Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 615489, 7 pages
doi:10.1155/2012/615489

Research Article

Study on the Compressive Modulus of Nylon-11/Silica Nanocomposites

Haseung Chung,[1] Sungjun Kong,[2] and Dongchoul Kim[2]

[1] *Department of Mechanical and System Design Engineering, Hongik University, 72-1 Sangsu-dong, Mapo-gu, Seoul 121-791, Republic of Korea*
[2] *Department of Mechanical Engineering, Sogang University, 1 Shinsoo-dong, Mapo-gu, Seoul 100-611, Republic of Korea*

Correspondence should be addressed to Dongchoul Kim, dckim@sogang.ac.kr

Received 22 January 2012; Accepted 13 March 2012

Academic Editor: Sevan P. Davtyan

This paper investigates the unusual characteristics regarding the mechanical properties of Nylon-11 filled with different volume fractions of silica nanoparticles by selective laser sintering (SLS) from numerical simulation. The compressive modulus was predicted by two different numerical models and compared with the experimentally measured one. While the two-phase model has a limited capability in explaining the unusual behavior shown in the compressive modulus obtained by experiments with 2% volume fraction of nanoparticles, the effective interface model can simulate the unexpected characteristic of nanocomposites according to the volume fraction of nanoparticles. We can conclude that the effective interface model should be employed to predict the mechanical properties of nanocomposites for efficiency and accuracy.

1. Introduction

Polymer systems often have light weight, ductile nature, and relatively ease of production while they have lower modulus and strength compared to metals or ceramics [1, 2]. Thus, various fillers including fibers, whiskers, platelets, or particles are employed to improve the mechanical properties of polymers as their advantages are maintained. Among the fillers, particles are usefully implemented for the enhanced mechanical performance of polymers for engineering applications in which strength and toughness are very important parameters to be taken into account. Especially, nanoparticles have unique features in improving stiffness and toughness compared to micro- or macroscale particles. Since the higher surface area of nanoparticles can promote stress transfer from the matrix to the particles, the mechanical strength of polymers can be more dramatically improved than that with micro- or macroscale particles [2–4]. Several experiments have investigated the effect of particle size and attained the enhanced mechanical properties of composites with decreasing particle size [5, 6]. On the other hand, a decreasing particle size may cause defects or flaws such as brittleness [7]. These defects or flaws can be reduced by distributing nanoparticles homogeneously in a matrix, and several researches have been conducted for homogeneous dispersion [8–10].

Recently, an advanced technique that incorporates deliberately designed transitions in materials composition and properties within a component in preferred directions to optimize the functional value of that component is presented, which is functionally graded materials (FGMs) [11]. The concept of FGMs is applicable practically in various engineering fields such as aerospace, nuclear energy, energy conversion, electronics, optics, and biosystems [12]. While the ability to manufacture complex components using FGMs is highly desirable, at present, efficient automated techniques to build such components realized as per design are limited. In this respect, layered manufacturing techniques such as selective laser sintering (SLS) have the potential to be ideal techniques to automatically build such components [2]. Chung and Das have tried to fabricate a one-dimensional FGM by SLS in the structure direction using micro- to

nanoparticulate-filled polymer and demonstrated its feasibility successfully. From their study, tensile and compression specimens were also generated by SLS and mechanical tests were conducted. In the case of Nylon-11 composites filled with silica nanoparticles, they showed that both the modulus increases and the strain at break decreases as the volume fraction of silica nanoparticles increases. However, there exists a critical composition at which these characteristics undergo an inversion in their trends [3]. This paper aims at examining this peculiar tendency of Nylon-11/silica nanocomposites by experiment from the theoretical viewpoint.

Several researches have focused on the simulation based on the continuum model to analyze the mechanical properties of composites. The unit cell model has been conducted widely to predict the mechanical properties because this model reduces the computational time and provides accurate mechanical properties [13–15]. These continuum models based on the macro/microlength and time scales presented that the elastic modulus of composites consistently increases with increasing volume fraction of particles [16, 17]. Atomic simulations such as molecular dynamics (MD) and Monte Carlo (MC) techniques are moreover employed to study the structure and properties of composites, especially for composites with nanoscale particles, whose analysis with a continuum model is impractical [18, 19]. However, both MD and MC techniques require excessive computational time as particle size increases. In this paper, we characterize the mechanical properties and the distinct tendency of Nylon-11/silica nanocomposites according to the volume fraction of nanoparticles whose diameter is 15 nm. Since MD or MC is impractical for analyzing composites filled with nanoparticles whose diameter is over 7 nm, we adopted a simulation model based on continuum and discussed unusual behavior presented from our experiments [3]. In this paper, we successfully demonstrate the unexpected characteristics regarding the mechanical properties of polymer nanocomposites according to the volume fraction of nanoparticles.

2. Effective Interface Model

The Mori-Tanaka model assuming that only two phase regions exist has been widely used to analyze the mechanical properties of composites [20–22]. For nanoscale particles, the interface region exiting physically between the particle and the polymer matrix cannot be considered as a continuous region, and the mechanical properties can no longer be determined through traditional micromechanical approaches [23]. It is inappropriate to be described as consisting of just two phase regions, and the interface region needs to be defined adequately. Thus, the effective interface model has been proposed, which incorporates an effective interface region between the particle region and the polymer matrix region. The phase regions are perfectly bonded to each other similar to the Mori-Tanaka model. The effective interface model has been employed to predict the mechanical properties of a composite with the interface of the same spherical shape as the particle. The effective interface has a finite size and is commonly referred to as an interphase or an interaction zone [1]. For this model, the bulk elastic stiffness tensor is

$$C = C^m + \left[\left(c^p + c^i\right)\left(C^i - C^m\right)T^{pi} + c^p\left(C^p - C^i\right)T^p\right] \times \left[c^m I + \left(c^p + c^i\right)T^{pi}\right]^{-1}, \quad (1)$$

where c^i, c^p, and c^m are the volume fractions of the effective interface, particle, and matrix, respectively, C^i, C^p, and C^m are the stiffness tensors of the effective interface, particle, and matrix, respectively, T^p and T^{pi} are the dilute strain-concentration tensors given by

$$T^p = I - S^p\left[S^p + (C^p - C^m)^{-1}C^m\right]^{-1}, \quad (2)$$

$$T^{pi} = I - S^p\left\{\frac{c^p}{c^p + c^i}\left[S^p + (C^p - C^m)^{-1}C^m\right]^{-1} + \frac{c^p}{c^p + c^i}\left[S^p + \left(C^i - C^m\right)^{-1}C^m\right]^{-1}\right\}, \quad (3)$$

where S^p is the Eshelby tensor [24]. For a spherical particle and an isotropic matrix, the components of the Eshelby tensor are

$$S^p_{1111} = S^p_{2222} = S^p_{3333} = \frac{7 - 5\nu}{15(1 - \nu)},$$
$$S^p_{1122} = S^p_{2233} = S^p_{3311} = S^p_{1133} = S^p_{2211} = S^p_{3322} = \frac{5\nu - 1}{15(1 - \nu)},$$
$$S^p_{1212} = S^p_{2323} = S^p_{3131} = \frac{4 - 5\nu}{15(1 - \nu)}. \quad (4)$$

The effective interface is modeled as having a finite size with a discrete transition even though the actual molecular structure has a gradual transition to the bulk molecular one. Since it is assumed that the dispersion of nanoparticle is homogeneous, the elastic modulus of nanocomposites is analyzed with the unit cell. Finite element simulations were performed within the framework of the small displacements theory and materials were assumed to behave as linear, elastic, and isotropic solids. While the model that the nanoparticle is bonded to Nylon-11 is composed of just two phases, the effective interface model has three phases where the effective interface was modeled as perfect spherical and existed between Nylon-11 and 15 nm silica nanoparticles. It is also assumed that the equivalent-continuum interfacial region is both continuous and homogeneous. Figure 1 shows a schematic description of unit cell in two-phase model and three-phase model, respectively.

3. Results and Discussion

3.1. Two-Phase Model. A two-phase model based on continuum has been used to analyze the mechanical property of composites filled with macro/microparticles in previous studies. In order to evaluate rationality to use the two-phase model for nanocomposites, the two-phase model was

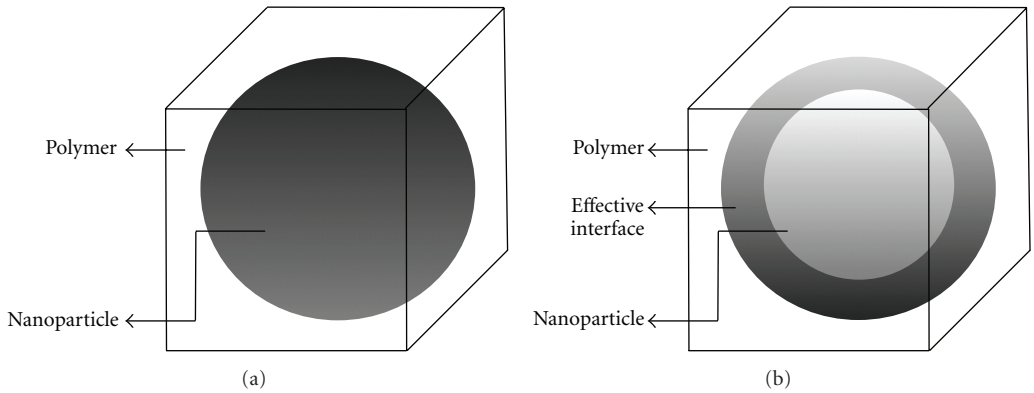


Figure 1: Unit cell of the nanocomposite in (a) the two-phase model and (b) an effective interface model.

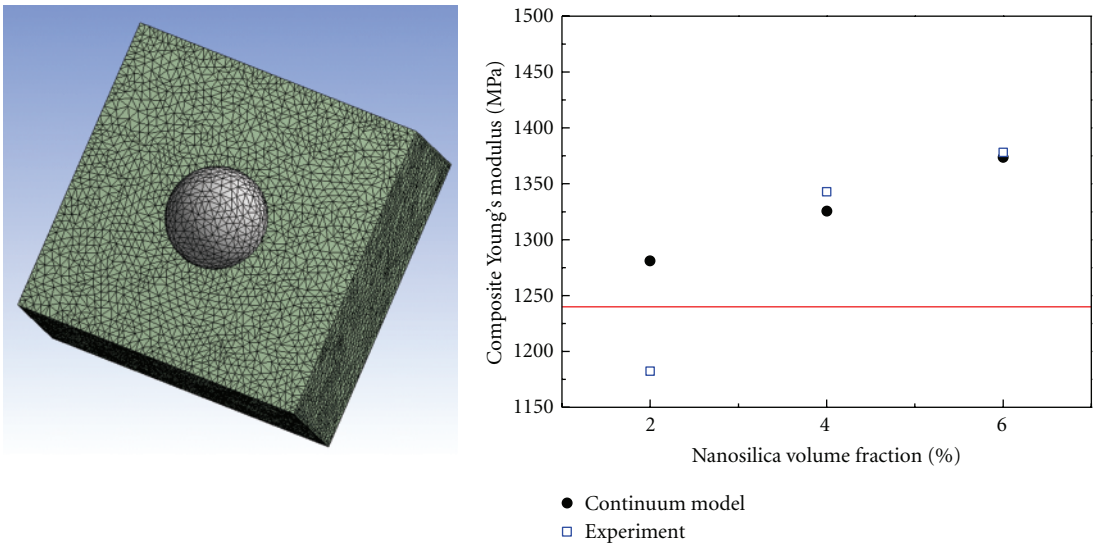
preferentially generated to predict the mechanical property of nanocomposites. The compressive modulus of Nylon-11/silica nanocomposite produced by SLS was investigated with respect to the volume fraction of nanoparticles by the two-phase model. Poisson's ratios of the particle and matrix are taken as 0.19 and 0.35, respectively. Young's modulus of silica particle is 88.7 GPa and that of Nylon-11 matrix is 1.24 GPa [2, 3]. Figure 2 shows a model of unit cell used in the two-phase model and compares the compressive modulus obtained from numerical simulations with experimental results presented elsewhere [3]. For experimental results, five specimens were generated for each composition, and accordingly compressive tests were conducted. All the values including 2% volume concentration represent the averaged values within 2% error range from five compressive tests.

As shown in Figure 2, the compressive modulus calculated from simulations continuously increases with increasing volume fraction of nanoparticles and is consistent with experimental results at 4% and 6% volume fraction of nanoparticles. However, the simulation result the by two-phase model presents an increased modulus at 2% volume fraction of nanoparticles while the compressive modulus from the experiment demonstrates the decreased modulus at 2% volume fraction of nanoparticles. The experimental results imply that there exists a critical composition at which the characteristics of compressive modulus as a function of volume fraction of nanoparticles undergo an inversion in their trends but the two-phase model is not able to reflect this behavior. The compressive modulus of the nanocomposite simulated by the two-phase model shows a good agreement with the experimental results up to 6% of volume fraction. This might have resulted from the assumption that the polymer matrix was perfectly bonded to nanoparticles because 15 nm fumed silica nanoparticles have a much higher Young's modulus than Nylon-11. However, the two-phase model has a limited capability in explaining the unusual behavior shown in the modulus obtained by experiments with 2% volume fraction of nanoparticles even if a polymer matrix experiences full melting and resolidification by SLS.

3.2. Effective Interface Model. As shown in Figure 2, the experimental compressive modulus at 2% volume fraction is even lower than the pure Nylon-11 even though the modulus increases as the volume fraction of nanoparticles increases from 4%. In order to explain why the compressive modulus at 2% volume fraction has a different tendency, it is proper to use the effective interface model. 15 nm fumed silicas are not perfectly bonded to the Nylon-11 polymer matrix due to their size relative to polymer chains. Thus, the region around nanoparticles embedded in the polymer matrix has a different density from that of a pure polymer, which is denoted as the effective interface region. The effective interface region has a lower Young's modulus than that of Nylon-11 due to sparse structure around nanoparticles. The effective interface region has a structural characteristic consisting of flexible polymer chains that are typically in sequences of adsorbed segments and unadsorbed segments, such as loops and tails. They are in turn entangled with other chains in their proximity and are necessarily bound to the surface. Hence, the density of the effective interface region becomes lower resulting from the weak interaction between chains and the surface because loops and tails extend farther into the matrix. This phenomenon is indicated by the smaller size of the particles, which is 15 nm.

In order to estimate Young's modulus of composite, the volume fraction and the mechanical properties of the effective interface are prerequisite. We have determined Young's modulus of the effective interface from an iterative procedure between calculations with the effective interface equations (1)–(4) and numerical calculations with finite element method. Various volume fractions of the effective interface are tried for each volume fraction of silica particles to analyze Young's modulus of composite. The procedure is summarized in Figures 3 and 4 shows a model of unit cell used in the effective interface model.

Figure 5 compares the compressive modulus obtained from the numerical simulations with the experimental results presented elsewhere [3]. As presented in Figure 5 and Table 1, the performed analysis demonstrates that the volume fraction of the effective interface plays an important role in the mechanical property of nanocomposites. We attempted to prove that our model expects an unusual characteristic of compressive modulus under various volume fractions of the effective interface. For the volume fraction



(a) (b)

Figure 2: (a) Model of unit cell in the two-phase approach. (b) Compressive modulus of nanocomposites with various volume fractions of silica particles.

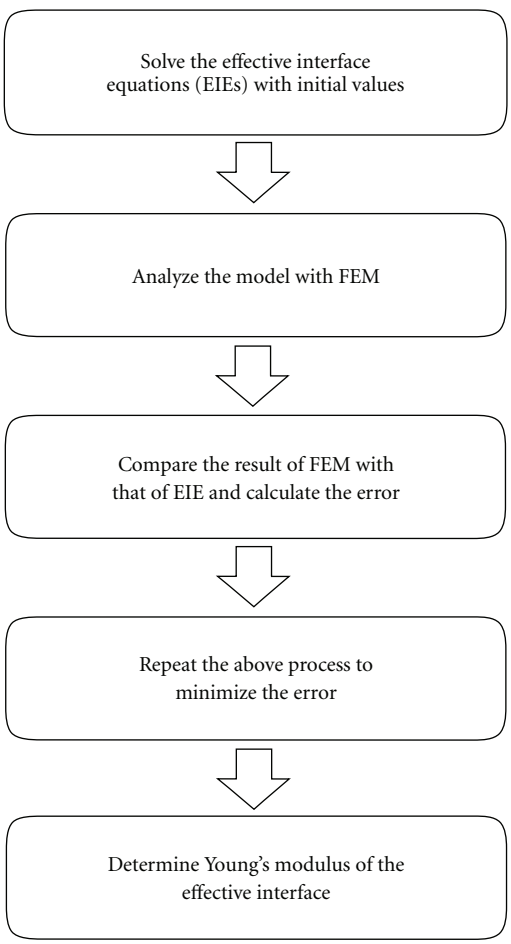


Figure 3: Procedure to calculate Young' modulus of an effective interface.

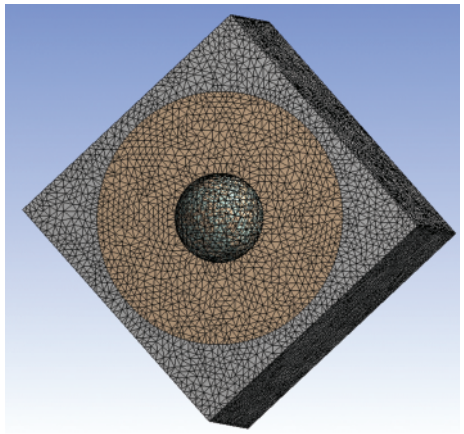


Figure 4: Model of unit cell in the effective interface approach.

of the effective interface, 10%, 15%, and 20% are tried. Figure 5 shows the compressive modulus as a function of volume fraction of the effective interface for nanocomposites with 2%, 4%, and 6% volume fraction, respectively. The compressive modulus of the nanocomposite increases with decreasing volume fraction of the effective interface while the compressive modulus of the nanocomposite decreases with decreasing Young's modulus of the effective interface for composites with 2% volume fraction of particles. With 4% and 6% volume fraction of particles, the compressive modulus of the nanocomposite increases with increasing volume fraction of the effective interface.

As shown in Figure 5(a), the compressive modulus of the nanocomposite with 2% volume fraction of particles decreases with increasing volume fraction of the effective interface and is even smaller than the neat polymer. However,

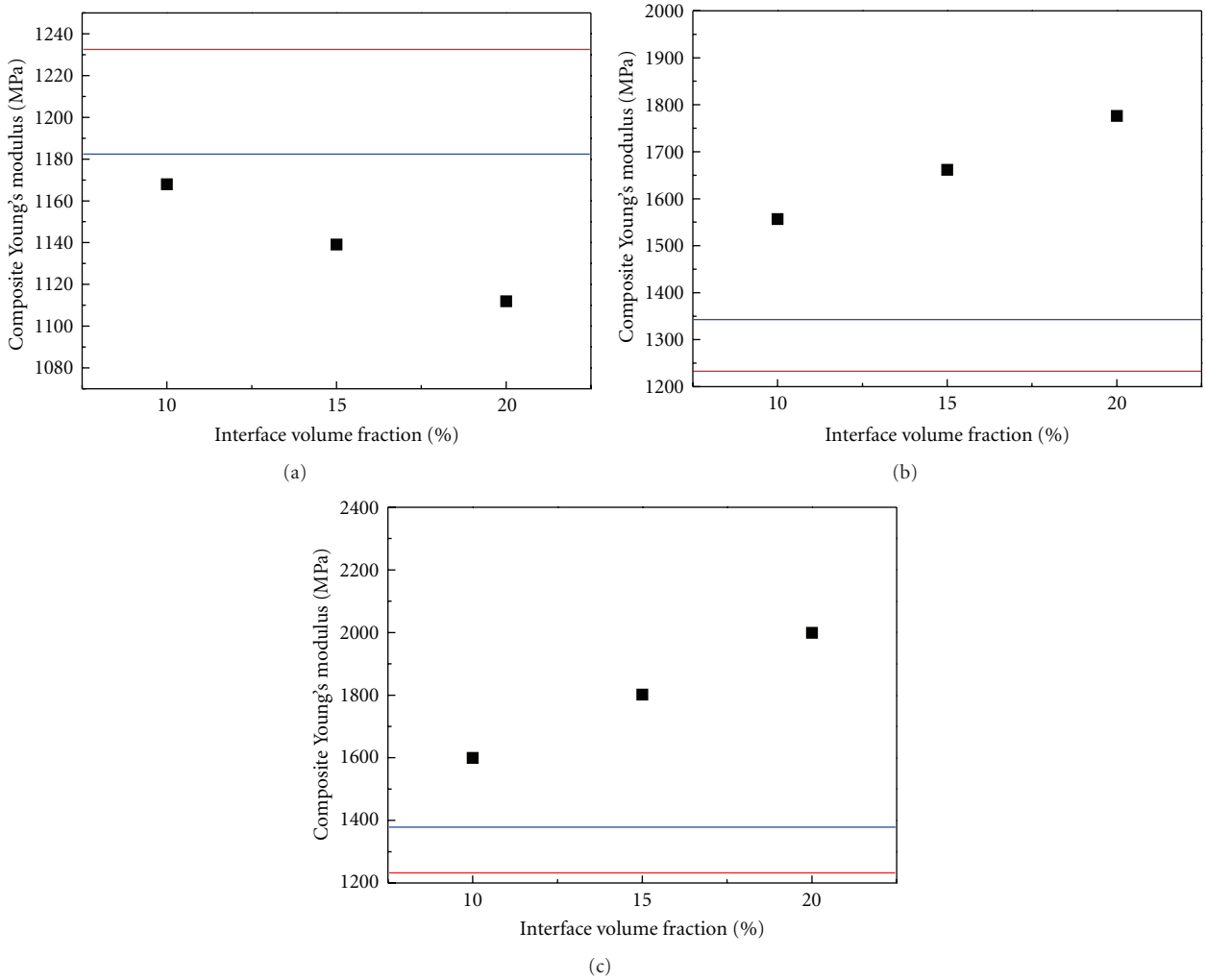


Figure 5: Young's modulus of nanocomposites with respect to the volume fraction of the effective interface. The volume fractions of particles are (a) 2%, (b) 4%, and (c) 6%. The red line is Young's modulus of Nylon-11. The blue line is Young's modulus of nanocomposites examined from experiments.

Table 1: Young's modulus of effective interface with respect to the volume fraction (MPa).

Volume fraction of particles	Volume fraction of effective interface			
	10%	15%	20%	25%
2%	577	627	657	678
4%	1012	723	637	614
6%	1332	1651	1932	1749

this trend becomes opposite in nanocomposites with 4% or larger volume fraction of nanoparticles. As the volume fraction of effective interface increases, the compressive modulus of nanocomposite also increases and is larger than the neat polymer. Figure 6 shows the compressive modulus as a function of volume fraction of nanoparticles under various volume fractions of the effective interface.

As shown in Figure 6, only for 2% volume fraction of nanoparticles, Young's modulus of the composite is smaller than that of the matrix as observed in the experiments. Young's modulus of matrix is depicted with a red line in Figure 6. All the calculated Young's moduli with different volume fractions of the effective interface are also consistent with the experimental observations as shown in Figure 6. The low density of the effective interface induces small Young's modulus of the effective interface. Thus, the effective interface behaves as a tender layer surrounding the nanoparticle and induces very small Young's modulus of composite such as the composite with 2% volume fraction of nanoparticles. As the volume fraction of the particle with high modulus increases, the effect of the effective interface is vanished by the increased amount of strong particles. Hence, it suggests that there must be the critical volume fraction of particles that induces the distinct influence of the effective interface on the mechanical property of nanocomposites.

While the two-phase model is not able to expect the unusual behavior shown in the modulus by the experiment with 2% volume fraction of nanoparticles, the compressive

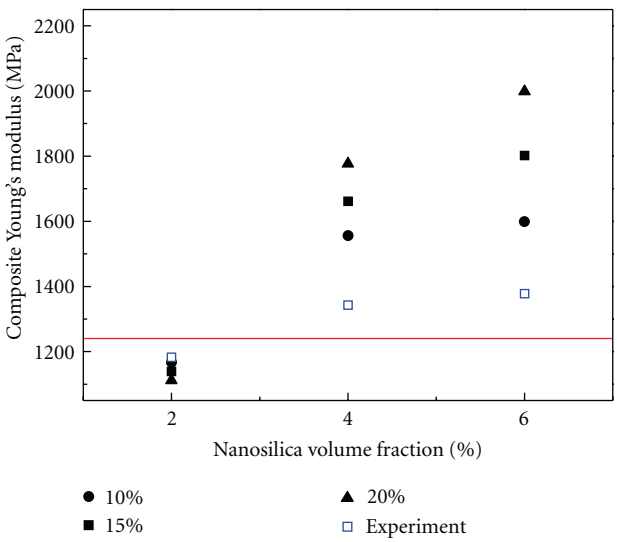


Figure 6: Compressive modulus of nanocomposites with respect to the volume fraction of silica particle. The red line is Young's modulus of Nylon-11.

modulus obtained by the effective interface model shows a good agreement with the experimental results overall. We can conclude that the effective interface model should be employed to predict the mechanical properties of Nylon-11 composites filled with silica nanoparticles for efficiency and accuracy.

4. Conclusions

This paper investigates the unusual characteristics regarding the mechanical properties of Nylon-11 filled with different volume fractions of silica nanoparticles by selective laser sintering (SLS) from numerical simulation. The compressive modulus was predicted by two different numerical models and compared with the experimentally measured one.

The compressive modulus calculated from the two-phase model continuously increases with increasing the volume fraction of nanoparticles and is consistent with the experimental results at 4% and 6% volume fraction of nanoparticles. However, the simulation result by the two-phase model presents an increased modulus at 2% volume fraction of nanoparticles while the compressive modulus from the experiment demonstrates the decreased modulus at 2% volume fraction of nanoparticles. The experimental results imply that there exists a critical composition at which the characteristics of the compressive modulus as a function of the volume fraction of nanoparticles undergo an inversion in their trends but the two-phase model is not able to reflect this behavior.

In order to explain why the compressive modulus at 2% volume fraction has a different tendency, the effective interface model was introduced here. The compressive modulus of the nanocomposite with 2% volume fraction of particles decreases with increasing volume fraction of effective interface and is even smaller than the neat polymer. However, this trend becomes opposite in nanocomposites with 4% or larger volume fraction of nanoparticles. As the volume fraction of the effective interface increases, the compressive modulus of the nanocomposite also increases and is larger than the neat polymer. Consequently, we could successfully demonstrate the unexpected characteristics regarding the mechanical properties of polymer nanocomposites according to the volume fraction of nanoparticles using the effective interface model. We can conclude that the effective interface model should be employed to predict the mechanical properties of nanocomposites for efficiency and accuracy.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2011-0011932, 2011-0029212) and no. 2010-0001913 funded by the Korean government (MEST) through the Multi-Phenomena CFD Engineering Research Center. This work was also supported by the Sogang University Research Grant of 200910020.

References

[1] G. M. Odegard, T. C. Clancy, and T. S. Gates, "Modeling of the mechanical properties of nanoparticle/polymer composites," *Polymer*, vol. 46, no. 2, pp. 553–562, 2005.

[2] H. Chung and S. Das, "Processing and properties of glass bead particulate-filled functionally graded Nylon-11 composites produced by selective laser sintering," *Materials Science and Engineering A*, vol. 437, no. 2, pp. 226–234, 2006.

[3] H. Chung and S. Das, "Functionally graded Nylon-11/silica nanocomposites produced by selective laser sintering," *Materials Science and Engineering A*, vol. 487, no. 1-2, pp. 251–257, 2008.

[4] F. N. Ahmad, M. Jaafar, S. Palaniandy, and K. A. M. Azizli, "Effect of particle shape of silica mineral on the properties of epoxy composites," *Composites Science and Technology*, vol. 68, no. 2, pp. 346–353, 2008.

[5] A. C. Roulin-Moloney, W. J. Cantwell, and H. H. Kausch, "Parameters determining the strength and toughness of particulate-filled epoxy-resins," *Polymer Composites*, vol. 8, no. 5, pp. 314–323, 1986.

[6] R. J. Cardoso, A. Shukla, and A. Bose, "Effect of particle size and surface treatment on constitutive properties of polyester-cenosphere composites," *Journal of Materials Science*, vol. 37, no. 3, pp. 603–613, 2002.

[7] M. I. Sarwar, S. Zulfiqar, and Z. Ahmad, "Polyamide-silica nanocomposites: mechanical, morphological and thermomechanical investigations," *Polymer International*, vol. 57, no. 2, pp. 292–296, 2008.

[8] M. Z. Rong, M. Q. Zhang, Y. X. Zheng, H. M. Zeng, R. Walter, and K. Friedrich, "Structure-property relationships of irradiation grafted nano-inorganic particle filled polypropylene composites," *Polymer*, vol. 42, no. 1, pp. 167–183, 2001.

[9] R. Y. Hong, H. P. Fu, Y. J. Zhang et al., "Surface-modified silica nanoparticles for reinforcement of PMMA," *Journal of Applied Polymer Science*, vol. 105, no. 4, pp. 2176–2184, 2007.

[10] X. Xu, B. Li, H. Lu, Z. Zhang, and H. Wang, "The effect of the interface structure of different surface-modified nano-SiO2 on the mechanical properties of nylon 66 composites," *Journal of Applied Polymer Science*, vol. 107, no. 3, pp. 2007–2014, 2008.

[11] B. Ilschner, "Processing-microstructure-property relationships in graded materials," *Journal of the Mechanics and Physics of Solids*, vol. 44, no. 5, pp. 647–656, 1996.
[12] Y. Miyamoto, "Development of functionally graded materials by HIP," *Materials Science Research International*, vol. 6, no. 1, pp. 3–8, 2000.
[13] K. S. Ravichandran, "A simple model of deformation behavior of two phase composites," *Acta Metallurgica Et Materialia*, vol. 42, no. 4, pp. 1113–1123, 1994.
[14] H. S. Kim, M. B. Bush, and Y. Estrin, "A phase mixture model of a particle reinforced composite with fine microstructure," *Materials Science and Engineering A*, vol. 276, no. 1-2, pp. 175–185, 2000.
[15] I. Tirtom, M. Güden, and H. Yildiz, "Simulation of the strain rate sensitive flow behavior of SiC-particulate reinforced aluminum metal matrix composites," *Computational Materials Science*, vol. 42, no. 4, pp. 570–578, 2008.
[16] J. Segurado and J. Llorca, "A numerical approximation to the elastic properties of sphere-reinforced composites," *Journal of the Mechanics and Physics of Solids*, vol. 50, no. 10, pp. 2107–2121, 2002.
[17] A. Pramanik, L. C. Zhang, and J. A. Arsecularatne, "An FEM investigation into the behavior of metal matrix composites: tool-particle interaction during orthogonal cutting," *International Journal of Machine Tools and Manufacture*, vol. 47, no. 10, pp. 1497–1506, 2007.
[18] T. Kairn, P. J. Daivis, I. Ivanov, and S. N. Bhattacharya, "Molecular-dynamics simulation of model polymer nanocomposite rheology and comparison with experiment," *Journal of Chemical Physics*, vol. 123, no. 19, Article ID 194905, 7 pages, 2005.
[19] A. Adnan, C. T. Sun, and H. Mahfuz, "A molecular dynamics simulation study to investigate the effect of filler size on elastic properties of polymer nanocomposites," *Composites Science and Technology*, vol. 67, no. 3-4, pp. 348–356, 2007.
[20] T. Mori and K. Tanaka, "Average stress in matrix and average elastic energy of materials with misfitting inclusions," *Acta Metallurgica*, vol. 21, no. 5, pp. 571–574, 1973.
[21] G. J. Weng, "The theoretical connection between Mori-Tanaka's theory and the Hashin-Shtrikman-Walpole bounds," *International Journal of Engineering Science*, vol. 28, no. 11, pp. 1111–1120, 1990.
[22] Y. Benveniste, "Some remarks on three micromechanical models in composite media," *Journal of Applied Mechanics*, vol. 57, no. 2, pp. 474–476, 1990.
[23] S. J. Lue, J. Y. Chen, and J. M. Yang, "Crystallinity and stability of poly(vinyl alcohol)-fumed silica mixed matrix membranes," *Journal of Macromolecular Science, Part B*, vol. 47, no. 1, pp. 39–51, 2008.
[24] T. W. Clyne and P. J. Withers, *An Introduction to Metal Matrix Composites*, Cambridge University Press, 1995.