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Estimation of interfacial properties of nanocomposites using an analytical interphase model

Hoi Kil Choi[a,b], Jaesang Yu[a,*], Eunho Kim[c], Eui Sup Shin[b]

[a] Multifunctional Structural Composite Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), Chudong-ro 92, Bongdong-eup, Wanju-gun, Jeollabukdo 55324, Republic of Korea

[b] Department of Aerospace Engineering, Chonbuk National University, Baekje-daero 567, Deokjin-gu, Jeonju 54896, Republic of Korea

[c] Division of Mechanical System Engineering & Automotive Hi-Technology Research Center, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju 54896, Republic of Korea

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ABSTRACT

In this study, an analytical interphase model is proposed to estimate the interfacial properties between a polymer matrix and carbon nanotubes (CNTs). A molecular dynamics (MD) simulation was performed to obtain the interaction energy and the geometrical parameters of the interphase. The CNTs had the different embedded surface area and functional groups. The interfacial shear strength and critical pull out force were estimated by using an analytical interphase model. The interfacial properties estimated by the proposed interphase model matched the results of the pull out test closely. The changes in the interaction energy and inter thickness introduced by the functionalization of CNTs improved the interfacial properties. These results show that the proposed assumptions were effective and the proposed interphase model using a MD simulation was useful for estimating the interfacial properties of nanocomposites.

1. Introduction

Nano-sized fillers, such as carbon nanotubes (CNTs), graphites, and nanoparticles have been widely used to improve the mechanical, electrical, and thermal properties of polymer matrix-based composites (PMCs) [1–3]. One of their major advantages is a large surface area of interphase (inter) and a lightweight due to tiny dimensions, allowing excellent interaction when contacting with a polymer matrix. A large surface area of inter between nanofillers and a polymer is a crucial factor determining the effective composite properties by the load transfer, electron hopping effect, and heat conduction. The state of an inter such as surface area, dimension of nanofillers, and type of polymer is fundamental and important information to design high performance nanocomposites.

Experimental investigation of an inter in the nanocomposites is difficult due to the size of the nanofiller. Accordingly, the analytical models and simulative method have been widely used to study the mechanical, thermal, and chemical behaviors of nanoscale material systems [4–7]. Molecular dynamics (MD) simulations, above all, focus on the atom-based nano-material [8–11]. A pull out simulation of nanofillers is the most popular method to analyze the interfacial behaviors. The main result of this type of simulation is the interaction energy between the nanofillers and the matrix. Previous works using a pull out simulation calculated the interfacial properties from the interaction energy and the geometrical parameters of nanofillers [12–16]. The interphase model in previous works assumed the inter as volumeless by considering the very high ratio of the embedded surface area to the thickness of the interphase. However, the ratio in case of the nanocomposites is low. The inter exists as the vacuous region, and it is maintained by the interaction between the nanofillers and the matrix. The interaction is determined by the van der Waals force between the atoms in the nanocomposite. The thickness of the inter is the distance for the equilibrium of the van der Waals force between the nanofillers and the matrix. The change of the thickness can affect to the interaction with the load transfer in the inter. Thus, the thickness of the inter could be considered as a main parameter for determining the interfacial properties of nanocomposites.

In addition, the previous interphase models [17] assume the force for the pull out as the friction force between the nanofillers and the matrix. It also focuses on the change of the interaction energy according to the displacement of the CNT. The interaction energy linearly decreases from the fully embedded position to completely pulled out position in the pull out simulation [18,19]. Then the friction force is defined as the spatial differential of the interaction energy according to the displacement of the CNT. It indicates that the friction force has a constant value regardless of the position of the CNT. However, in the

* Corresponding author.
E-mail address: jamesyu@kist.re.kr (J. Yu).

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pull out tests of a CNT embedded in the polymer matrix [20–22], the CNT rarely moves on the fully embedded position until the pull out force reached to the critical value. The required force decreases with the interaction energy after reaching to the critical value. If the critical force was the friction force, the force is identical to every position of the CNT. This shows that the pull out was occurred from the critical force to break the interaction between the nanofillers and the matrix. Thus, the interphase model for determining the interfacial properties of the nanocomposites should focuses on the interaction energy and the critical pull out force on fully embedded position.

An analytical interphase model for CNT/polymer composites is proposed in this work. CNTs with different embedded surface area and functional groups were considered in the MD models of nanocomposites. The interaction energy and geometrical parameters of the inter were calculated by performing a pull out MD simulation of CNTs embedded in a polymer matrix. The interfacial shear strength and the critical pull out length were estimated by the proposed interphase models. The estimated results were compared to the results in the literature [20]. The influence of functionalization on the interfacial properties was examined in a comparative study between the nanocomposites containing the different functionalized CNTs.

2. Methodologies

2.1. A pull out MD simulation

A pull out simulation has been used to estimate the characteristics in the inter between two different materials. In the case of the CNT/polymer composites, the CNTs are assumed as hollow thin walled structures, and they are embedded in a polymer matrix [23]. An interphase (inter) is a vacuous region between the CNTs and the matrix. The inter has a potential energy by the van der Waals interaction of the CNTs and the matrix. The interaction energy (U) in the inter is expressed as [24,25]

$$U = U_{comp} - (U_{CNT} + U_{matrix}), \tag{1}$$

where U_{comp}, U_{CNT}, and U_{matrix} are the van der Waals energies of the overall composite, the CNT, and the matrix, respectively. While the polymer matrix is constrained in all degrees of freedoms, the CNT moves along its longitudinal direction with uniform incremental of the displacement, from fully embedded position in the matrix to completely pulled out position. The interaction energy is calculated in each incremental step.

2.2. An analytical interphase model

An analytical model for the inter between the nanofillers and the matrix is proposed in this section. This model has three assumptions: [1)]the inter is an elastic solid, [2)]the inter is broken when its strain energy reached to the maximum value of the interaction energy, [3)]the inter has an effective thickness between the CNTs and the matrix. Fig. 1 schematically illustrates the analytical interphase model under the pull out force. When a pull out force (F) was applied on the CNT embedded in the matrix, a shear force on the embedded surface results in shear deformations of the inter like Fig. 1 (b). Then, the normal strains of the CNT rarely appears due to no constraint of the CNT. The relations of the pull out force, the shear stress (τ), and shear strain (γ) of the inter are expressed as

$$\tau(F) = \frac{F}{A} = \frac{F}{2rL\pi}, \tag{2}$$

$$E(F) = \frac{V}{2}\tau(F)\gamma(F) = \frac{V\tau^2(F)}{2G} = \frac{((r+t)^2 - r^2)L\pi}{2G}\tau^2(F), \tag{3}$$

where A, r, and L are the embedded surface area, radius, and embedded length of CNTs, respectively. E is the strain energy of the inter introduced by the shear deformations. V and t indicate the volume and thickness of the inter, respectively. G is the shear modulus of the inter. A displacement of the CNT (Δx) is occurred from the shear strain of the inter. The maximum value of the interaction energy between the CNT and the matrix can be changed by the displacement of the CNT. The displacement of the CNT and the maximum interaction energy are expressed as

$$\Delta x(F) = t\tan(\gamma(F)) = t\tan\left(\frac{F}{2rL\pi G}\right), \tag{4}$$

$$U(\Delta x(F)) = U_0 - \frac{U_0}{L_{pullout}}\Delta x(F), \tag{5}$$

where U_0 is the maximum interaction energy in the fully embedded position. $L_{pullout}$ is the distance from a fully embedded position to a completely pulled out position. It differs from the embedded length due to the cut off distance where the non-bonding interaction between atoms does not apply. The relationship of the maximum interaction energy and the displacement of the CNT is found in the literature about the pull out MD simulations [18,19]. The inter is broken when the strain energy reached to the critical value. The maximum interaction energy is one of good candidate of the critical value. Both the strain energy and the maximum interaction energy are defined as a function of the pull out force in Eqs. (3) and (5). A failure criterion for the inter is expressed as

$$U(\Delta x(F)) = U_0 - \frac{U_0}{L_{pullout}}t\tan\left(\frac{F}{2rL\pi G}\right) \leqslant E(F) = \frac{((r+t)^2 - r^2)L\pi}{2G}\left(\frac{F}{2rL\pi}\right)^2. \tag{6}$$

The minimum pull out force that satisfies Eq. (6) is defined as a critical pull out force. The interfacial shear strength (ISS) then is calculated from Eq. (2) and the critical pull out force.

2.3. Simulation details

The single walled structured CNTs were used in the MD simulations. The different embedded surface area and various functional groups were employed. Fig. 2 shows the representative model for the pull out MD simulation. A periodic boundary system with dimensions of 3.5 nm × 3.5 nm × (embedded length) nm was constructed by considering a cut off distance of 1.5 nm and a CNT diameter of 0.8 nm. The polymeric chains crosslinked with epoxy (Epon 826) and hardener (Jeffamine D230) packed a vacuous region excluding the CNT. The density of the polymer matrix was 1.13 g/m^3 at room temperature and atmospheric pressure. An energy minimization was performed with a smart algorithm to relax the potential energies of the MD models including the CNTs and the polymeric matrix. The relaxed MD models were stabilized under isothermal and isobaric conditions (NPT ensemble). The temperature and pressure in the NPT ensemble were 298 K and 1 atm, and the ensemble time was 500 ps with a time step of 1 fs. For the pull out MD simulations, the length of the stabilized systems was expanded by considering an embedded surface area and a cut off distance. The displacement of the CNT increased 0.2 nm per one simulation step. Every simulation was performed by a COMPASS II force field in Materials Studios software [26], and an explanation of the energy equations can be found in the literature [27].

3. Results and discussions

3.1. Effects of an embedded surface area on interfacial properties

In the MD simulations, the CNTs had different embedded surface areas of 2.1, 4.1, 8.3, 10.3, 20.6, 41.1, 82.3, and 164.6 nm^2 with identical diameter of 0.8 nm. The shear modulus of the inter was obtained from a simple mixture theory as 1.37 GPa [28]. Then, the used