First principles study of breaking energy and mechanical strength of Kevlar-29

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Abstract. The first principles study is performed for the mechanical strength of Kevlar-29, and is based on density functional theory. The bond strength is investigated relative to the displacement of central nitrogen atom along X , Y and Z directions, respectively. The structural property analysis explains the asymmetric nature. A higher bond breaking energy is observed during compression along Z direction and vice versa for elongation. It is an insulator of forbidden energy gap which increases while compression and reduces during elongation. Crystal orbital overlap population reveals the higher strength of anti-bonding orbitals. It is mechanically stronger along the Z -axis and weaker along the Y -axis.

Keywords. SIESTA; density functional theory; DOS; COOP; tensile stress.

1. Introduction

Kevlar is a well-known high-strength reinforcement fibre for plastic composites [1,2]. Kevlar (poly para-phenylene terephthalamide) is taking an important practice today for the study of fibre, it is made of para-phenylene diamine and terephthaloyl chloride [3–6]. It has a high degree of orientation/crystallinity, high elastic modulus, high breaking stress and low breaking strain [7,8]. It is widely used in applications of ballistic protection due to flexibility and high strength to weight ratio [9–14]. The molecular structures of Kevlar are well known for thermal enhancement of compressive properties by the formation of inter-chain cross linking and the disruption of hydrogen bonds [5]. Due to its good mechanical properties, thermal stability and energy absorption properties, it is extensively used in the fields of aerospace, military, marine, mountaineering etc. [15–17].

Fibre composite materials are replacing the conventional metals, secondary aerospace and aircraft structural elements because of their superior mechanical properties, very high-tech and a high level of working ability [18,19]. Kevlar is an example of an elastic polymer fibre with a high elastic modulus, a high breaking stress and a low breaking strain; it is several times stronger than steel [20,21]. In this paper, a further theoretical analysis is performed to investigate the breaking energy and mechanical strength of Kevlar-29 with the help of density functional theory.

2. Methodology

Simulation is performed by using a computational program Spanish Initiative for Electronic Simulations with

Thousands of Atoms (SIESTA), which is based on density functional theory [22,23]. For exchange and correlation potential; a Generalized Gradient Approximation of Perdew–Burke–Ernzerhof is used [24]. Core electrons are modelled with Troullier–Martins norm-conserving pseudopotentials [25] and the valence electrons functions are expanded in double zeta polarized basis set [26,27] of localized orbitals and the real space grid is set to be 300 Ry. The structure is relaxed until the Hellmann–Feynman forces acting on all components of each atom are smaller than $0.01 \text{ eV } \text{\AA}^{-1}$.

3. Results and discussion

The equilibrium configurations of (Kevlar-29), (Kevlar-29)- x , (Kevlar-29)- y and (Kevlar-29)- z are shown in figure 1a–d, where x , y and z are representing the variation in the displacement of central N-atomic position to respective bond is broken along X , Y and Z axes, respectively. There is a little variation in the bond lengths between C and central atom N of a Kevlar-29 (K-29) during 10% displacement of lattice constants along Y and Z axes, the C–N bond is broken for the elongation along X and Z axes and Y axis, hence, it exhibits an asymmetric nature of Kevlar-29 [28].

To know the bond strength, the bond breaking energy of Kevlar-29 is calculated during bond (C–N) compression/elongation along X , Y and Z axes and tabulated in table 1. A higher compression energy is required to break the bond along Z -axis; it is 194.584 eV and smaller along the Y -axis; it is 15.562 eV. During elongation of a bond, larger energy is required along the X -axis; it is 18.703 eV and is smaller

Figure 1. Equilibrium configurations of: (a) Kevlar-29, (b) Kevlar-29-*x*, (c) Kevlar-29-*y* and (d) Kevlar-29-*z*, where *x*, *y* and *z* represent the breaking of structure during the variation of central N-atomic position along *X*, *Y* and *Z* axes, respectively.

Table 1. C–N bond breaking energy.

Kevlar-29		(Kevlar-29)-x	(Kevlar-29)-y	(Kevlar-29)-z
Bond breaking energy in eV (when bond length of C–N is compressed/elongated from its equilibrium position)	During compression	44.810	15.562	194.584
	During elongation	18.703	4.557	1.219

Figure 2. DOS at equilibrium positions of Kevlar-29, Kevlar-29-x, Kevlar-29-y and Kevlar-29-z, where x, y and z are representing the strain applied along X, Y and Z axes, respectively.

along the Z-axis; it is 1.219 eV. Hence, to break a bond (C–N), larger bond breaking energy is required along the Z-axis for compression and smaller energy during elongation; it is analogous to our previous work [29].

To investigate the nature of amorphicity in response to strain, the density of states (DOS) are analysed. In Kevlar-29, the higher occupied energy state of valence band is at -1.85 eV, the lowest unoccupied energy state is at 2.1 eV and the forbidden energy gap (E_g) is 3.95 eV (as shown in figure 2), it exhibits the insulating nature of Kevlar-29. The Fermi energy is represented by 0 eV. If strain is applied along all axes respectively, there is little change in the forbidden energy gap; it is 4.25 eV for X-axis, 4.0 eV for Y-axis and 4.0 eV for Z-axis, which can be observed in figure 2, all values of E_g and Fermi energy are tabulated in table 2. By applying strain, E_g is increased and there is larger variation along the X-axis. A few energy states are also found in the forbidden

Figure 3. DOS for tensile strain of K-29 along X, Y and Z axes.

region, just below and at higher energy states of Fermi level, which reduces the crystallinity and increases the amorphicity of K-29.

By comparing the forbidden energy gaps obtained in compression and elongation of bonds, it is observed that for strain produced in compression, energy gap is little larger when compared to elongation, and it decreases gradually on further elongation and for higher values of strain, it is shown in figure 3. Crystal orbital overlap population (COOP) analysis gives more insight into the bonding characteristics of systems [30,31]. The curves are energy resolved plots of Mulliken orbital overlap population between two atoms or orbitals, which provides a quantitative description of the bonding, non-bonding and anti-bonding interactions between two atoms. The Y-axis of figure 4a gives the magnitude of the anti-bonding (lower side) and bonding (upper side) nature of molecular orbitals of Kevlar-29. The maximum overlapping between C2p–N2p, C2p–N2s, C2p–O2p, C2p–O2s, C2s–O2p, C2p–C2p and C2s–C2s atomic orbitals and C–C atoms is observed.

Table 2. Fermi energy and forbidden energy gap.

System	Kevlar-29	(Kevlar-29)-x	(Kevlar-29)-y	(Kevlar-29)-z
Fermi energy (eV)	– 4.263	– 4.342	– 4.339	– 4.344
Forbidden energy gap (eV) ($\pm 5\%$)	3.950	4.250	4.000	4.000

Figure 4. COOP of: (a) Kevlar-29, (b) Kevlar-29-*x*, (c) Kevlar-29-*y* and (d) Kevlar-29-*z*.

We have the resultant strength of anti-bonding orbitals than bonding orbitals, hence, it reduces the crystallinity of Kevlar-29 and increases the amorphicity. By applying stress along all

Table 3. Tensile stress and strain along the axes.

Strain applied along axis	Strain	Tensile stress in GPa	Experimental values in GPa [33]
X-axis	−0.013	−0.223	−0.185
	0.047	1.460	1.850
	0.077	2.230	
Y-axis	−0.040	−0.181	−0.185
	0.070	0.377	1.850
	0.100	0.509	
Z-axis	−0.041	−2.253	—
	0.018	1.099	—
	0.048	2.657	—

Figure 5. Energy vs. strain along X, Y and Z axes.

axes, respectively, a little variation in the orbital distribution and overlapping in orbital states is observed and it is shown in figure 4b–d, but the overall resultant anti-bonding orbital strength is observed in all cases.

The tensile stress is calculated by applying a strain along X, Y and Z axes by following equation [32]:

$$\sigma = (1/\Omega(\varepsilon))\partial E/\partial \varepsilon \quad (1)$$

where σ is tensile stress, E is total energy and $\Omega(\varepsilon)$ is volume at given strain (ε). All calculated values are tabulated in table 3, the negative values of strain and tensile stress represent the compression and positive values represent elongation of C–N bond of Kevlar-29. The results of compression are approximately equal to the experimental values [33] along X and Y axes.

For elongation, the calculated values along the X axis are nearly equal to the experimental value [33], but for Y axis these are too small. Due to unavailability of experimental values along the Z-axis, stress values could not be compared. But it is comparable to the experimental values of K-29 irrelevant of axes [34].

According to tabulated values in table 3, there is a higher tensile stress required during elongation of a bond than compression; it is around 10 times higher along the X-axis and

Figure 6. Stress vs. strain along X, Y and Z axes.

2–3 times along the Y-axis. Along the Z-axis a higher tensile stress is required for compression than the first value of stress of elongation and approximately equal to second value.

A graphical analysis of total energy of Kevlar-29 with respect to strain is shown in figure 5, it shows that the total energy of a system is increased during compression as well as for elongation along all axes. To produce the same strain, the ratio of increasing of energy is higher along the Z-axis and lower along the Y-axis. Figure 6 shows the linear relation between stress and strain for all axes, to produce the same strain; higher stress is required to apply along the Z-axis and smaller along the Y-axis, i.e., Kevlar-29 is mechanically stronger along its Z-axis and weaker along the Y-axis.

4. Conclusions

The structural property exhibits an asymmetric nature of Kevlar-29. A higher bond breaking energy is required for compression of a C–N bond along the Z-axis and vice versa for elongation. DOS explains the insulating nature and the amorphicity of K-29 relative to stress. At equilibrium condition, on applying strain, the forbidden energy gap is increased, it is larger along the X-axis. In compression, the forbidden energy gap is little larger than that of elongation. For higher values of stress in elongation, the energy gap decreases gradually.

COOP gives the resultant strength of anti-bonding orbitals than bonding orbitals, which explains the reduction in crystallinity and increase in amorphicity. To produce the same strain, K-29 is mechanically stronger along its Z-axis and weaker along the Y-axis.

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