A molecular dynamics simulation study on mechanical properties of nanocellulose-graphene layered composites

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Research Article

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Abstract

Inspired by bioinspired layered materials with excellent mechanical and chemical property due to their interface cohesive force, a nanocellulose-graphene layered structure with covalent linkaged (C-C bond) is constructed. The mechanical properties are systematically studied by molecular dynamics (MD) simulations in terms of the effects of temperature, strain rate and the covalent bond contents. The elastic modulus and tensile strength of layered nanocomposites are sensitive to temperature and much higher than these of the pristine nanocellulose at the same temperatures. They also increase significantly with the increase of strain rate and covalent bond coverage. The results showed significant improvements in the mechanical properties by addition of grapheme layers due to the covalent bonding interactions and Van der Waals force interactions at the interfaces. These findings can be useful in further modelling of other graphene-based polymers at the atomistic scales, which are critical for their potential applications as functional materials.

Introduction

Nanocellulose has characteristics of good mechanical properties, chemical modification, and biocompatibility, which can be extracted from trees, plants, and other various biomass resources (Wu et al. 2014; Mazeau et al. 2008). It has motivated a lot of experimental and theoretical investigations to exploit its properties as well as in combination with other materials. For example, the uniform deformation and nano-indentation method are used to explore the stress-strain response and inter crystal sliding friction of nanocellulose and calculated the Poisson's ratio, elastic modulus, stiffness, and other mechanical parameters of cellulose (Dri et al. 2015; Wu et al. 2020). While experimental measurements meet significant difficulties for the uncontrollable operating conditions in these tests, for the crystal structure, defects, percent crystallinity of cellulose keep changing during the tests (Tanaka et al. 2006; Pakzad et al. 2012). More recently, molecular dynamics (MD) simulation as a valuable tool has been used to research the mechanical properties of nanocellulose at molecular-scale, which could provide the deformation and the microstructure evolution of the materials and predict the stress-strain response under tensile deformation by physical statistical method (Eichhorn et al. 2006; Wu et al. 2013; Liu et al. 2020). In addition, some researches have shown that different arrangements of nanocellulose in polymer matrix may enhance the polymer (Peng et al. 2020; Khakalo et al. 2020).

The bioinspired layered materials have drawn significant interest recently due to their the extraordinary properties. Particularly, the excellent mechanical properties of the bioinspired layer are attributed to the synergistic strengthening effect of the interaction between the building modules and the interface (Cheng et al. 2015; Papageorgiou et al. 2017; Zhang et al. 2016). Graphene is one of the best candidates for preparing bioinspired layered materials due to its excellent physical properties. Recently, many papers have reported that the mechanical properties of graphene-based layered nanocomposites are dramatically improved. It has been found that adding carbon series materials to the polymer system can significantly improve the mechanical properties of composites by using MD simulations (Gao et al. 2020; Islam et al. 2020; Li et al. 2017). Hu et al. studied the mechanical performances and processing

approaches of polymer-graphene layered nanocomposites and revealed that processing conditions and interfacial interactions control these materials'mechanical and other physical properties (Hu et al. 2014); Kamaraj et al. investigated the role of graphene as matrix reinforcement in fiber-reinforced polymer composites and found that the flammability and water absorption of flax/epoxy composites decreased with the increase of graphene content, and the tensile and bending strength of the composites increased significantly (Kamaraj et al. 2020). The unique mechanical properties of graphene-based layered materials are attributed to the micro/nanoscale interface interactions. Typical interface interactions of graphene-based artificial materials can be divided into non-covalent bonds and covalent bonds. Compared with covalent bonds formed by chemical reactions, the interaction of non-covalent bonds is relatively weak (Liu et al. 2021; Dai et al. 2017; Song-Moo et al. 2018; Mohan et al. 2018).

In the current study, a nanocellulose-graphene layered structure with covalent linkages is designed in order to improve the mechanical property of nanocellulose. Molecular dynamics (MD) simulations are applied to research the stress-strain relationship and nanostructure deformation by comparing pristine nanocellulose and nanocellulose-graphene layered composites. The simulation results could provide some important connections between mechanical behavior and covalent bonding at graphene layered nanocomposites, and it could provide some basic theories and insights for optimizing the mechanical properties of polymers.

Models And Simulation Method

All the MD simulations are performed on the pristine nanocellulose and nanocellulose-graphene with covalent linkaged layered structure owning three-dimensional size of nearly 6.4 nm (X)×3.8 nm (Y)×2.3 nm (Z). As shown in Fig. 1(b), the covalent linkages are randomly distributed between the grapheme layer and nanocellulose layer with different coverages varying from 0–8%. The coverage of the covalent linkages is defined as the number of the covalent linkages of each layer divided by the total number of carbon atoms of grapheme layer. The covalent linkages are generated by removal of one H atoms from nanocellulose chains and bonding to the carbon atom of grapheme layer. Axial strains were applied in the tensile direction X and remained unchanged in other directions.

The MD simulations are carried out by the LAMMPS code. The C/H/O bond interaction of nanocellulose is described by ReaxFF potential function which is previously developed for C-C interactions and hydrocarbon oxidation (Nishiyama et al. 2002; Mattsson et al. 2010). The ReaxFF force field is expressed as a function of bond order and shown to accurately characterize the mechanical calculation data of hydrocarbons, graphite, and other carbon nanocomposites (Dong et al. 2020). For all simulations, a constant integration time step of 0.5 fs is used. Periodic boundary conditions are applied in all directions to eliminate end effect. The Berendsen thermostat is applied to control the system temperature. Before starting the tensile simulation, the nanostructures reach the global energy minimum using the steepest decent minimization algorithm. After equilibration, the system is stretched for 200 ps with different strain rates under an NVT ensemble. The stresses are derived by dividing the applied force to the cross-section area. The elastic modulus are computed according to Hooke's law.

Results And Discussion

Effect of temperature on mechanical property

The calculated mechanical properties of pristine nanocellulose and nanocellulose-graphene layered structure with the temperature of 300K, 400K and 500K are shown in Fig. 2. The maximum tensile stresses of nanocellulose-graphene layered structure are 7 times higher than that of pristine nanocellulose. The tensile strengths of these two nanocomposites are both correlated negatively with the temperature which are well agreed with the experimental research (Dri et al. 2020). When the temperature increases from 300K to 500K, the maximum tensile stress of nanocellulose-graphene layered composite decreases significantly. Figure 3 shows the effect of temperature on the elastic modulus for pristine nanocellulose and nanocellulose-graphene layered structure. The measured elastic modulus decreases from 448.20GPa to 410GPa for layered structure and from 152.6GPa to 113.64GPa for pristine nanocellulose as the temperature increases. These results are indicated that the nanocellulose-graphene layered structure exhibits better mechanical behavior than pristine nanocellulose. Van der Waals forces and covalent bonds are essential factors to maintain the structure stability of layered structures. With the increase of temperature, the Van der Waals forces and the covalent interaction which maintain the stability of the simulation system become weaker. In addition, the effect of interface adhesion between graphene and cellulose chain also become weaker. The decrease of stress transfer capacity at the interface lead to the decrease of the elastic modulus of tensile strength.

The deformation states of the simulation element with temperature are shown in Fig. 4. It can be seen that an obvious local stress concentration phenomenon appears in the pristine nanocellulose composite. However, the layered structure has better structural stability than that of the pristine nanocellulose with the increase of temperatures. It is because the thermal stability of interchain hydrogen bonds and intra-chain hydrogen bonds in pristine nanocellulose is destroyed due to the increasing temperature, which makes the nanocellulose chain more easily deformed (Araujo et al. 2018). For nanocellulose-graphene layered structure, the arrangement of atoms in the graphene layer appears some distortion and the C-C bonds between nanocellulose and graphene layers are broken, however the nanocellulose chains are observed no apparent breakage.

Effect of strain rate on mechanical property

Figure 5 presents the tensile stress of the two structures with different strain rates. When the strain rates increases from 0.0001fs to 0.0005 fs, the maximum tensile stresses of pristine nanocellulose and nanocellulose-graphene layered composite increase 5% and 9%, respectively. The elastic modulus of pristine nanocellulose and nanocellulose-graphene layered composite also increase proportionally to the strain rates, as shown in Fig. 6. In addition, although the overall performance is tensile deformation, a negative stress is observed at the limit strain of the two structures, which usually corresponds to compression condition. The local compression in the structure may lead to such emergence of negative stress, which should be induced by the cellulose molecular chain breaking (Wu et al. 2014).

In order to explore the underlying mechanism for the strain rate effect on the mechanical properties of the two nanocomposites, the atoms in detail at different strain rates are shown in Fig. 7. It is observed that an obvious local stress concentration phenomenon appears in the pristine nanocellulose composite. The layered structure has better structural stability than pristine nanocellulose with the increase of strain rates. It can be concluded that the covalent interfacial interaction can enhance the mechanical properties of layered structure. The main reason is that the C-C bonds at the interface can strength the stress transfer capacity. The interface adhesion of the layered structure could not produce obvious stress concentration and cellulose molecular chain fracture phenomenon.

Effect of covalent bond coverage on mechanical property

The calculated mechanical properties that perform the correlated positively of the nanocellulose-graphene layered structure with the C-C bond contents are shown in Fig. 8. When the bond content increases from 0–8%, the maximum tensile stress of nanocellulose-graphene layered composite increases 72.36%. Figure 9 shows the effect of C-C bond content on the elastic modulus for nanocellulose-graphene layered structure. The measured elastic modulus increases from 414.79GPa to 448.2GPa for layered structure as the C-C bond content increases. Compared with the pristine nanocellulose composite, the nanocellulose-graphene layered structure exhibit better mechanical behavior. These results indicate that the graphene layers can significantly strengthen polymer materials due to the presence of graphene/polymer interfaces which have greater strength than that of the polymer matrix (Young et al. 2018). The mechanical strength of the covalent bond is the highest, and the interfacial adhesion and load transfer effect of composite materials are significantly enhanced through covalent bonding. Moreover, van der Waals forces also provide part of the interface strength due to the large specific surface area between nanocellulose and graphene.

Conclusion

In this file, the mechanical properties of the nanocellulose-graphene layered structure with covalent linkaged are investigated by molecular dynamics simulation. It is found that the layered structure with graphene can prominently improve the mechanical properties of nanocellulose due to the covalent interaction and van der Waals forces at the interface. The elastic modulus and tensile strength negatively correlate with temperature but have a positive relationship with strain rate and content of the C-C covalent bond. These results have a particular incentive effect on the theoretical research and practical applications of polymers with layered structure.

Declarations

CRediT authorship contribution statement

Xingli Zhang: Methodology, Investigation; Zhiyue Chen: Software, calculate ,Writing; Hao Chen: review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

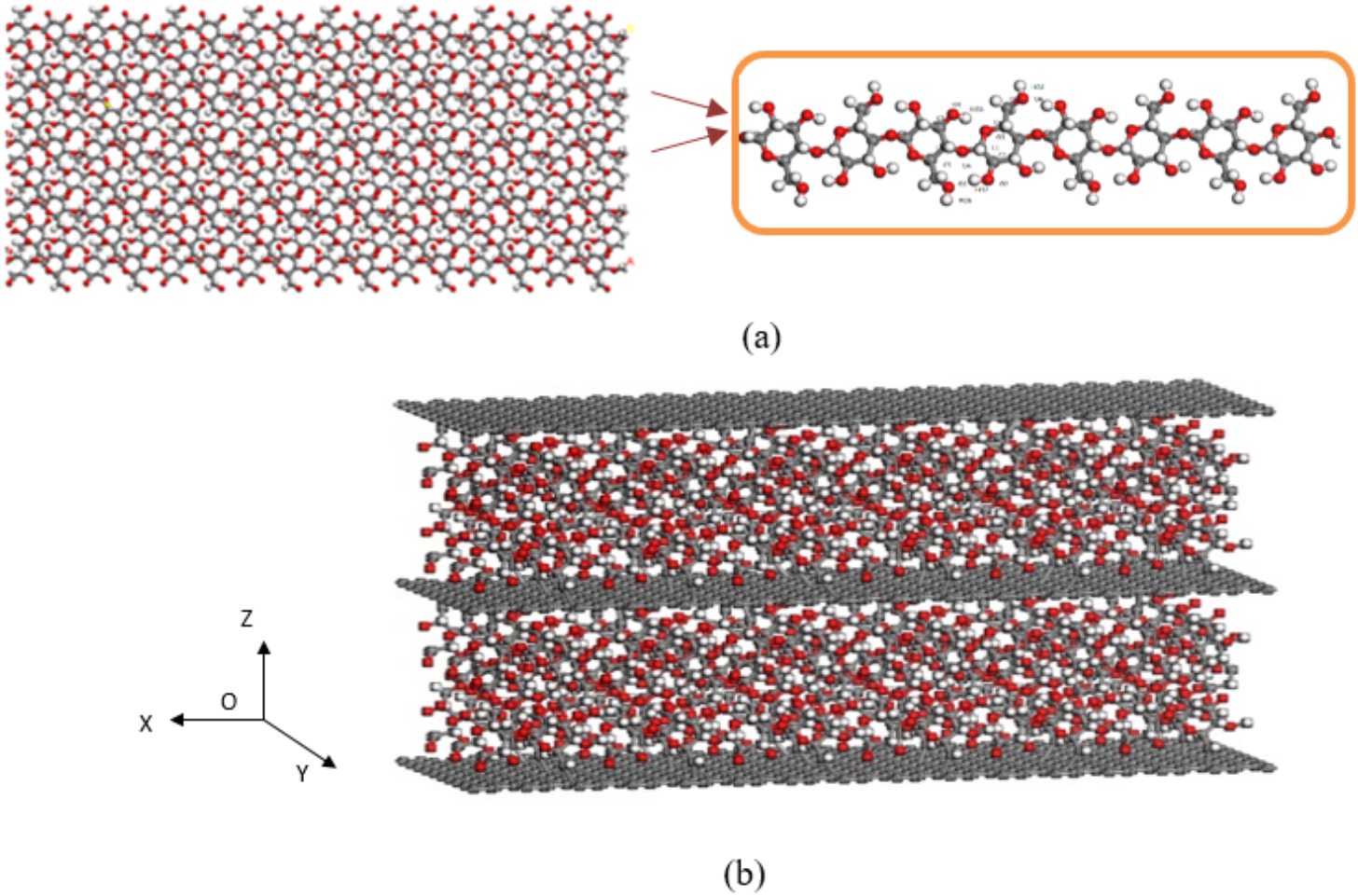

Figure 1

Atomic structure (a) Pristine nanocellulose (Silver is C atoms, red is O atoms, white is H atoms) (b) Nanocellulose-graphene layered composite

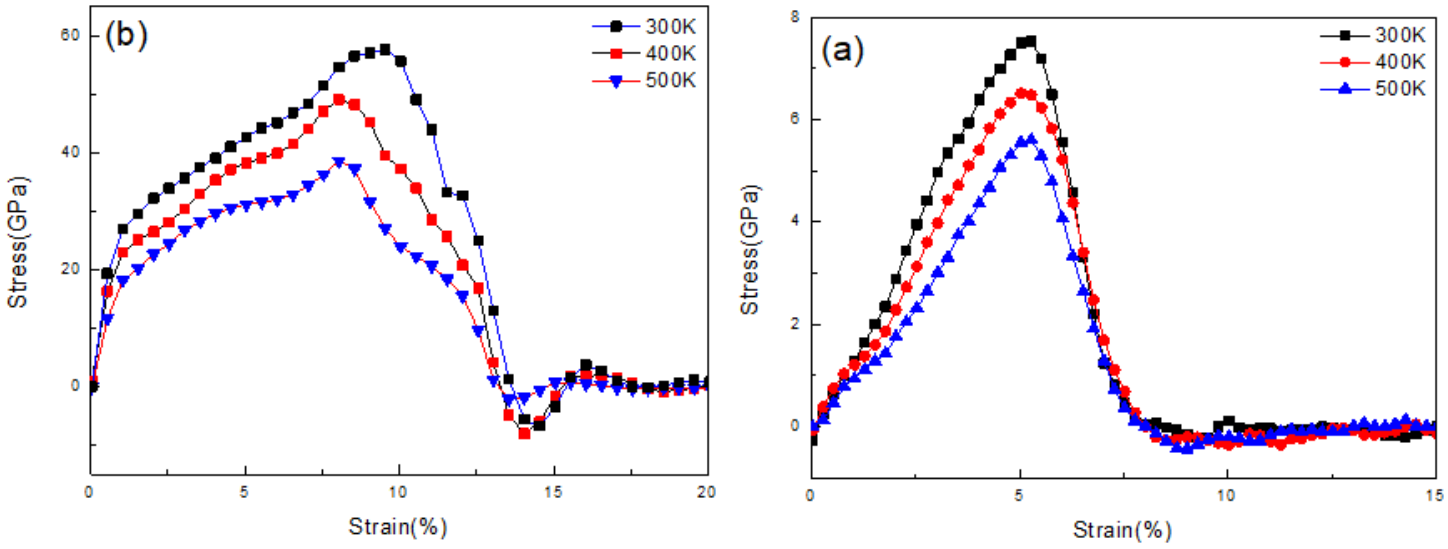

Figure 2

Stress-strain relationship at different temperatures. (a) Pristine nanocellulose. (b) Nanocellulose-graphene layered composite.

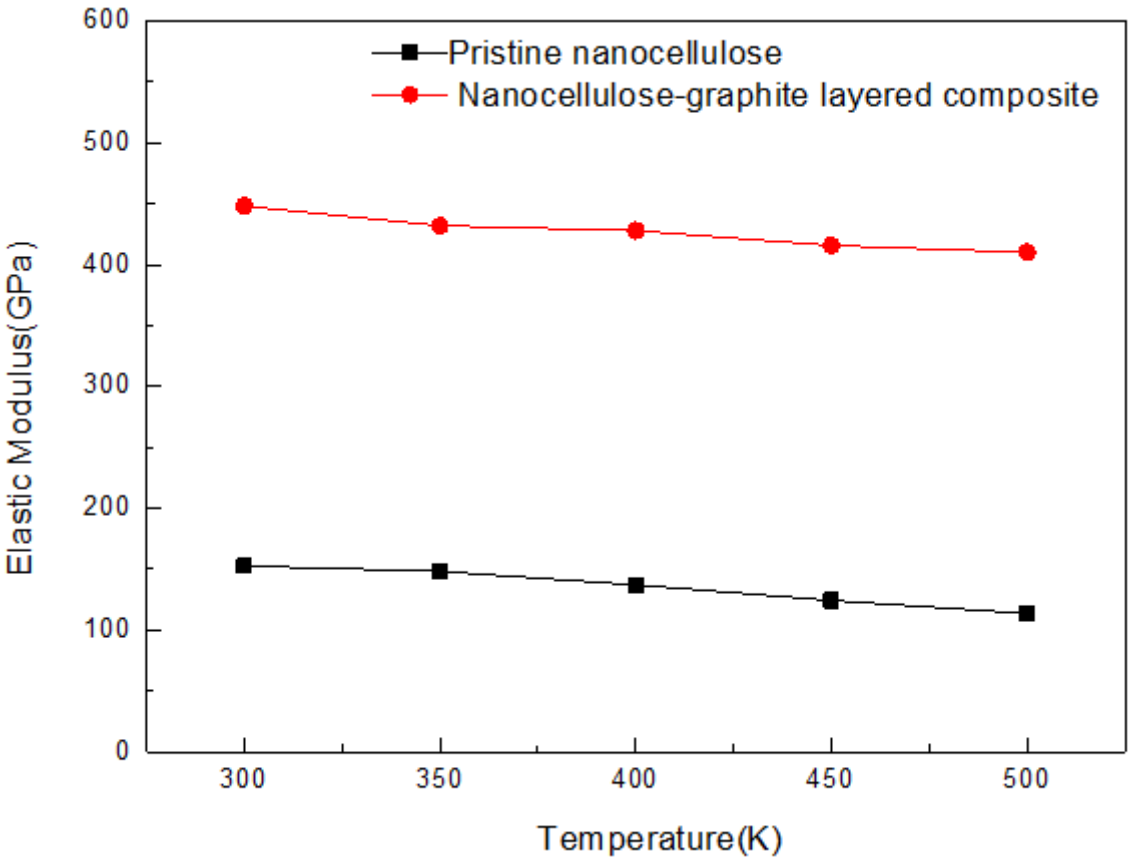

Figure 3

A comparison of elastic modulus of pristine nanocellulose and nanocellulose-graphene layered composite

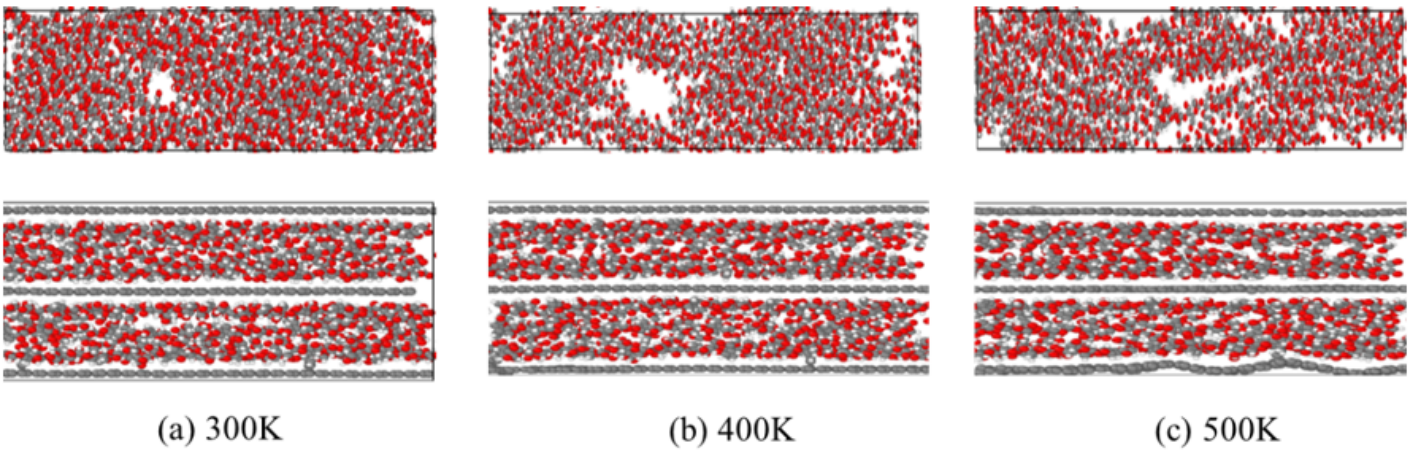

Figure 4

Comparison of the atoms configuration of two composites under tensile stresses at different temperatures

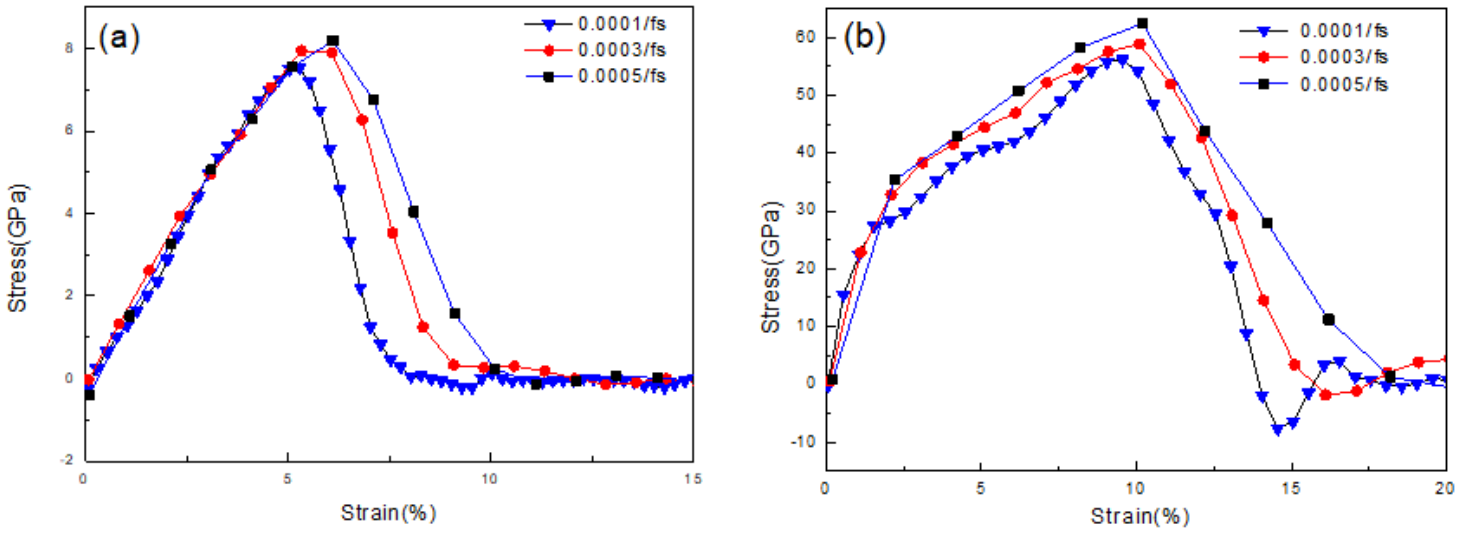

Figure 5

Stress - strain relationship at different strain rates. (a) Pristine cellulose. (b) Nanocellulose-graphene layered composite.

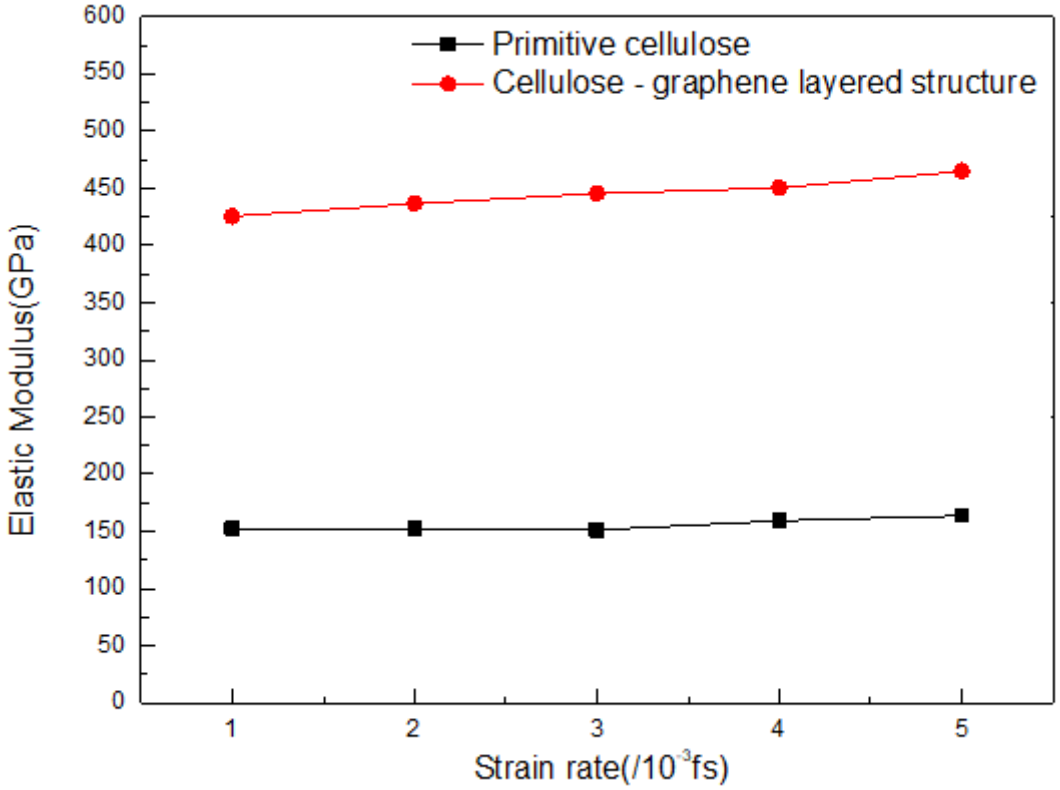

Figure 6

Comparison of the variation trend of elastic modulus of pristine cellulose and nanocellulose-graphene layered structure with strain rate

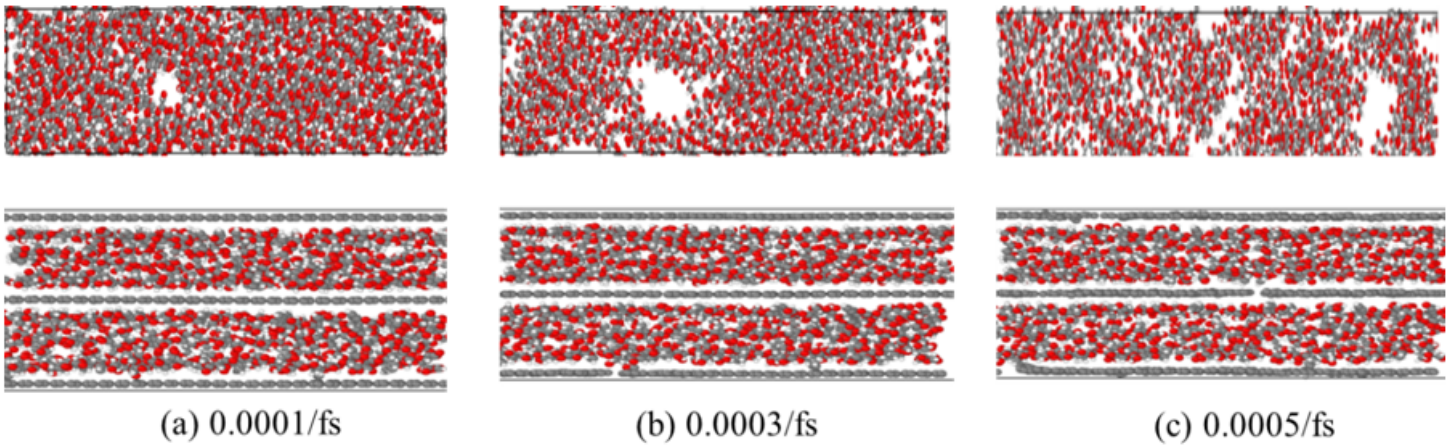

Figure 7

Comparison of the atoms configuration of two composites under tensile stresses

with different strain rates

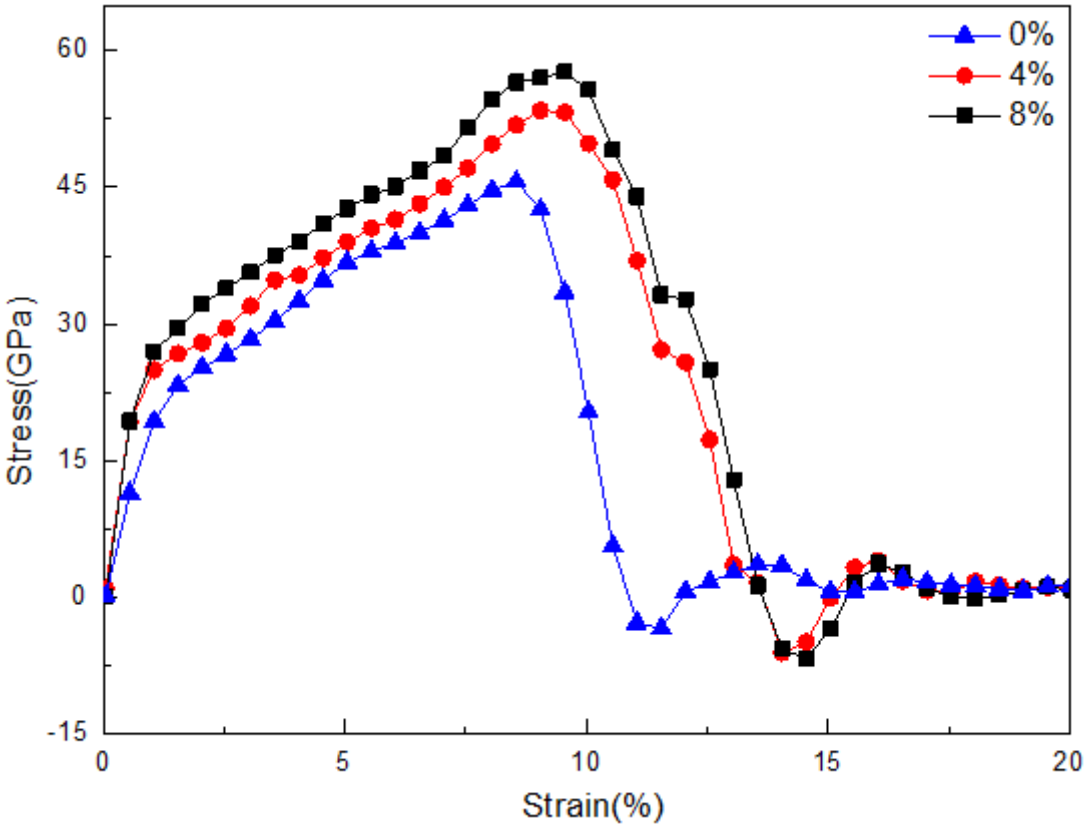

Figure 8

Stress-strain curve of layered structure with different C-C bond contents

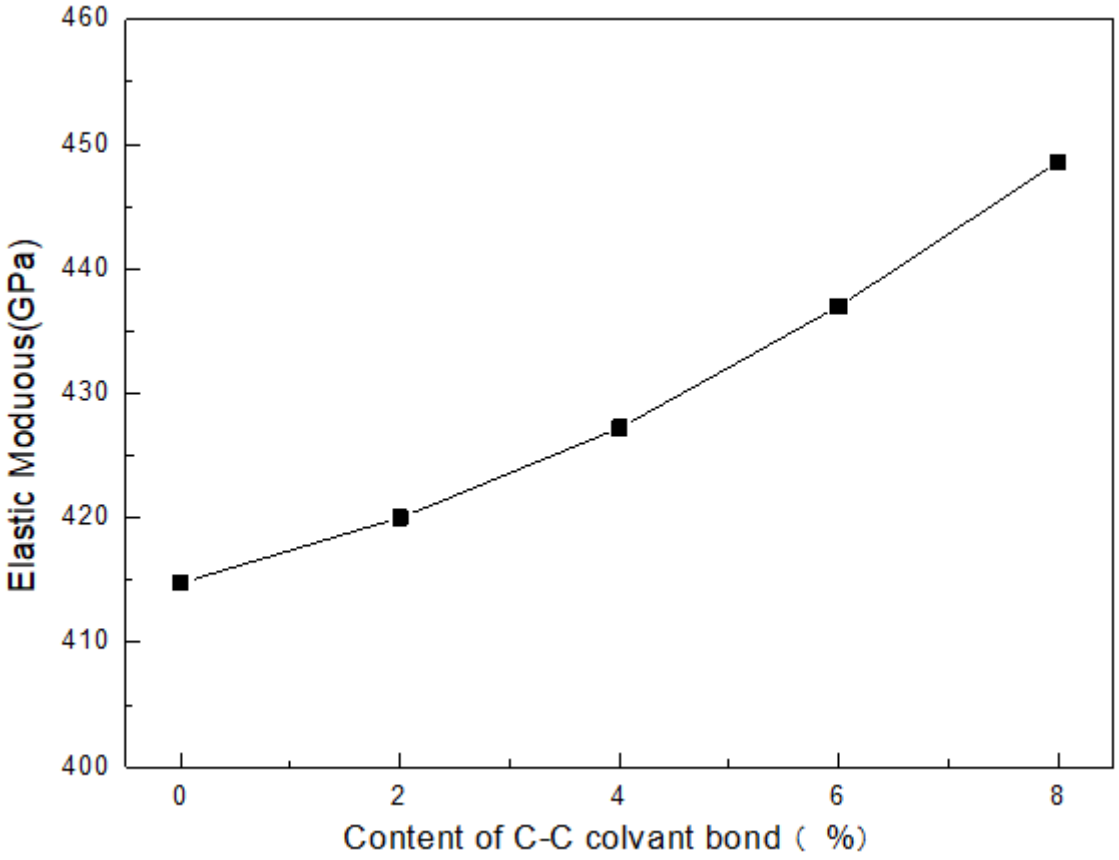

Figure 9

Elastic modulus of layered structure with different C-C bond content