Polymer 129 (2017) 92–104

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

# A molecular dynamics-based analysis of the influence of strain-rate and temperature on the mechanical strength of PPTA crystallites

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ARTICLE INFO

*Article history:*
Received 21 April 2017
Received in revised form
12 September 2017
Accepted 16 September 2017
Available online 23 September 2017

*Keywords:*
Kevlar®
Aramid fibers
Molecular dynamics
Reactive potentials
Rate-dependence
Temperature-dependence
Fracture

ABSTRACT

Molecular dynamic simulations are used to quantify how the mechanical behavior of PPTA crystallites, the fundamental building blocks of aramid fibers such as Kevlar®, depend on strain-rate, temperature, and crystallite size. The (axial) crystallite elastic modulus is found to be independent of strain-rate and decreases with increasing temperature. The crystallite failure strain increases with increasing strain rate and decreases with increasing temperature and crystallite size. These observations are consistent with crystallite failure being driven by stress-assisted thermal fluctuations of bonds within PPTA crystallites and the concepts of the kinetic theory of fracture. Appealing to reliability theory, a model is proposed that predicts the onset of both primary and secondary bond failure within a crystallite as of function of strain rate, temperature, and crystallite size. The model is parameterized using bond failure data from constant strain-rate molecular dynamic strain-to-failure simulations and is used to compute the activation volume, activation energy, and frequency for both primary and secondary bond ruptures.



## 1. Introduction

Synthetic polymer fibers play a key role in many engineering applications including fiber-reinforced composites, sporting equipment, and woven fabrics. Among the strongest of man-made polymer fibers are aromatic polyamides, or aramid fibers, with well-known examples being Kevlar® and Twaron®. Aramid fibers consist of long-chain molecules made from the monomer poly(*p*-phenylene terephthalamide) (PPTA), pictured in Fig. 1. Northolt et al. [1] showed through X-ray diffraction that the microstructure of PPTA fibers can be defined by an orthogonal unit cell of single PPTA monomers with polymer chains parallel to the fiber axis. Over the years, a number of studies [2–7] have observed that PPTA fiber microstructure is comprised of crystallites between 60 and 600 nm in diameter made from PPTA chains of about 200 nm in length, with periodic defect planes consisting of collections of chain-ends located every 20–40 nm along the fiber axis. Additionally, the fibers exhibit a 0.1–1.0 nm thick outer skin where chain-ends are distributed randomly along the fiber axis, rather than organized into defect planes.

In our previous work [8], molecular dynamics (MD) simulations were conducted to study the dynamic tensile deformation response of PPTA crystallites containing different distributions of chain-end defects, but did not explore the strain-rate dependence of the crystallite response in detail. Yet, this is an important topic to address: aramid fibers used in projectile-resistant fabrics and armor are subjected to high rates of tensile loading, with strain-rates in the range of 1000–10,000 $s^{-1}$. Hence, the dependence of the fiber constitutive response on the rate of loading merits special attention. Dynamic tensile loading experiments performed on single yarns and fiber bundles have yielded conflicting results on this matter, with some experiments showing an increase in fiber modulus and tensile strength with increasing tensile strain rate [9–11], while others find no strain-rate sensitivity of the fiber mechanical properties [12–14]. Shim et al. [15] have postulated that the strain-rate sensitivity observed in their experiments is caused by differing fiber failure mechanisms, specifically failure by polymer chain scission along the backbone versus inter-chain sliding and hydrogen bond rupture between chains, which are activated at different rates; of course, this hypothesis cannot be easily verified experimentally. The lack of clarity on the existence

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https://doi.org/10.1016/j.polymer.2017.09.037
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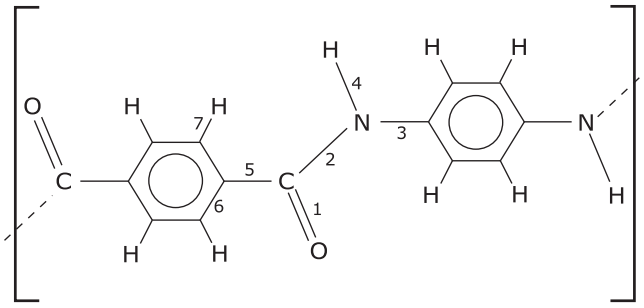


**Fig. 1.** Diagram of a single PPTA monomer. Unique bond types are labeled 1 through 7.

and extent of rate-sensitivity in the mechanical properties of aramid fibers hinders the development of accurate constitutive models for fibers subjected to ballistic impact loading rates.

In this work, constant tensile strain-rate MD simulations are conducted on molecular models of PPTA crystallites in an effort to characterize their strain-rate dependent mechanical behavior. The crystallite is chosen as the subject of study due to its role as the fundamental building block of PPTA fibers and its length-scale compatibility with the limitations of MD modeling with respect to system size. Two interatomic potentials are employed to model PPTA: the reactive bond-order force field ReaxFF [16–19] is used to study situations where crystallite failure occurs by both primary and secondary (hydrogen) bond failure, while the classical PCFF force field [20] is used when failure occurs via hydrogen bond rupture only (the latter situation occurs when chain-end defects are clustered closely together, see Ref. [8]). The influence of temperature and crystallite size is also studied here in order to provide a more complete picture of the constitutive response of the crystallites. The results of these simulations show that the crystallite modulus decreases with increasing temperature but is unaffected by strain-rate and crystallite size, while crystallite strength depends prominently on strain-rate, temperature, and crystallite size. The findings on strength indicate that failure of PPTA crystallites is governed by thermal fluctuations of atomic bonds, which is consistent with the kinetic theory of fracture for failure in solids [21–23]. Leveraging this observation, a model for bond failure based on reliability theory is proposed, and it is shown that the onset of both primary and secondary bond failure in PPTA crystallites can be predicted with good accuracy over a range of strain-rates and temperatures.

The remainder of this article is organized as follows: Section 2 presents the details of the MD simulation methodology used here, including creation of the atomistic model of PPTA crystallites, interatomic force field selection, and the implementation. Section 3 presents the results of simulations concerning the sensitivity of the crystallite mechanical response to strain-rate, temperature, and unit cell size. In Section 4, a model for predicting bond failure based on the principles of reliability theory is presented and its predictive capacity is assessed. Concluding remarks and a discussion of the application of these results to creating a rate-dependent constitutive model of PPTA fibers are offered in Section 5.

## 2. Methods

### 2.1. Force field selection

The primary potential used in the simulations performed in this work is the ReaxFF force field [16–19]. ReaxFF is a reactive bond-order force field capable of dynamically modeling the breakage and formation of covalent bonds during a simulation. ReaxFF has been used extensively to study fracture events in atomistic solids [24–29], as well as specifically for PPTA [8,30,31], making it a good candidate for studying bond rupture events and the failure behavior of crystalline PPTA. While no ReaxFF parameter set has been specifically developed to model PPTA, our previous work [8] demonstrated that the parameter set developed by Liu et al. [32] is able to represent the behavior of PPTA reasonably well, and as such, this parameter set is again adopted for the simulations conducted here.

ReaxFF is a complex and computationally expensive force field, and its use is only necessary when performing simulations in which covalent bonds are expected to rupture. Therefore, for some of the simulations performed in this work, the more computationally efficient PCFF force field is used instead. PCFF is a Class-II force field [20] parameterized from *ab initio* calculations, and is designed specifically to model polymers and organic compounds. PCFF has been successfully used in several MD studies of PPTA [33–36], as well as in our previous work [8]. More recently, the COMPASS force field [37] (based on PCFF but modified to more accurately reproduce PVT relations in condensed matter) was employed by Grujicic et al. [38–43] to conduct a variety of MD simulations of PPTA, exploring, among others, the effects of various classifications of defects and the effect of different static loading conditions on the material response. Given that PCFF was parameterized to model organic compounds like PPTA, and that it has been successfully used (along with its similar counterpart COMPASS) to model PPTA in previous MD studies, it is deemed a reasonable choice for modeling PPTA in cases where hydrogen (as opposed to covalent) bond rupture is of exclusive interest.

### 2.2. Molecular model

All the simulations performed in this work were conducted using LAMMPS [44], a parallelized MD code capable of handling large-scale atomic simulations. Initial atomic models of crystalline PPTA were created with the aid of Materials Studio [45]. Perfect crystal models were created from an atomic topology file based on the X-ray diffraction measurements by Northolt [1]. A perfect crystal model of any size can be created from this starting point by replicating the crystalline unit cell $N_x$, $N_y$, and $N_z$ times in the $x$, $y$, and $z$ directions, respectively. Some simulations in this work involve simulations of a crystallite containing chain-end defects. Chain-end defects are introduced by removing the amide linkage between two aromatic rings along the chain backbone and capping the aromatic rings with hydrogen atoms, as shown in Fig. 2.

The MD simulations make use of periodic boundary conditions to represent PPTA crystallites in a bulk environment. Hence, these simulations are most representative of the crystallites in the core of

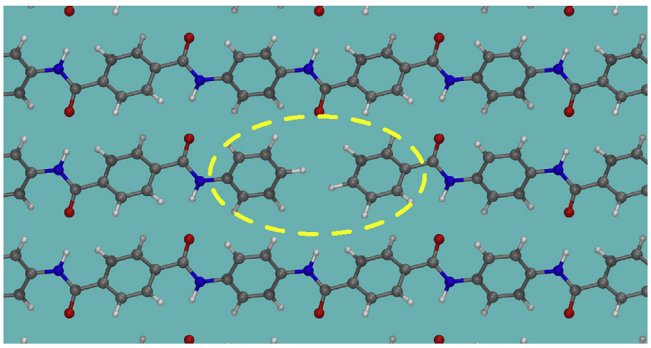

**Fig. 2.** A chain-end defect is introduced by removing the bonds linking two aromatic rings, and capping the rings with hydrogen atoms. The colors gray, blue, red, and white represent C, N, O, and H atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)