

Micromechanical Models for Carbon Nanotube and Cellulose Nanowhisker Reinforced Composites

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Different micromechanical models which account for the presence of dispersed and agglomerated nanofillers, specifically carbon nanotubes (CNTs) and cellulose nanowhiskers (CWs), in a polymeric matrix and consider the effect of a percolation threshold on the elastic modulus of the composite are derived and compared. We demonstrate that the critical filler volume fraction where a percolating network is forming marks a ‘turning point’ in the reinforcement efficiency. The suitability of these models is verified by comparing simulated values with experimental data from literature. The results show that the models are able to predict mechanical properties over a wide range of testing conditions. POLYM. ENG. SCI., 00:000–000, 2012. © 2012 Society of Plastics Engineers

INTRODUCTION

Nanocomposites are a class of composites in which one of the dimensions of the reinforcement phase is in the range of 1–100 nm. Because of the filler nanometer size characteristics, nanocomposites possess superior properties by comparison with more conventional composites reinforced with micron sized fillers [1]. Such properties are mainly due to filler high specific surface areas (of the order of 100s of $\text{m}^2 \text{g}^{-1}$) and aspect ratios (100–1000). Moreover, the properties of nanocomposites seem to be primarily affected by the onset of a 3D network at a filler concentration labeled as the percolation threshold (V_c). The effect of the mechanical percolation is extremely dependent on the degree of interaction between fillers. Therefore systems reinforced with a percolated network of weakly interacting fillers may behave differently from systems reinforced with a strongly connected percolated network of fillers. The prediction of the mechanical properties of systems with percolating dispersed fillers remains a challenge and classical mechanical models such as Halpin–Tsai or the rule of mixtures prove not to be accurate.

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In this study, we compare the mechanical percolation effect of two different nanofillers, namely carbon nanotubes (CNTs) and cellulose nanowhiskers, on the elastic modulus of polymer based composites. The Takayanagi Models I and II are applied to better account for the effect of a percolating network. In addition, the change in reinforcement efficiency and network formation at temperatures below and above the T_g is discussed.

Composites Containing Cellulose Nanowhiskers

Nanometric monocrystals of cellulose, commonly referred as whiskers, can be obtained from various sources such as wood [2], tunicin [3], ramie [4], cotton [5], wheat straw [6], bacterial cellulose [7], and sugar beet [8]. In addition, other important natural whiskers comprise chitin whiskers [9] as well as starch crystals [10].

The addition of nanowhiskers into a polymer matrix has been showed to have a remarkable effect on the mechanical performance of the system. Let us consider different polymers such as latex, poly(vinyl chloride) or atactic polypropylene (aPP). Below the glass transition temperature (T_g) the modulus of the neat polymer does not vary significantly with temperature, however it drops rapidly to a few MPa once the T_g is reached (◆ in Fig. 1). The polymer then behaves as a viscous liquid with the stiffness decreasing with increasing the temperature. When nanowhiskers are added to a polymer matrix, the behavior is also different below and above the T_g . Generally, for temperatures below the T_g , the presence of nanowhiskers does not affect the composite modulus to a great extent (○,* in Fig. 1). In this case the elastic moduli of the whiskers, E_w , and of the matrix, E_m , are not that different ($E_w/E_m \geq 1$) to render a reinforcement effect with only a small amount of filler. On the other hand, above the T_g , the reinforcement efficiency of the whiskers changes. The ratio between the filler-to-matrix modulus is now extremely high ($E_w \gg E_m$) and the reinforcement effect becomes apparent. The modulus of the composite is higher than the one of the neat polymer and the drop observed due to the glass–rubber transition is reduced as compared to the neat polymer (Fig. 1). At such

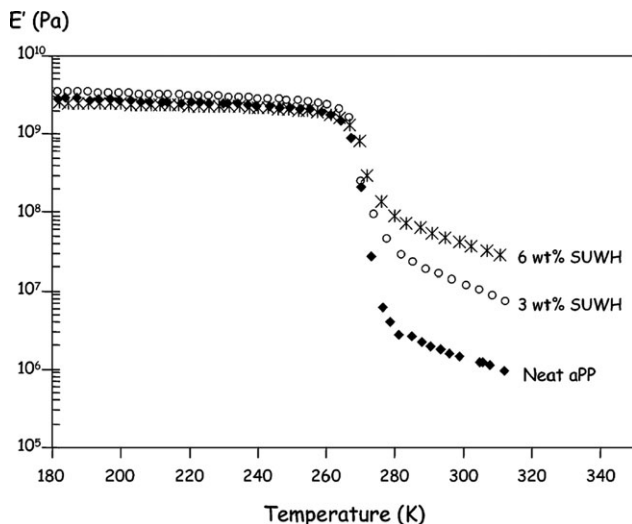


FIG. 1. Temperature dependence of storage modulus curves for aPP and composites reinforced with 3 and 6 wt% nanowhiskers. Reprinted with permission from [11]. © American Chemical Society (2005).

temperatures and for volume fractions above the threshold, the reinforcement observed has shown to drastically increase with the volume fraction of whiskers.

These results have been attributed to the formation of a stiff cellulose whisker network, which occurs when processing enables the formation of strong hydrogen bonds between the whiskers. This effect is generally present in composites prepared by an evaporation process which allows whisker contact and enables the formation of a strong network due to the hydrogen bonding between the hydroxyl groups on their surface. The system moduli observed experimentally in the situation above are higher than predicted with a classical model like the Halpin–Kar-

dos model [11]. The results suggest that interactions between the whiskers induce the mechanical percolation of the fillers. The influence of this effect on the mechanical properties of the system can be calculated following the method of Ouali et al. in their adaptation of the percolation theory to the parallel-series model of Takayanagi.

Takayanagi et al. developed a two-phase mechanical model to predict the modulus of a crystalline polymer, taking into consideration the crystalline and noncrystalline phases of a polymer and the fact that those different parts of the crystalline phase can undergo different deformation under the application of stress [12]. The Takayanagi model was used successfully to analyze tensile properties for polymer blends and for composite systems with diverse filler morphologies [13, 14].

Ouali et al. extended the parallel-series model of Takayanagi by introducing a percolating concept [15]. This enabled the application of the model to predict mechanical properties for polymer composites reinforced with cellulose nanowhiskers and polymer blends [13]. Recently we have extended the series-parallel model of Takayanagi to include the percolating concept and use it to predict mechanical properties of carbon nanotube reinforced composites [16].

A schematics for the series-parallel (Model I) and parallel-series (Model II) models is shown in Fig. 2a and b. Parameters λ and ϕ or their combinations reflect volume fractions of the system components [16].

Following the schematics of the models shown in Fig. 2a and b, we define $1 - \lambda$ the volume fraction of the percolating phase and $\lambda\phi$ the volume fraction of the dispersed phase. It follows that the volume fraction of the filler (F) is given by [16]:

$$V_F = 1 - \lambda + \lambda\phi \quad (1)$$

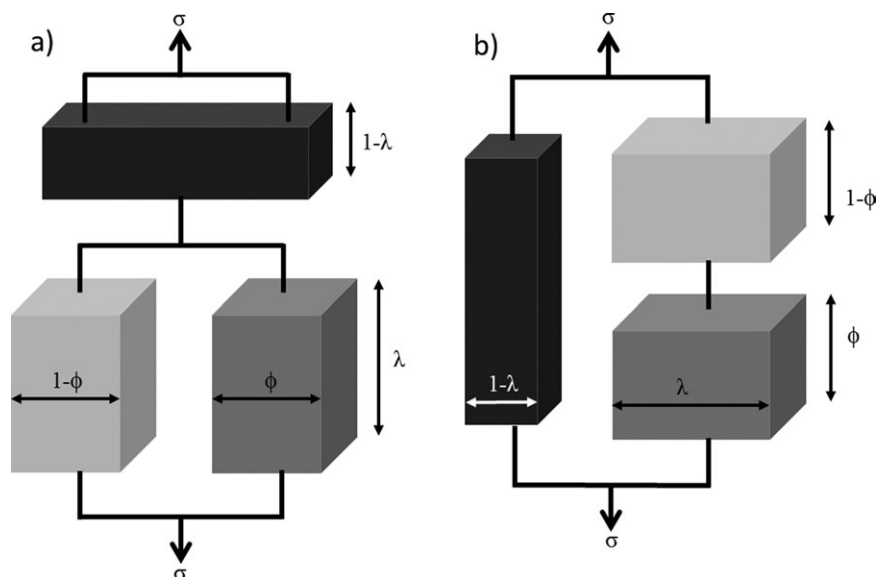


FIG. 2. Schematic representation of Takayanagi Model I (a) and II (b). ϕ is a function of the volume fraction of the parallel element and λ of the series element. Models I and II are also known as the series-parallel and parallel-series model, respectively.

The percolation threshold, V_c , can be obtained experimentally as well as estimated theoretically as a function of the filler aspect ratio (η). Based on the excluded volume concept, Celzard et al. [17] and Balberg et al. [18] estimated the percolation threshold to be:

$$V_c = \frac{0.5}{\eta} \quad (2)$$

where $\eta = l/d$. In systems with large distributions of aspect ratio, the percolation threshold can be lower than the value predicted by Eq. 2.

The percolation behavior in the vicinity of the percolation threshold is well described by Chatterjee [19] using a “switching function”, f_s , defined as:

$$\begin{aligned} f_s(V_F) &= 0 & V_F < V_c \\ f_s(V_F) &= 1 - e^{-A(V_F/V_c - 1)^{0.474}} & V_F \geq V_c \end{aligned} \quad (3)$$

where A is an adjustable parameter which modulates the width of the transition. The choices for f_s in Eq. 3, have the advantage that the domain within which the percolation probability exhibits power-law behavior can be appropriately confined to the vicinity of the threshold by a suitable choice of the parameter A [19]. Hence, one can differentiate between the fraction of well dispersed and agglomerated fillers present in the system by adjusting A [16, 19]. As a result, when $V_F > V_c$, a fraction $V_F^{agg} = f_s V_F$ of the fillers in the system belongs to the percolating network, whereas the remaining rods $V_F^{dis} = (1 - f_s)V_F$ are treated as being uniformly dispersed within the polymeric matrix.

According to the Model I shown in Fig. 2a, the modulus of the composite E_c is given by [16]:

$$E_c = \frac{(1 - V_F)E_m E_F^{agg} + (V_F + \lambda - 1)E_F^{dis} E_F^{agg}}{(1 - \lambda)(1 - V_F)E_m + (1 - \lambda)(\lambda + V_F - 1)E_F^{dis} + \lambda^2 E_F^{agg}} \quad (4)$$

where E_F^{agg} , E_F^{dis} , and E_m are the Young’s moduli of the percolated filler network, dispersed fillers and matrix phase, respectively and V_F is the filler volume fraction.

For $V_F < V_c$, $\lambda = 1$ and Eq. 4 reduces to the rule of mixtures (upper bound):

$$E_c = (1 - V_F)E_m + V_F E_F^{dis} \quad (5)$$

For the Model II shown in Fig. 2b, the elastic modulus of the composite can be written as [16]:

$$E_c = \frac{(1 - \lambda)(1 - V_F)E_F^{dis} E_F^{agg} + (1 - \lambda)(V_F + \lambda - 1)E_m E_F^{agg} + \lambda^2 E_m E_F^{dis}}{(1 - V_F)E_F^{dis} + (V_F + \lambda - 1)E_m} \quad (6)$$

Details for the derivation of Eqs. 4 and 6 can be found in [16]. For $V_F < V_c$, $\lambda = 1$ and Eq. 6 simply reduces to the series model (lower bound):

$$E_c = \frac{E_m E_F^{dis}}{(1 - V_F)E_F^{dis} + V_F E_m} \quad (7)$$

We employ Takayanagi Model II to describe the mechanical behavior of composites containing cellulose whiskers at temperatures above the glass transition temperature. For whisker volume concentrations below the percolation threshold, Takayanagi Model II assumes that only dispersed nanowhiskers are present in the system. The two phases, matrix and whiskers are in a series arrangement and the composite modulus is described by a lower bound. This fits the physical picture of a soft matrix above the glass transition temperature and a high modulus filler at relatively low concentrations. It is also worthwhile mentioning that when considering the dispersed nanowhiskers, this phase may also contain isolated aggregates. However the filler concentration is not sufficient for a 3D network to form. Once the amount of whiskers increases above the percolation threshold, a 3D network is formed throughout the matrix. At this point, three phases, namely matrix, dispersed nanowhiskers and the percolated network are present in the system. Further increase in the filler concentration will increase both the network density and the amount of individual dispersed nanowhiskers. According to Takayanagi Model II, the network of whiskers will elongate as much as the combined matrix and dispersed whiskers phases. The strong 3D whisker network linked by hydrogen bonds will support a higher load than the matrix or the dispersed whiskers. The stiffness of the percolated network is strongly affected by the nature of cohesive forces among its constituents. For instance, it has been reported that the cohesion between percolating individualized whiskers is stronger than the cohesion between aggregates [11]. Also, once water is present in the system, water-nanowhiskers interactions prevail over filler–filler interactions and the network stiffness is tremendously reduced [20]. Filler surface modifications or the presence of surfactants may also alter the 3D network properties.

Figure 3 shows three examples of the application of the Takayanagi Model II for fitting experimental data from literature. The composites prepared by Capadona et al. are based on a rubbery ethylene oxide–epichlorohydrin copolymer (EO-EPI) and tunicates-cellulose nanowhiskers isolated from sea cucumbers [20]. The individual tunicates have a modulus of ~ 143 GPa, whereas films prepared from the tunicates show a modulus of 4 GPa [20]. The authors have also shown that water could act as a chemical regulator for the whisker-whisker interaction, tremendously reducing the network stiffness. Figure 3 shows that Takayanagi Model II fits very well the experimental results for both dry EO-EPI/whisker nanocomposites as well as the ones conditioned by equilibrium swelling in de-ionized water. Note in Fig. 3 that parameter “ A ” in Chatterjee’s “switching function” was changed from 0.2 to 0.15 and the Young’s modulus of the aggre-

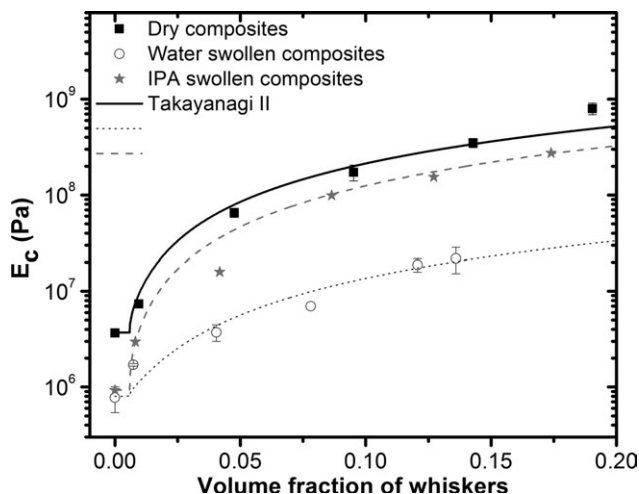


FIG. 3. Tensile storage moduli of EO-EPI/whisker nanocomposites as function of volume fraction of cellulose whiskers. Dry composites (■,—) reported [20] whiskers and matrix material parameters: $l = 2.2 \mu\text{m}$, $d = 26 \text{ nm}$, $E_m = 3.66 \text{ MPa}$; $E_{\text{whi}}^{\text{dis}} = 143 \text{ GPa}$, $E_{\text{whi}}^{\text{agg}} = 4 \text{ GP}$, fitting parameter: $A = 0.2$. Water swollen composites (○,.....) reported [20] whiskers and matrix material parameters: $l = 2.2 \mu\text{m}$, $d = 26 \text{ nm}$, $E_m = 0.78 \text{ MPa}$; $E_{\text{whi}}^{\text{dis}} = 143 \text{ GPa}$, fitting parameters: $E_{\text{whi}}^{\text{agg}} = 300 \text{ GPa}$, $A = 0.15$. Isopropanol (IPA) swollen composites (★,—) reported [20] whiskers and matrix material parameters: $l = 2.2 \mu\text{m}$, $d = 26 \text{ nm}$, $E_m = 0.928 \text{ MPa}$; $E_{\text{whi}}^{\text{dis}} = 143 \text{ GPa}$, $E_{\text{whi}}^{\text{agg}} = 4 \text{ GPa}$, fitting parameter: $A = 0.1$.

gated whiskers was changed from 4 GPa to 300 MPa to reflect a change in network formation due to the presence of water. The 300 MPa value was obtained by curve fitting since the moduli of water soaked whisker films has not been reported in the literature. To confirm that the results obtained were not just due to the plasticization of the material swollen in water, composites have been conditioned by equilibrium swelling in isopropanol (IPA), a solvent which swells neat EO-EPI but do not disperse cellulose whiskers. Again the results are fitted well by the Takayanagi model suggesting the network formation. In employing Takayanagi Model II we have used material parameters determined experimentally with the exception of the modulus for the swollen whisker network which we considered to be an order of magnitude lower than the dry one. In addition, to take into account the different mechanism of network formation for IPA swollen composites parameter “A” was modified [19, 21].

Composites Containing CNTs

Because of their outstanding electrical, thermal and mechanical properties, carbon nanotubes (CNTs) show great potential for many applications and are considered to be ideally suited for the next generation of nanocomposite materials [22]. During the last decade, a great deal of effort has been given toward maximizing the promise of CNTs as reinforcing agents in polymer matrix composites. Despite this effort, the full potential of CNT-reinforced composites has not been realized due to current technological limitations in obtaining homogene-

ous dispersions of CNTs and sometimes to lack of matrix/nanotube interfacial adhesion. Results from different micromechanical models such as the widely known Halpin-Tsai, predict that composites containing CNTs should exhibit exceptional mechanical properties whereas the experimental evidence is contradictory to such predictions at filler volume fractions above a threshold value.

Reports in the literature have shown that the enhancement of properties due to the addition of CNTs takes place up to a certain concentration of fillers, after which the reinforcement efficiency decreases [23]. In fact, numerous reported experimental results have suggested that at low concentrations of CNTs, the composite modulus increases linearly with the amount of filler whereas after some point, increasing the amount of CNTs leads to a less significant improvement in properties [23, 24].

Because of strong interactions, carbon nanotubes tend to aggregate and above a critical concentration form a percolating network throughout the polymeric matrix. However, differently from nanowhiskers, carbon nanotubes form a geometrical percolating network without strong hydrogen bonds, and we have shown that the network formation can be detrimental to the system mechanical properties [25]. It is interesting to remark that the change in the filler reinforcement efficiency usually takes place at volume fractions coincident with the percolation threshold (V_c).

We have recently formulated and compared different micromechanical models for the prediction of mechanical properties of CNT reinforced polymers, considering the presence of agglomerated CNTs and the percolation of the fillers. Below the critical percolation threshold, the system is comprised of two phases, namely a relatively stiff matrix at temperatures below the glass transition temperature and the dispersed carbon nanotubes. These nanotubes can agglomerate but their concentration is too low to render a network. These two phases are in a parallel arrangement in the mechanical model and the system properties will define an upper bound. Above the percolation threshold, a 3D network is formed which can support a higher load than the matrix or the dispersed carbon nanotubes [16, 26, 27]. However, this network is not strengthened by hydrogen bonds and consequently it cannot reinforce the system to the same extent as individually dispersed nanotubes. This is why experimentally the “negative” turning point is observed.

Takayanagi Model I can satisfactorily fit the mechanical behavior of nanocomposites. Figure 4 shows two examples of the application of the Takayanagi Model I for the fitting of experimental data from literature. The Young’s moduli of 3D networks of CNTs used during simulations were in the range of values published for the moduli of CNT buckypapers [28]. The Takayanagi Model I captures well the change in CNTs reinforcing efficiency once the percolation concentration is reached (Fig. 4a). In addition, the result presented in Fig. 4b shows that up to

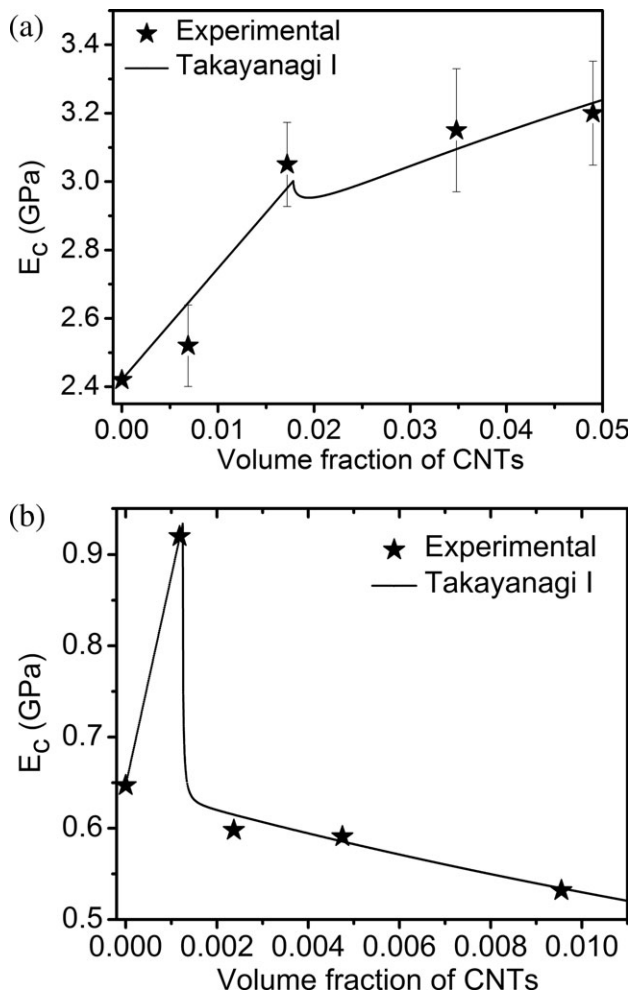


FIG. 4. Comparison of experimental and simulated elastic modulus of different CNT based composites. (a) MWCNT/polyamide composites; reported [24] MWCNTs and matrix material parameters: $l = 1.68 \mu\text{m}$, $d = 60 \text{ nm}$, $E_m = 2.42 \text{ GPa}$; fitting parameters: $E_{\text{NT}}^{\text{dis}} = 35 \text{ GPa}$, $E_{\text{NT}}^{\text{agg}} = 10 \text{ GPa}$, $A = 0.6$. (b) MWCNT/ultrahigh-molecular-weight polyethylene composites; reported [25] MWCNTs and matrix material parameters: $l = 10 \mu\text{m}$, $d = 25 \text{ nm}$, $E_m = 0.65 \text{ GPa}$; fitting parameters: $E_{\text{NT}}^{\text{dis}} = 230 \text{ GPa}$, $E_{\text{NT}}^{\text{agg}} = 0.028 \text{ GPa}$, $A = 9$.

the critical percolation threshold, the CNTs reinforce the polymer matrix but at higher volume fractions of CNTs the percolated network has a detrimental effect on the modulus. The composite modulus drops to values even below the modulus of the neat resin. These rather unexpected results are very well captured by Takayanagi Model I.

DISCUSSION

The mechanical percolation of fillers has a distinct effect on composites reinforced with CNTs and whiskers. For the case of whiskers, at temperatures above the T_g and volume fractions above the threshold, a strong percolated network of filler species linked by hydrogen bonds is formed. The Takayanagi Model II with a percolation concept captures well the change in reinforcement efficiency above the threshold (Fig. 5). For this case the

threshold marks a positive “turning point” in the mechanical behavior of the system, after which the modulus increases drastically. Takayanagi Model II assumes that the filler network will support much higher loads than the matrix, a reasonable assumption for systems at temperatures above the matrix glass transition temperature.

For CNTs, we also observe the formation of a percolated network at volume fractions above a threshold value. However, for this case the network is not linked by strong hydrogen bonds and it can have a detrimental effect on the mechanical behavior of the system. The Takayanagi Model I captures well such behavior (Fig. 5). The threshold marks a negative “turning point” in the mechanical performance of the composite and for volume fractions above the threshold a decrease in reinforcement efficiency is observed. Takayanagi Model I differentiates between the deformation of the dispersed and percolated CNTs. It assumes that the dispersed CNTs will support a larger portion of the load applied to the composite in comparison to the matrix. It also considers that the individual CNTs can elongate as much as the matrix itself. The model also assumes that the filler network phase will support more load than the matrix or the dispersed filler phase and, as the network is not sufficiently strong, a change in reinforcement efficiency is observed.

CONCLUSIONS

The formation of a percolating network marks a negative turning point for reinforcement in the case of composites with CNTs at temperatures below the T_g of the matrix. By contrast, in the case of cellulose whiskers the

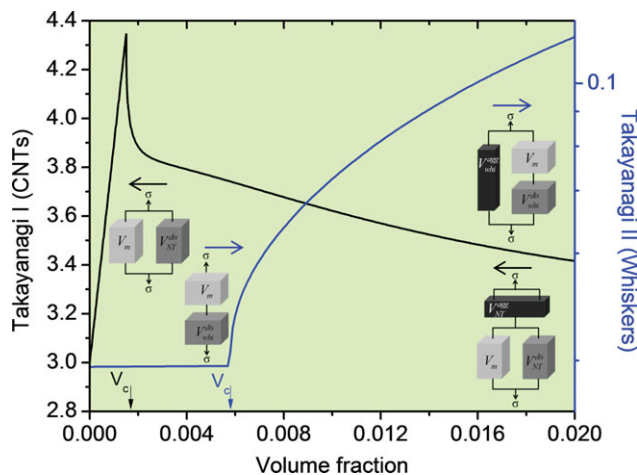


FIG. 5. Elastic modulus of a CNT-reinforced composite according to the Takayanagi Model I at $T < T_g$ and whisker reinforced composite according to the Takayanagi Model II at $T > T_g$. Arrows in the figure point to the model used in the simulations. For CNT reinforced composite the simulation parameters used are: $E_{\text{NT}}^{\text{agg}} = 50 \text{ GPa}$, $E_{\text{NT}}^{\text{dis}} = 900 \text{ GPa}$, $E_m = 3 \text{ GPa}$, $l = 5 \mu\text{m}$, $d = 15 \text{ nm}$, $A = 1.2$; and for whisker reinforced composites the simulation parameters are $E_{\text{whi}}^{\text{agg}} = 13 \text{ GPa}$, $E_{\text{whi}}^{\text{dis}} = 143 \text{ GPa}$, $E_m = 16 \text{ MPa}$, $l = 1.9 \mu\text{m}$, $d = 22 \text{ nm}$, $A = 0.4$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of a percolating network marks a positive turning point in the reinforcing behavior in composites at temperatures above the glass transition temperature of the matrix.

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NOMENCLATURE

List of Symbols

T_g	glass transition temperature
E_w	elastic modulus of the whiskers
E_m	elastic modulus the matrix phase
E_F^{agg}	elastic modulus of the percolated filler network. $F \equiv NT$ for CNTs and $F \equiv whi$ for whiskers;
E_F^{dis}	elastic modulus of the dispersed fillers. $F \equiv NT$ for CNTs and $F \equiv whi$ for whiskers
V_c	filler concentration labeled as the percolation threshold
V_F	volume fraction of the filler
V_m	volume fraction of the matrix
V_{NT}^{dis}	volume fraction of the dispersed CNTs
V_{NT}^{agg}	volume fraction of agglomerated CNTs
l	length
d	diameter
η	aspect ratio
$l - \lambda$	volume fraction of the percolating phase
$\lambda\phi$	volume fraction of the dispersed phase
f_s	“switching function” describing the percolation behavior in the vicinity of the percolation threshold
A	adjustable parameter which modulates the width of the percolation transition

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