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Crystallographic defect-induced interfacial strengthening of carbon nanotube reinforced polymer composites

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ABSTRACT

This study investigates the effect of crystallographic 5-7-7-5 defect of carbon nanotube on the interfacial strength and overall transversely isotropic elastic stiffness of carbon nanotube reinforced polypropylene composites. To establish the structure-property relationship between 5-7-7-5 defect of CNT and overall properties of composites, the number of defect is gradually increased and the resultant change of the elastic moduli of the composites are estimated from molecular dynamics simulations. At the same time, non-bond interaction energy between defected CNT and surrounding matrix is compared with that between perfect CNT and matrix. As a result, interfacial adhesion characteristics between CNT and matrix has been shown to increase as the number of 5-7-7-5 defect increases. Addressing simple stiffness tensor rotation in micromechanics of composites materials, how the 5-7-7-5 defect can contribute to the effective isotropic properties of randomly distributed CNT reinforced composites is discussed.

1. INTRODUCTION

In polymer nanocomposites incorporating carbon nanotubes(CNT) and graphene,

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the properties of the nanocarbon as well as interfacial strength between the embedded nanocarbon and polymer matrix are important design variables. In general, there are several kinds of intrinsic defects in carbon nanotubes such as vacancy(Jin, 2008), adatom defect, and Thrower-Stone-Wales(TSW) defect(Meyer, 2008). Since these defects destroy sp^2 carbon bonds or changes the electronic band structure of sp^2 carbon, and degrade the properties of CNT, they have been regarded as negative factors.

On the other hand, chemical reactivity of the side wall of CNTs is known to be tailored by the intrinsic defects. Of the three defects, the TSW defect also known as crystallographic 5-7-7-5 defect has been found to have stronger chemisorption and physisorption characteristics than pristine sites(Meng, 2002). Since interfacial strength between pristine CNT and engineering polymer is weak in nature, TSW defect can be a useful interfacial design parameter to promote the overall properties of nanocomposites.

In characterizing the interfacial and overall properties of polymer nanocomposites, molecular dynamics(MD) simulation has been primarily applied to establish structure-property relationship. However, most of the previous molecular level simulation and multiscale modeling approaches rarely dealt with the defected CNT in nanocomposites. In order to consider TSW defect engineering of CNT in design of nanocomposites, understanding the characteristics of the TSW defect and its contribution to the interfacial and overall properties of CNT reinforced nanocomposites is of primary importance. In this study, thus, we investigate the interfacial strength of TSW-defected CNT reinforced polypropylene(PP) composites by molecular dynamics simulations. Quantitative examination of the defect density of TSW defect on the elastic stiffness of nanocomposites is performed by uniaxial and shear tests of transversely isotropic unit cell structure. To evaluate the enhancement of interfacial strength, the MD simulation results are compared with the properties estimated from continuum micromechanics model.

2. MOLECULAR MODELING AND SIMULATION

2.1 Construction of unit cell

In order to study the effect of TSW defect density, in total of four different (15,0) nanotubes; pristine, 5defected, 10 defected, 15defected are considered. Amorphous PP matrix is consists of 56 chains of isotatic PP polymer composed of 40 propylene monomers. Since typical random distribution of CNT in real nanocomosites is impossible in MD simulations for their excessive computational costs, we constructed transversely isotropic nanocomposites unit cell by embedding one CNT into PP matrix as shown in Fig.1. The density of the nanocomposites is set as 0.88g/cc. To eliminate finite size effect, periodic boundary conditions are applied to all the direction of the unit cell, thus, the embedded CNT has infinite length. As typical aspect ratio of CNT in nanocomposites is about ~1000, this is a good representative of the nanocomposites microstructure.

Once the unit cell structure is constructed, total potential energy is minimized using the conjugate gradient method. Since the glass transition temperature of PP matrix is below room temperature, we investigated the elastic stiffness of nanocomposites at glassy state of the PP matrix. Therefore, isothermal ensemble simulation is

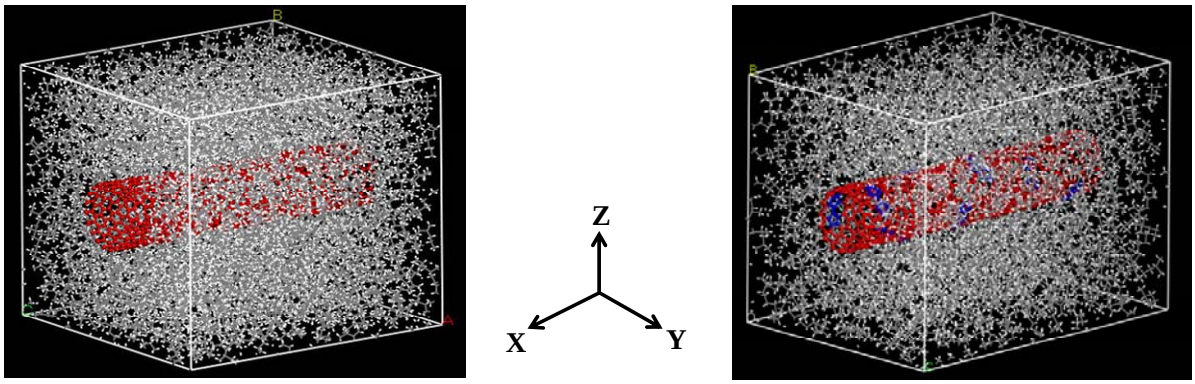

Fig. 1 Transversely isotropic nanocomposites unit cell structure, left: pristine CNT right: 10 TSW defected CNT

implemented for 50 ps at 200K followed by 3ns of isothermal-isobaric ensemble simulation at 200K and 1atm to equilibrate the unit cell at target temperature.

2.2 Production run to obtain elastic constants

The transversely isotropic elastic constants of nanocomposites unit cell are obtained from stress-strain relation of nanocomposites. Thus, three different tensile simulation along the longitudinal and transverse direction of the embedded CNT are applied at a constant true strain rate of 0.0001/ps until the true strain of the nanocomposites reaches 0.02%. Similarly, three different shearing simulation distorting the tilt angle of the unit cell are implemented at the same true strain rate. The resultant stress of the nanocomposites at each strain step is calculated from the virial theorem.

Since the elastic properties of CNT are also affected by the TSW defect, the transversely isotropic elastic moduli of CNT according to the TSW defect are calculated by molecular mechanics simulation. To calculate the elastic moduli, the equivalent continuum structure of the CNT is assumed to be a solid cylinder with an effective wall thickness of 0.34nm. The details of the process to calculate the moduli of CNT from strain energy density to elastic constant relation can be found elsewhere(Yang, 2012).

3. RESULTS AND DISCISSION

3.1 Elastic moduli of CNT

The elastic moduli of CNTs according to the TSW defect are shown in Table 1. In all cases, the elastic moduli of CNT decrease as the number of TSW defect increases. Above 5 TSW defects, the moduli of CNT rapidly decrease. Among all the components, the longitudinal shear modulus shows the most drastic degradation by the TSW defect. Recalling a simple rule of mixtures, the results in Table 1 makes an intuitive decision that the TSW defect degrades the overall properties of nanocomposites. However, the overall elastic properties of nanocomposites does not solely depend on the degradation of the CNTs by the TSW defects as follows

3.2 Elastic moduli of nanocomposites

Table 1. Transversely isotropic elastic stiffness of CNTs [GPa].

No. of TSW defects	E_L	E_T	G_L	G_T	K_T
0	767	74.6	334.8	20.2	269.4
5	767	74.8	302.7	20.2	270.0
10	756	69.9	285.1	18.8	268.2
15	731	70.5	266.3	18.9	265.0

The transversely isotropic elastic moduli of nanocomposites obtained from MD simulations are compared with those from the Mori-Tanaka continuum micromechanics solutions in Fig.2. The longitudinal Young's modulus of nanocomposites decreases as the number of TSW defect increases. This is due to the degradation of the longitudinal Young's modulus of CNTs by the TSW defect. Therefore, it can be concluded that the degradation of the CNT is rather dominant factor in longitudinal property. One distinguishable feature in longitudinal Young's modulus is that the result from MD simulation is higher than the Mori-Tanaka model prediction. The reason for this discrepancy is that the Mori-Tanaka model prediction does not consider the densified interphase zone formed right in the vicinity of the CNTs(Yang, 2012)..

On the other hand, the transverse Young's modulus and two shear moduli show different tendency; they are improved by the TSW defects. With a pristine CNT, all these moduli are smaller than the Mori-Tanaka model prediction and even smaller than those of pure P matrix. This result indicates that, even considering the contribution of the densified interphase zone, the interfacial strength between pristine CNT and PP matrix is weak in nature. As the number of TSW defect increases, however, the moduli increase and approach to the Mori-Tanaka model prediction. Since the Mori-Tanaka model considered in this study assumes that the CNT and matrix are perfectly bonded, the variation in Fig.2 indicates that the weak interfacial bonding between CNT and PP matrix is promoted by the TSW defect. Since the transverse Young's modulus and the two shear moduli of CNT is degraded by the TSW defect, the improvement of the interfacial strength is unusually strong to overcome the degradation of CNTs. The result implies a possibility of TSW defect engineering of CNT as a new strategy to improve overall properties of nanocomposites.

4. CONCLUSION

In this study, we examined the effect of the crystallographic 5-7-7-5 defect on the interfacial properties of CNT reinforced composites. Even if the properties of CNTs were found to decreased by the TSW defect, due to the improvement of interfacial strength between the CNT and PP matrix, overall elastic moduli of nanocomposites could be improved by the TSW defect. The results shown in this study support the

potential of defect engineering of CNT to improve and tailor the properties of nanocomposites.

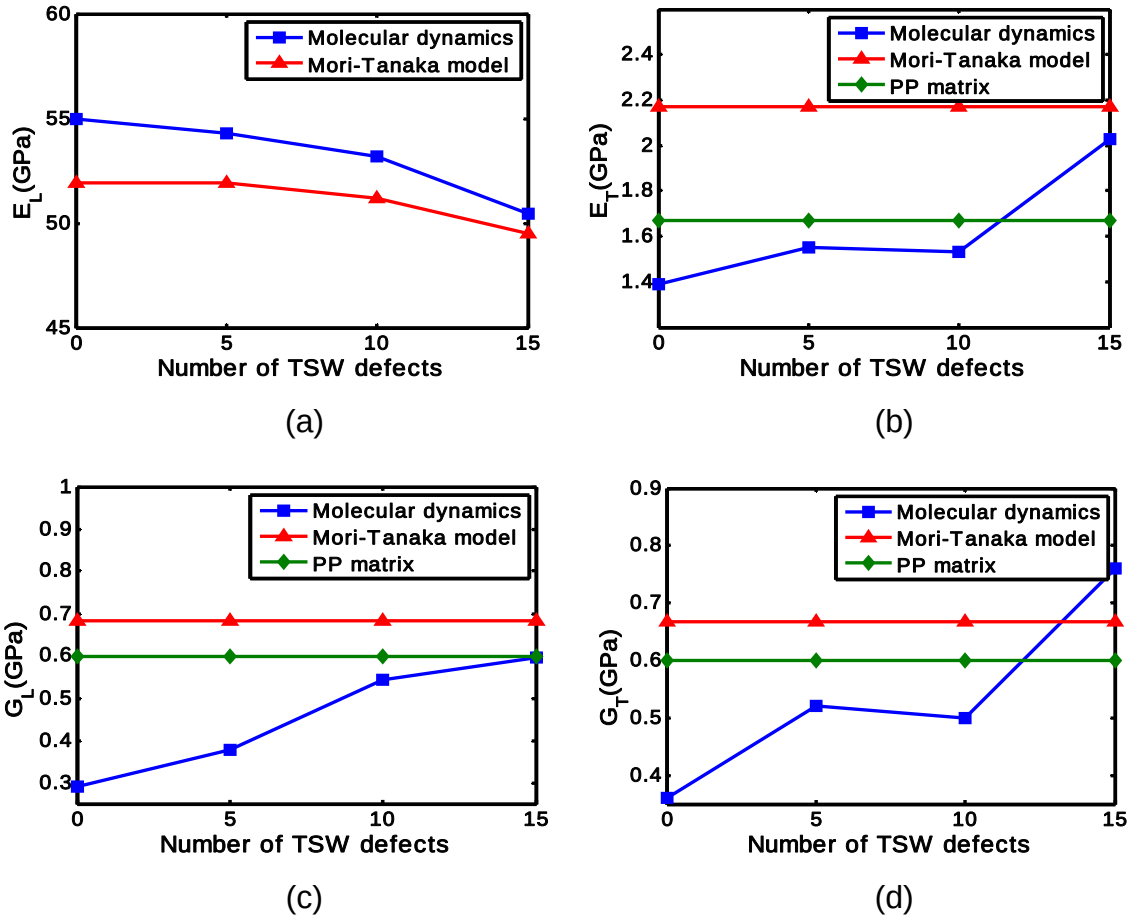

Fig. 2 Transversely isotropic elastic moduli of CNTs reinforced composites (a) longitudinal Young's modulus (b) Transverse Young's modulus (c) Longitudinal shear modulus (d) In-plain shear modulus.

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