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A molecular dynamics study of the effects of hydrogen bonds on mechanical properties of Kevlar® crystal

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ABSTRACT

Effects of loading direction and hydrogen bonds on the anisotropic elastic and strength properties of p-phenylene terephthalamide (PPTA) crystal (i.e. Kevlar®) are studied using molecular dynamics simulations with reactive force field ReaxFF. Simulations of monotonic tension, compression and shear loadings of the crystal indicate that the elastic properties exhibit orthotropic symmetry but strengths in the various crystal directions are anisotropic and highly dependent on the direction of loading. Tensile strength in the chain axis of the crystal fails by chain scission at a stress level that is twenty times higher than the compression strength governed by chain buckling. To study the effects of hydrogen bonds, simulations are repeated by removing the hydrogen bonding interactions from the ReaxFF force field parameter file. Simulation results indicate that hydrogen bonds do not affect the axial properties that are dominated by covalent bonds in the chains. However, in the absence of hydrogen bonds, transverse tensile, compressive and shear moduli (40–44%) and strengths (47–69%) are reduced significantly. The absence of hydrogen bonding on changes in failure modes for the various loading directions are identified. The results presented in this study provide insight into moisture induced property degradation mechanisms of Kevlar® reported in the literature attributed to reduction in hydrogen bonding.

1. Introduction

Due to superior specific tensile stiffness, strength and energy absorbing capability, Kevlar® fibers are widely used in various protective systems in the form of either woven fabric or composites [1]. The fiber has a multi-length scale hierarchical core-shell structure [2]. At the lower length scales, p-phenylene terephthalamide (PPTA) crystal forms a fibrillar structure comprised of 10–50 nm diameter fibrils [3–5]. Fibrils are connected through a network of hydrogen bonds (H-bonds) and non-bonded van der Waals (vdW) and coulombic interactions. At higher length scales, these fibrils combine into a macro-fibril structure (100–600 nm) and ultimately the fiber having a nominal diameter of about 12 μm.

Kevlar® fibers are commonly used as protective materials in applications such as helmets and body armor. In these applications, ballistic fibers are subjected to multi-axial high strain rate loadings while being exposed to long term environmental conditions (e.g. variable temperature and humidity). Environmental conditions can weaken the bonded and non-bonded inter-atomic interactions in the crystal and fibrillar structure and may degrade fiber performance. There are numerous studies that focus on mechanical properties of Kevlar® under static and dynamic loading [5–15]. In contrast very few studies on the performance of Kevlar® fiber under different environmental conditions have been conducted. Mercer et al. [16] studied the influence of strain rate and temperature on the mechanical properties of PPTA crystal using molecular dynamics simulations. They have reported that tensile failure strain in the fiber direction increases with increasing strain-rate and decreasing temperature. Leal et al. [17] showed experimentally that moisture content in the Kevlar® like organic M5 fiber reduces H-bond density and reduces compressive strength in the fiber direction. They postulated that under humid condition, reduction in the H-bond density weakens inter-fibril interactions. As a result, fibrils can easily shear under axial compressive deformation resulting in compressive strength reduction due to kink band formation. Hageman et al. [18] compared two different configurations (i.e., sheet like and bi-directional structures) with two different levels of H-bond density. Through analytical modeling, where interaction energy is obtained from density functional theory (DFT) calculations, they report that sheet like crystal structure with low H-bond density gives higher shear modulus and compressive strength compared to bi-directional crystal structure with

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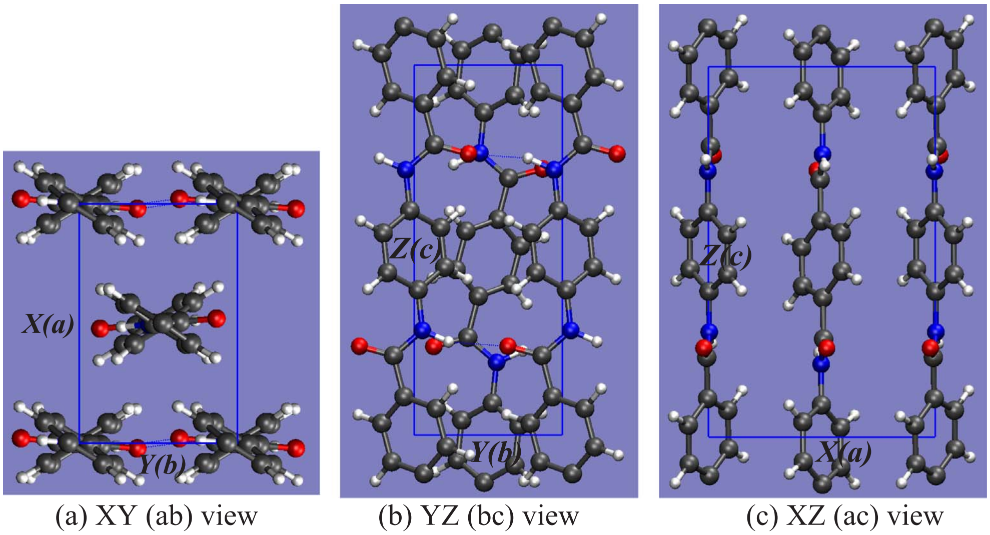

(a) XY (ab) view (b) YZ (bc) view (c) XZ (ac) view

Fig. 1. Kevlar® unit cell. (Atom Color: Carbon-Black, Hydrogen-White, Oxygen-Red, Nitrogen-Blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

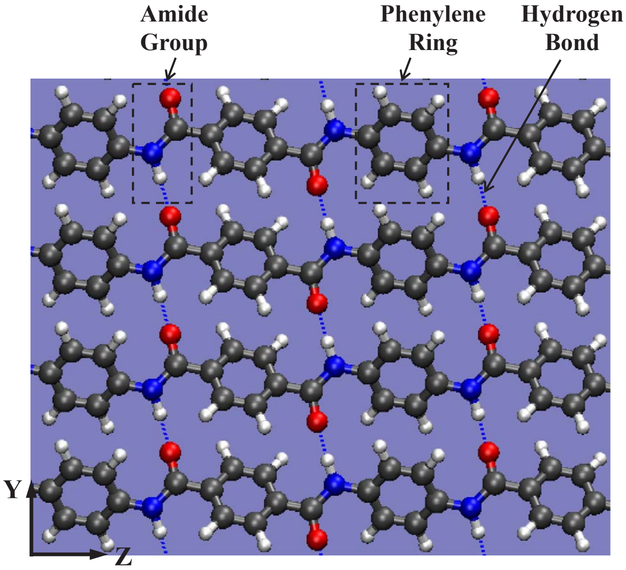

Fig. 2. Kevlar® sheet with inter-chain H-bonds (dotted blue lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

high H-bond density. They concluded that there is competition between H-bonds and other inter-chain interactions giving rise to lower compressive properties. This suggests that H-bond network structure in the crystal influences crystal properties in a complex manner.

In Kevlar®, H-bonds occur at two length scales – within the fibril crystal and at the surface of fibrils within the network. H-bonds at both length scales are affected by moisture [17,19]. Under hygrothermal conditioning, Kevlar® and M5 fiber absorb a significant amount of moisture (8–19 wt%) [17,20]. Leal et al. [17] showed that water ingress significantly reduces inter-fibril H-bonds density. Jackson et al. [19] showed that in the as polymerized PPPT, about 30–40% of the amide sites of the crystals, located near the exterior region of the crystal, are exchanged with water (i.e., breakage of the crystal H-bonds). About 25% amide sites are exchanged in Kevlar® 29 and Kevlar® 49, and about 10% amide sites are exchanged in Kevlar® 149 fibers. Experimental studies [19,21] show that asymmetric polar water molecules attract polar −NH groups of Kevlar and break the H-bond in Kevlar. Therefore, under hygrothermal environment water goes into inter-fibril regions as well as inside the crystals and break H-bonds. In this paper, the effects of H-bonds on crystal mechanical properties are investigated. Bounds are established by comparing crystal atomic structure and mechanical properties with all H-bond interactions removed to the baseline response. Since H-bonds exist at the atomic length scale, the influence of H-bonds at the crystal level is modeled using molecular dynamic simulations to provide an in depth understanding of failure.

Molecular dynamics methods [22] are an excellent tool to analyze the structure at molecular, nano- and even sub-micron length scale. In this paper, the effects of H-bond interaction on the axial, transverse and shear properties of the Kevlar® crystal are predicted by using all-atom molecular dynamics (MD) simulations. Molecular simulations are carried out using open source MD code LAMMPS [23] where atomic interactions are modeled with reactive force field ReaxFF [24]. VMD [25] is used for model visualization.

2. Simulations details

2.1. Model development

Northolt et al. [26,27] and Tashiro et al. [28] determined the orthorhombic crystalline structure of the PPTA crystal through X-ray diffraction analysis. Fig. 1 shows the crystal unit cell which has dimensions 0.787 × 0.518 × 1.29 nm [27,28]. Chains are aligned along the Z (c) direction while H-bonds are aligned along the Y (b) direction. H-bonds are formed between the NH and CO groups of the adjacent chains in the YZ (bc) plane (dotted blue lines in Figs. 1b and 2). The three-dimensional model (Fig. 3) is created by replicating the unit cell in the X (a), Y (b) and Z (c) directions. The model contains 13,440 atoms with dimensions 4.722 × 5.180 × 5.160 nm. The model is expected to be anisotropic since the covalent bonds are stronger than H-bonds and H-bonds are stronger than non-bonded vdW and coulomb interactions. The crystal should have higher axial stiffness and strength along Z (c) axis, intermediate transverse properties along Y (c) axis and lowest transverse properties along the X (a) axis. The influence of loading direction (tension, compression and shear) on failure modes within the crystal are studied.

2.2. Force field

Reactive force field ReaxFF is used to describe the inter-atomic interactions. Details about the ReaxFF functions are available in [29]. ReaxFF can capture bond scission under large deformation. Bond