)–(110) interface has a higher fracture energy than the (200)–(200) interface, which is attributed to different molecular interactions dominating at the interface; hydrogen bonding for (110)–(110) and van der Waals for (200)–(200). Shearing simulations show a common mechanism and common shape of the shear energy landscape for both the (110)–(110) and (200)–(200) interfaces. During shearing, fibrils move between local energy minima along the interface due to the geometry of the surfaces, while also exhibiting an underlying increase in energy. The distance between these energy minimums is observed to be a function of the surface geometry, whereas the magnitude of the energy barrier that must be overcome to reach the next minimum is a function of the dominant molecular interaction mechanism. Based on the results of SMD simulations, analytical models are proposed to describe the energy landscape of interactions between CNC elementary fibrils. These analytical models will allow us to develop a coarse-grained description of CNC elementary fibrils that is capable of modeling the potential energy landscape of both separation and shearing of adjacent fibrils. This will be useful in future work that will focus on an examination of macroscale cellulosic materials, such as CNC neat films and CNC-polymer composites, which would be impractical to explore with fully atomistic simulations.

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