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Моделирование параметра передачи напряжений на границе раздела в полимерных наноккомпозитах с углеродными нанотрубками

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С использованием модели Pukanszky определен параметр передачи напряжений на границе раздела s в модели Callister. Уравнение для параметра s учитывает прочность полимера, размер углеродных нанотрубок и сдвиговую прочность границы раздела. На его основе построены зависимости параметра s от указанных величин. Полученные результаты демонстрируют высокую точность данного уравнения при описании наноккомпозитов с углеродными нанотрубками. Показано, что параметр s сильно зависит от сдвиговой прочности границы раздела и не зависит от прочности матрицы. Наличие в композите углеродных нанотрубок большой длины и толщины приводит к увеличению параметра s , при их уменьшении параметр s снижается. Однако незначительное изменение s в разных диапазонах размеров углеродных нанотрубок свидетельствует о слабом влиянии размера углеродных нанотрубок на его значение. Параметр s напрямую зависит от параметра B в модели Pukanszky, так как оба этих параметра описывают межфазные свойства. Несмотря на то что соотношение длины и толщины углеродных нанотрубок определяет площадь поверхности наночастиц, данная величина слабо влияет на значение s .

Ключевые слова: полимерные наноккомпозиты с углеродными нанотрубками, параметры межфазных границ, моделирование, сдвиговая прочность границы раздела

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Modeling of the interfacial stress transfer parameter for polymer/carbon nanotube nanocomposites

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The main aim of this paper is to define the interfacial stress transfer parameter s in the Callister model using the Pukanszky model. The parameter s is expressed by the polymer strength, carbon nanotube (CNT) size, and interfacial shear strength. The developed equation is applied to plot the roles of all parameters in the value of s . The reasonable outputs of the developed equation show its accuracy for the CNT nanocomposites. The interfacial shear strength directly handles the parameter s , but the matrix strength has no effect. Thin and long CNT increase the value of s , but thick and short CNT deteriorate it. However, the negligible variation of s within different ranges of CNT dimensions indicates that the CNT size slightly affects the value of s . The parameter B in the Pukanszky model directly handles the parameter s , which is logical because both B and s show the interfacial/interphase properties. In addition, although the aspect ratio of CNT determines the surface area of nanoparticles, it insignificantly manipulates the parameter s .

Keywords: polymer/CNT nanocomposites, interfacial/interphase parameters, modeling, interfacial shear strength

1. Introduction

There is an increasing concentration on the nanotechnology and nanostructures specially nanocomposites in recent years [1–7]. The large aspect ratio, poor density and good chemical constancy as well as the

outstanding electrical and mechanical properties of carbon nanotubes (CNT) have justify the preparation and analysis of polymer CNT nanocomposites [8–13]. Actually, the high number of CNT benefits produces the high-quality nanocomposite samples for various

applications. However, the van der Waals attraction between CNT makes the aggregates/agglomerates in nanocomposites [14, 15], which should be prevented by modification of CNT, because the desirable dispersion of CNT in the polymer matrix is mandatory to progress the mechanical possessions of nanocomposites [16, 17].

The big surface area of nanofillers and the powerful interfacial interaction/adhesion between polymer matrix and nanoparticles build the interphase region in nanocomposites [18–21]. The interphase properties such as thickness, strength and modulus were characterized in the previous papers [19, 22]. Since the experimental management of interphase zone includes the description of interfacial interaction at nanoscale, the models for the mechanical properties of nanocomposites simplify the interphase examinations [23, 24]. There are many modeling studies on the interphase region in nanocomposites [25–27]. Moreover, many researchers have tried to characterize the interphase proprieties through characterizing the tensile strength and modulus of nanocomposites [28, 29].

The amplified properties of nanocomposites compared to the neat polymers significantly depend on the interfacial attachment of CNT to the polymer matrix [30–32]. Furthermore, the interfacial interaction significantly changes the composition, structure and properties in a thin layer of polymer surrounding the nanoparticles [33]. As a result, the third phase as interphase between polymer matrix and CNT has different properties from both polymer matrix and nanoparticles and it is essential to understand the interphase properties to simulate the unforeseen performance of nanocomposites.

Many models have been suggested for the tensile strength of polymer nanocomposites. For example, Callister [34] and Pukanszky [35, 36] models have shown good agreement with the experimental data of tensile strength in nanocomposites. These models contain the interfacial parameters. Parameter B in Pukanszky model is a determinate parameter as a function of filler and interphase properties [35, 36]. However, the parameter s in Callister model is an undefined parameter. In this work, we try to define the s by linking the Callister and Pukanszky models. We define the parameter s by polymer, CNT and interfacial parameters. We use the developed equation to plot the roles of all parameters in the parameter s . Clearly, the logical outputs of the developed equation show its accuracy for the nanocomposites. This study helps to find and optimize the main parameters affecting the parameter s in nanocomposites.

2. Methodology

Callister model expresses the tensile strength of polymer nanocomposites by material and interfacial interaction parameters [34] as

$$\sigma_r = \frac{\sigma_c}{\sigma_m} = 1 + \left(\frac{\alpha s}{\sigma_m} - 1 \right) \varphi_f, \quad (1)$$

where σ_r is relative strength, σ_c and σ_m are the strengths of nanocomposite and polymer matrix, respectively, α is the aspect ratio of nanofiller as $\alpha = l/d$; l and d show the length and diameter of nanoparticles, respectively, s is an interfacial stress transfer parameter as the extent of interfacial adhesion at the interface, and φ_f is filler volume fraction.

Pukanszky [37] also suggested a simple model for tensile strength of polymer nanocomposites as

$$\sigma_r = \frac{1 - \varphi_f}{1 + 2.5\varphi_f} \exp(B\varphi_f), \quad (2)$$

where B is the capability of stress transfer between polymer matrix and nanoparticles. Parameter B is a function of the thickness and strength of interphase as

$$B = (1 + A_c d_f t) \ln \left(\frac{\sigma_i}{\sigma_m} \right), \quad (3)$$

where A_c and d_f show the specific surface area and density of nanofiller, respectively, t and σ_i denote the thickness and strength of interphase region, correspondingly. So, both s and B parameters can express the extents of interphase properties in polymer nanocomposites by the experimental data of tensile strength.

Now, these equations are linked to develop an equation for the parameter s .

In function changes Eq. (2) to

$$\ln \left(\sigma_r \frac{1 + 2.5\varphi_f}{1 - \varphi_f} \right) = \ln \sigma_r + \ln \left(\frac{1 + 2.5\varphi_f}{1 - \varphi_f} \right) = B\varphi_f. \quad (4)$$

Substituting of σ_r from Eq. (1) into above equation gives:

$$\ln \left[1 + \left(\frac{\alpha s}{\sigma_m} - 1 \right) \varphi_f \right] + \ln \left(\frac{1 + 2.5\varphi_f}{1 - \varphi_f} \right) = B\varphi_f. \quad (5)$$

When $\varphi_f \rightarrow 0$, the logarithmic terms are approximated as

$$\ln \left[1 + \left(\frac{\alpha s}{\sigma_m} - 1 \right) \varphi_f \right] \cong \left(\frac{\alpha s}{\sigma_m} - 1 \right) \varphi_f, \quad (6)$$

$$\ln \left(\frac{1 + 2.5\varphi_f}{1 - \varphi_f} \right) \cong 3.4\varphi_f. \quad (7)$$

Now, Eq. (5) can be rearranged to

$$\left(\frac{\alpha s}{\sigma_m} - 1\right)\varphi_f + 3.4\varphi_f = B\varphi_f, \quad (8)$$

which correlates B and s as

$$B = \frac{\alpha s}{\sigma_m} + 2.4. \quad (9)$$

Restructuring of above equation expresses s by

$$s = \frac{(B - 2.4)\sigma_m}{\alpha}. \quad (10)$$

Moreover, B was related to CNT dimensions and interfacial parameters in our previous study [38] as

$$B = 2.04 + \frac{\eta_o \alpha \tau}{\sigma_m}, \quad (11)$$

where η_o is an orientation factor, which is 1 for full alignment of nanoparticles, 3/8 for arbitrarily in-plane two-dimensional (2D) orientation and 1/5 for randomly 3D organization of nanoparticle, τ is interfacial shear strength. In this paper, $\eta_o = 1/5$ for 3D arrangement of CNT in nanocomposites.

When B from above equation is replaced into Eq. (10), s is given by

$$s = \frac{1}{\alpha} \left(\frac{\eta_o \alpha \tau}{\sigma_m} - 0.36 \right) \sigma_m, \quad (12)$$

correlating s to CNT, polymer and interfacial parameters.

3. Results and discussion

In this section, we discuss the roles of all parameters in s based on the developed equation.

Figure 1 depicts a contour plot for the roles of interfacial shear strength and polymer matrix strength in s at average $R = 10$ nm and $l = 10$ μ m. The maximum level of s as 3.5 MPa is obtained at $\tau > 17.5$ MPa,

Fig. 1. A contour plots for s as a function of interfacial shear strength and polymer matrix strength at average $R = 10$ nm, $l = 10$ μ m (color online)

while s significantly reduces to 1 MPa at $\tau < 7.5$ MPa. However, it is shown that the polymer strength does not affect s . Therefore, the interfacial shear strength directly controls s , but the matrix strength has no effect. In fact, the tensile strength of polymer matrix does not change s in the nanocomposites.

These results are reasonable. The interfacial shear strength may represent the strength of interface/interphase in nanocomposites. In other words, high interfacial shear strength shows the strong interface, while a poor interface/interphase indicates the low interfacial shear strength. Moreover, s demonstrates the extent of interfacial/interphase properties in nanocomposites. Since both s and interfacial shear strength depend on the interfacial/interphase properties, they display a direct relation. These outputs indicate that the developed equation properly shows the role of interfacial shear strength in s . The polymer strength has no impact on s . This trend is also meaningful, because s is a function of interfacial/interphase characteristics and the polymer strength is not effective on the interfacial aspects. In fact, the interfacial/interphase strength does not depend on the strength of polymer matrix and so, the interfacial parameter s does not correlate to the polymer strength. The logical dependence of s on the polymer strength supports the accuracy of the developed equation for s .

Figure 2 illustrates the impacts of R and l parameters on s using the developed equation. The high levels of s are calculated at low R and high l , while high R and short l reduce s . Actually, thin and long CNT increase s , but thick and short CNT weaken it. Nevertheless, the minor variation of s at different ranges of CNT dimensions indicates that CNT size has minor effects on s . In other words, this plot demonstrates

Fig. 2. Dependence of s on R and l parameters using Eq. (12) at $\sigma_m = 30$ MPa and $\tau = 10$ MPa (color online)

Fig. 3. Correlation of s to B using Eq. (12) at $R = 10$ nm, $l = 10$ μ m and $\sigma_m = 30$ MPa

Fig. 4. Variation of s at different CNT aspect ratio according to Eq. (12) at $\sigma_m = 30$ MPa and $\tau = 10$ MPa

that the CNT size slightly change s in nanocomposites. It can be said that s only depends on the interfacial interaction/adhesion between components and the interfacial area as a function of filler size is ineffective.

As mentioned, s is different from B , because B mainly depends on the filler radius/thickness and the thin nanoparticles increase B . Our previous study on the tensile strength of polymer clay nanocomposites assuming the incomplete interfacial adhesion between polymer matrix and clay (by the average normal stress in clay platelets) reported that the clay size changes s when incomplete interfacial adhesion between the polymer matrix and nanoparticles is considered [39]. However, Eq. (12) reveals that the CNT size has no influence on s .

Figure 3 plots the effect of B on s at $R = 10$ nm, $l = 10$ μ m and $\sigma_m = 30$ MPa. It is observed that s directly correlates to B . A high level of $B = 55$ produces $s = 3.2$ MPa, while $B = 5$ reduces s to 0.2 MPa. So, B directly manipulates s in polymer nanocomposites. This correlation is logical, because both B and s show the interfacial power between polymer matrix and nanoparticles [39, 40].

It means that the high levels of both B and s indicate the strong bonding between polymer and nanoparticles, while the slight values of these parameters show the poor interfacial/interphase properties in the nanocomposites. According to this explanation, the direct relation between B and s is reasonable certifying the developed equation.

Figure 4 reveals the effect of CNT aspect ratio on s according to Eq. (12) at $\sigma_m = 30$ MPa and $\tau = 10$ MPa. A high CNT aspect ratio increases s , but a poor s is observed at low CNT aspect ratio. The aspect ratio of 100 causes $s = 1.89$ MPa, while s reaches to 1.99 at the aspect ratio of 1000. So, the aspect ratio directly influences s . Although the aspect ratio directly mani-

pulates s , it slightly changes s . In other words, the aspect ratio insignificantly handles s in nanocomposites. Even though the aspect ratio of CNT determines the surface area of nanoparticles, it cannot manipulate s . In fact, this plot indicates that the s does not depend on the aspect ratio of nanoparticles. It means that s is not a function of interfacial/interphase area in nanocomposites. However, it was reported that B correlated to the filler radius in polymer nanocomposites [38, 40].

4. Conclusions

The parameter s was defined by polymer strength, CNT size and interfacial shear strength using Pukanzsky model. The maximum level of s as 3.5 MPa was obtained at $\tau > 17.5$ MPa, while s suggestively reduced to 1 MPa at $\tau < 7.5$ MPa. However, it was shown that the polymer strength did not affect s . The high levels of s were calculated by thin and long CNT, but the minor variation of s at different ranges of CNT dimensions indicated that CNT size has minor effect on s . It was said that s only depends on the interfacial interaction/adhesion between components and the interfacial area as a function of filler size is ineffective. A high level of $B = 55$ produced $s = 3.2$ MPa, while $B = 5$ reduced s to 0.2 MPa. Therefore, B directly manipulated s in polymer nanocomposites. A high CNT aspect ratio increased s , but a poor s was observed at low CNT aspect ratio. However, the aspect ratio slightly changed s . It means that s is not a function of interfacial/interphase area, while B depends on the filler radius in nanocomposites.

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