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Modeling the effect of interfacial conductivity between polymer matrix and carbon nanotubes on the electrical conductivity of nanocomposites

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This article presents the role of interfacial conductivity between the polymer matrix and nanoparticles in the electrical conductivity of polymer carbon nanotube (CNT) nanocomposites (PCNT) by simple equations. In this methodology, CNT size, CNT conductivity, CNT waviness and interfacial conductivity express the effective length and effective concentration of CNT in PCNT. Additionally, the percolation threshold and the percentages of CNT in the conductive networks are defined by the above mentioned terms. Finally, a simple model is developed to suggest the electrical conductivity of PCNT by CNT dimensions, CNT conductivity, CNT waviness, interphase thickness, interfacial conductivity and tunneling distance. The developed model is applied to show the roles of all parameters in the conductivity. Also, the experimental levels of percolation threshold and conductivity for several samples are compared to the predictions to validate the developed equations. The interfacial conductivity directly controls the electrical conductivity of nanocomposites. In addition, thick interphase, low waviness and short tunneling distance increase the conductivity. Moreover, the predictions show good agreement with the experimental measurements, providing evidence in support of the developed equations.

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1 Introduction

The electromagnetic shielding and electrical conductivity (summarized as conductivity in this paper) of polymer nanocomposites containing carbon nanotubes (CNT) and graphene provide applications in electronics, biomedical tools, sensors, automobile and aerospace industries.^{1–20} The CNT networks are formed above the percolation threshold, *i.e.* the percolation threshold is the minimum volume fraction of nanoparticles establishing continuous networks.^{21,22} The percolation threshold is considered as the volume fraction of conductive nanoparticles in which the conductivity significantly improves, due to the formation of networks.

The main mechanism for electrical conductivity of polymer CNT nanocomposites (PCNT) was suggested as electron tunneling in which the charges are transferred by tunneling effect.^{23,24} So, the adjacent CNT cause the conductivity by electron jumping in the tunneling regions. Additionally, the tunneling effect only depends on the tunneling properties between CNT such as tunneling distance, tunneling resistivity due to insulated polymer layer and contact area.^{25,26} However, many authors have neglected the dominant tunneling conductivity in PCNT. The electrical conductivity of PCNT depends on many parameters attributed to CNT such as concentration,

conductivity, dimensions and waviness.^{27,28} Moreover, the recent papers have indicated that some parameters such as the network size and interphase properties also affect the conductivity of PCNT.²⁹ Some modeling studies have considered the roles of the latter terms in the conductivity,^{29–31} but many researches have investigated the percolation threshold and conductivity of PCNT by conventional views. Therefore, the earlier works commonly have not considered the roles of novel terms in the conductivity of nanocomposites.

Many nanocomposites show an inadequate interfacial adhesion between polymer matrix and nanoparticles, which deteriorates the performance of nanocomposites such as modulus, because the poor interfacial regions cannot assign the outstanding properties of nanoparticles to the polymer matrix.^{32,33} This occurrence is due to the incompatibility or less compatibility between polymer matrix and nanoparticles as well as the poor dispersion and agglomeration of nanofiller in nanocomposites.^{34–36} The extent of interfacial properties can also control the percolation threshold and conductivity of nanocomposites, because the super conductivity of nanoparticles should be transferred to surrounding polymer matrix. In fact, a strong interfacial adhesion can efficiently assign the filler conductivity to polymer matrix, whereas a poor interface cannot provide it. Therefore, the roles of interfacial adhesion in the percolation threshold and conductivity of nanocomposites are important, although the limited studies in this field have not explained this subject.

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In this study, “ L_c ” term is defined as the minimum length of CNT essential for efficient transferring of conductivity from nanofiller to adjacent polymer matrix. “ L_c ” is a function of CNT properties and interfacial conductivity, which considers the role of interfacial adhesion in the percolation threshold and conductivity. Also, the effective length and concentration of CNT are expressed by CNT dimensions, CNT conductivity, CNT waviness and interfacial conductivity. Additionally, the percolation threshold and the percentages of CNT in the conductive networks are defined by simple equations assuming the mentioned terms. Finally, a simple model is developed, which can suggest the conductivity of nanocomposites by CNT dimensions, CNT conductivity, CNT waviness, interphase thickness, interfacial conductivity and tunneling distance. The roles of all parameters in the conductivity are expressed and explained using the developed model. Also, the experimental results of percolation threshold and conductivity of some samples are compared to the predictions to validate the developed equations. The developed model can replace the conventional approaches for estimation of conductivity in PCNT.

2 Theoretical expressions

A poor interfacial adhesion cannot stand the high interfacial stress during the stress loading, which causes yielding or failing at or near the interface. In this condition, a high portion of nanotubes is not completely loaded weakening the strengthening effect of nanoparticles.^{37,38} The role of interfacial adhesion in the conductivity of nanocomposites can be described by the similar attitude. An incomplete interfacial adhesion cannot completely transfer the maximum filler conductivity (σ_f) to surrounding polymer matrix.

“ L_c ” is the minimum length of CNT, which perfectly transfer the maximum conductivity of CNT to neighboring polymer matrix as:

$$L_c = \frac{\sigma_f D}{2k} = \frac{\sigma_f R}{k} \quad (1)$$

where “ D ” and “ R ” are the diameter and radius of CNT, respectively and “ k ” denotes the interfacial conductivity.

The profile of normal conductivity (σ) in a nanotube is exhibited in Fig. 1. When $0 \leq x \leq 2L_c$ (the first condition), the entire length of CNT cannot reach “ σ_f ”, but in the second case, “ σ ” can reach “ σ_f ” indicating the effective conductivity transferring from nanofiller to near polymer matrix.

The average normal conductivity ($\bar{\sigma}$) is identical to “ σ_f ” when CNT are perfectly bonded to polymer matrix; but, “ $\bar{\sigma}$ ” is less than “ σ_f ” in the case of incomplete interfacial adhesion. So, the effective length of CNT (l_{eff}) is assumed as:

$$\bar{\sigma} l = \sigma_f l_{\text{eff}} \quad (2)$$

where “ l ” is CNT length.

“ l_{eff} ” and effective filler concentration (ϕ_{eff}) in the case of $x < 2L_c$ (case 1) are defined³⁷ as:

$$l_{\text{eff}} = \frac{l^2}{4L_c} \quad (3)$$

$$\phi_{\text{eff}} = \phi_f \frac{l}{4L_c} \quad (4)$$

where “ ϕ_f ” is volume fraction of nanofiller in nanocomposite. Moreover, when $l > 2L_c$ (case 2), “ l_{eff} ” and “ ϕ_{eff} ” are stated³⁷ as:

$$l_{\text{eff}} = l \left(1 - \frac{L_c}{l} \right) \quad (5)$$

$$\phi_{\text{eff}} = \phi_f \left(1 - \frac{L_c}{l} \right) \quad (6)$$

Assuming that the CNT include $x < 2L_c$ and $x > 2L_c$ regions, “ l_{eff} ” and “ ϕ_{eff} ” parameters are expressed assuming the latter equations as:

$$\begin{aligned} l_{\text{eff}} &= \frac{2L_c}{l} \left(l - \frac{l}{4L_c} \right) + \left(\frac{l - 2L_c}{l} \right) l \left(1 - \frac{L_c}{l} \right) \\ &= \frac{l}{2} + (l - 2L_c) \left(1 - \frac{L_c}{l} \right) \end{aligned} \quad (7)$$

$$\begin{aligned} \phi_{\text{eff}} &= \frac{2L_c}{l} \left(\phi_f \frac{l}{4L_c} \right) + \left(\frac{l - 2L_c}{l} \right) \phi_f \left(1 - \frac{L_c}{l} \right) \\ &= \phi_f \left[\frac{1}{2} + \left(\frac{l - 2L_c}{l^2} \right) (l - L_c) \right] \end{aligned} \quad (8)$$

The effective factors are suggested as a function of interfacial conductivity by replacing of “ L_c ” from eqn (1) into eqn (7) and (8) as:

$$l_{\text{eff}} = \frac{l}{2} + \left(l - \frac{2\sigma_f R}{k} \right) \left(1 - \frac{\sigma_f R}{kl} \right) \quad (9)$$

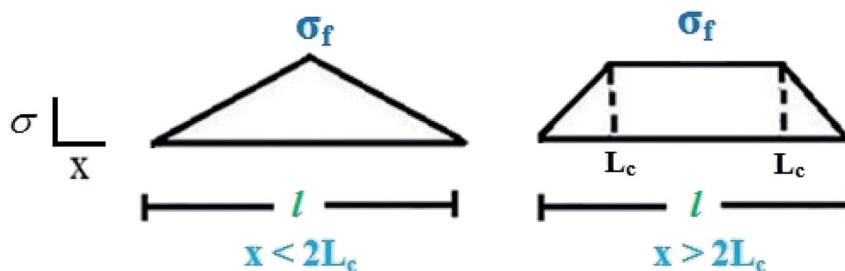


Fig. 1 The profile of normal conductivity at $x < 2L_c$ and $x > 2L_c$.



$$\phi_{\text{eff}} = \phi_f \left[\frac{1}{2} + \left(\frac{l - \frac{2\sigma_f R}{k}}{l^2} \right) \left(l - \frac{\sigma_f R}{k} \right) \right] \quad (10)$$

However, the significant length of CNT causes the waviness in nanocomposites,³⁹ which lessens their effectiveness. An equivalent length (l_{eq}) as the minimum distance between two ends of each nanotube is considered in a waviness parameter as:

$$u = \frac{l}{l_{\text{eq}}} \quad (11)$$

where $u = 1$ displays the straight CNT (no waviness), but a higher “ u ” displays more waviness.

Also, the waviness deteriorates the nature conductivity of CNT.³⁹ Consequently, the conductivity of waved CNT is expressed by:

$$\sigma_{\text{CNT}} = \frac{\sigma_f}{u} \quad (12)$$

Assuming the waviness parameter in eqn (9) and (10) modifies the effective factors to:

$$l_{\text{eff}} = \frac{l}{2u} + \left(\frac{l}{u} - \frac{2\sigma_f R}{uk} \right) \left(1 - \frac{\sigma_f R}{kl} \right) \quad (13)$$

$$\begin{aligned} \phi_{\text{eff}} &= \phi_f \left[\frac{1}{2} + \left(\frac{\frac{l}{u} - \frac{2\sigma_f R}{uk}}{\frac{l^2}{u^2}} \right) \left(\frac{l}{u} - \frac{\sigma_f R}{uk} \right) \right] \\ &= \phi_f \left[\frac{1}{2} + \left(\frac{l - \frac{2\sigma_f R}{k}}{l^2} \right) \left(l - \frac{\sigma_f R}{k} \right) \right] \end{aligned} \quad (14)$$

However, only a fraction of CNT participates in the conductive networks and others are dispersed in the polymer matrix.

The percentage of networked CNT³¹ is calculated by:

$$f = \frac{\phi_f^{1/3} - \phi_p^{1/3}}{1 - \phi_p^{1/3}} \quad (15)$$

where “ ϕ_p ” is percolation threshold of nanoparticles in PCNT.

When the effective filler fraction (eqn (14)) is substituted into the latter equation, “ f ” is suggested as:

$$f = \frac{\phi_{\text{eff}}^{1/3} - \phi_p^{1/3}}{1 - \phi_p^{1/3}} \quad (16)$$

which determines the volume fraction of networked regions as:

$$\phi_N = f\phi_{\text{eff}} \quad (17)$$

The percolation threshold of casually dispersed CNT in PCNT was assumed⁴⁰ by:

$$\phi_p = \frac{V}{V_{\text{ex}}} \quad (18)$$

where “ V ” and “ V_{ex} ” are the volume and excluded volume of nanoparticles, respectively. The excluded volume involves the volume about an object into which the center of a similar object cannot arrive.

“ V ” and “ V_{ex} ” in PCNT were suggested⁴⁰ as:

$$V = \pi R^2 l \quad (19)$$

$$V_{\text{ex}} = \frac{32}{3} \pi R^3 \left[1 + \frac{3}{4} \left(\frac{l}{R} \right) + \frac{3}{32} \left(\frac{l}{R} \right)^2 \right] \quad (20)$$

The interphase layer about CNT can hasten the development of conductive networks in nanocomposites.^{41–43} Also, the interfacial conductivity and waviness change the effective length of CNT (eqn (13)). As a result, the excluded volume develops by the mentioned terms as:

$$V_{\text{ex}} = \frac{32}{3} \pi (R+t)^3 \left[1 + \frac{3}{4} \left(\frac{l_{\text{eff}}}{R+t} \right) + \frac{3}{32} \left(\frac{l_{\text{eff}}}{R+t} \right)^2 \right] \quad (21)$$

where “ t ” is interphase thickness.

The percolation threshold of CNT assuming eqn (19) and (21) into eqn (18) is given by:

$$\phi_p = \frac{\pi R^2 l}{\frac{32}{3} \pi (R+t)^3 \left[1 + \frac{3}{4} \left(\frac{l_{\text{eff}}}{R+t} \right) + \frac{3}{32} \left(\frac{l_{\text{eff}}}{R+t} \right)^2 \right]} \quad (22)$$

which suggests valuable predictions for percolation threshold of CNT in PCNT.

When eqn (14) and (22) are replaced into eqn (16) and (17), the volume fraction of networks is calculated.

Deng and Zheng⁴⁴ suggested a simple model for conductivity of PCNT as:

$$\sigma = \sigma_0 + \frac{f\phi_f\sigma_f}{3} \cong \frac{\phi_N\sigma_f}{3} \quad (23)$$

where “ σ_0 ” is the conductivity of polymer matrix. The insignificant value of “ σ_0 ” as about $10^{-15} \text{ S m}^{-1}$ can be disregarded from this equation. This model assumes the roles of filler fraction, filler conductivity and percolated networks in the conductivity, but it ignores the CNT waviness, interfacial conductivity, interphase thickness and tunneling effect. Moreover, this equation linearly correlates the conductivity to the filler concentration disregarding the percolation-like improvement of conductivity in nanocomposites as a function of filler concentration.

Accordingly, this model is developed for conductivity of PCNT assuming the declared terms as:

$$\sigma = \frac{\phi_N^2 \sigma_{\text{CNT}}}{3 \left(\frac{d}{z} \right)^3} = \frac{(f\phi_{\text{eff}})^2 \sigma_f}{3 \left(\frac{d}{z} \right)^3 u} \quad (24)$$

where “ d ” is tunneling distance between adjacent CNT and “ z ” is a tunneling parameter ($z = 1 \text{ nm}$). This model can predict the conductivity of PCNT when “ f ” and “ ϕ_{eff} ” are replaced from eqn (14) and (16). So, this model assumes the filler dimensions, waviness, network size, interfacial conductivity, interphase size



and tunneling distance in the conductivity of nanocomposites. These equations were suggested and developed for nanocomposites containing cylindrical nanofiller like CNT. Therefore, the suggested equations are not proper for the systems including different filler geometries.

3 Results and discussion

3.1 Parametric analysis

The effects of different parameters on the predicted conductivity by the developed model are expressed and justified in this section. 3D and contour plots demonstrate the roles of two parameters in the conductivity at average values of other factors. The average levels are considered as $\phi_f = 0.01$, $R = 10$ nm, $l = 15$ μm , $\sigma_f = 10^5$ S m^{-1} , $u = 1.2$, $t = 10$ nm, $k = 400$ S m^{-1} and $d = 2$ nm.

Fig. 2 reveals the influences of “ l ” and “ k ” parameters on the conductivity of nanocomposites. The maximum conductivity of 0.025 S m^{-1} is obtained at $l > 27$ μm and $k > 800$ S m^{-1} , but the conductivity approaches to 0 at $k = 100$ S m^{-1} or $l < 15$ μm and $k < 290$ S m^{-1} . As a result, both “ l ” and “ k ” parameters as CNT length and interfacial conductivity directly change the conductivity of nanocomposites and the high levels of these parameters are necessary to increase the conductivity. On the other hand, short CNT and poor interfacial conductivity cannot enhance the conductivity of nanocomposites.

The length of CNT affects the effective fraction and percolation threshold of nanofiller in the nanocomposites. The long CNT increase the effective filler concentration and decrease the percolation threshold. So, large CNT produce a high level of “ f ” (eqn (16)) displaying the large and dense networks in nanocomposite. In fact, the large CNT produce the big conductive networks in the nanocomposites, which effectively improve the conductivity. Therefore, the developed model properly predicts the conductivity at different CNT lengths. Moreover, a high level of interfacial conductivity causes a desirable conductivity, because the filler conductivity can be suitably transferred to the insulated polymer matrix. A high level of “ k ” decreases the “ L_c ” term (eqn (1)), which raises the effective concentration

(eqn (14)) and effective length (eqn (13)) of CNT. Accordingly, a high level of interfacial conductivity decreases the percolation threshold and enhances the percentages of CNT in the conductive networks. In other words, a high level of interfacial conductivity produces the desirable networks containing CNT and interfacial/interphase regions. According to these evidences, the developed model correctly shows the role of interfacial conductivity in the conductivity of nanocomposites.

Fig. 3 illustrates the roles of “ u ” and “ d ” parameters in the conductivity of nanocomposites. The low levels of these parameters significantly improve the conductivity, but the conductivity decreases at high values of “ u ” and “ d ”. As observed, the conductivity can reach 0.09 S m^{-1} at $u = 1$ and $d = 1$ nm, but $d > 2.3$ nm dominantly cause the conductivity of about 0. As a result, low waviness and short tunneling distance increase the conductivity, while the conductivity mainly decreases by large tunneling distance. These results obviously show the detrimental effects of waviness and large tunneling distance on the conductivity of PCNT.

The waviness reduces the equivalent length of CNT in nanocomposites, which undesirably affects the effective CNT length and percolation threshold. So, “ f ” parameter decreases by waviness causing small networks in nanocomposites. In addition, the nature conductivity of CNT weakens by waviness. As a result, the dimensions and conductivity of networks deteriorate by waviness, which decreases the conductivity of PCNT, as suggested by the developed model. A large tunneling distance also negatively governs the conductivity of nanocomposites, because it decreases the extent of charge transferring thorough tunneling regions. In fact, the electrons cannot pass *via* large tunneling distance, because the tunneling spaces include the insulated polymer matrix. In other words, a big tunneling distance introduces a high tunneling resistance against the electron transportation, which limits the conductivity of nanocomposites. Other authors also reported the same relation between nanocomposite conductivity and tunneling distance.^{39,45} So, the developed model properly shows the positive role of short tunneling distance in the conductivity of PCNT.

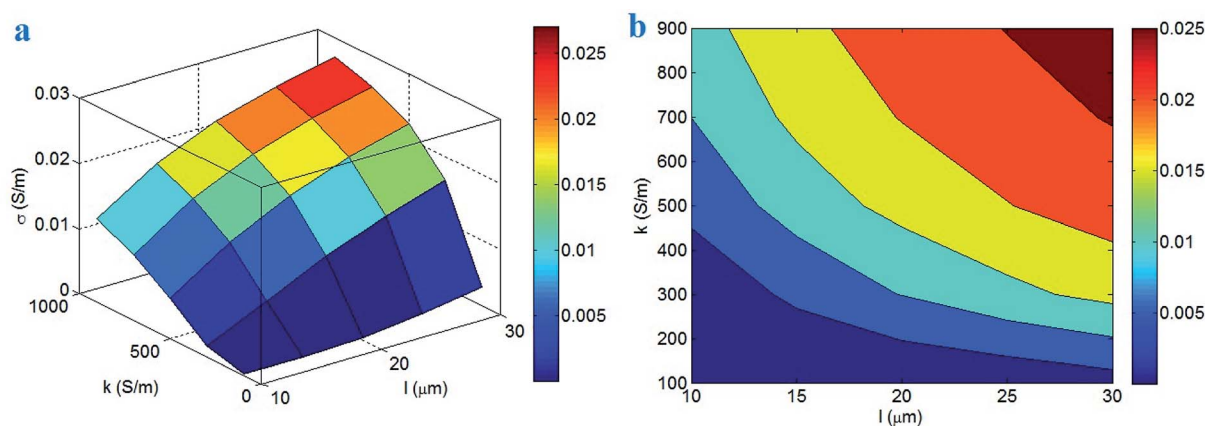


Fig. 2 Significances of “ l ” and “ k ” parameters on the conductivity of nanocomposites based on the developed model by (a) 3D and (b) contour plots.



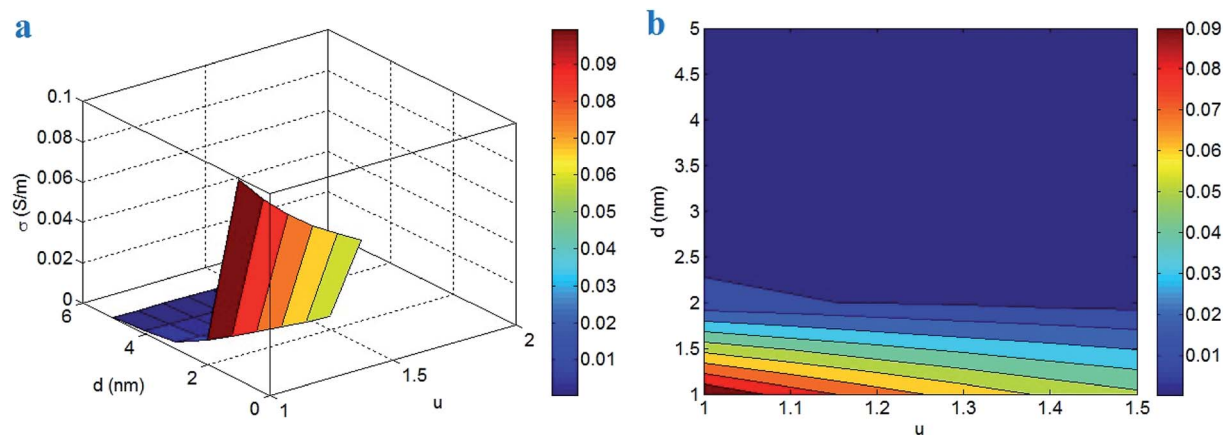


Fig. 3 Calculations of conductivity at different levels of “ u ” and “ d ” parameters by (a) 3D and (b) contour schemes.

Fig. 4 depicts the dependencies of conductivity on filler concentration and percolation threshold according to the developed model. $\phi_f = 0.04$ and $\phi_p = 0.001$ produce the highest conductivity of 0.45 S m^{-1} , but the conductivity decreases to about 0 at $\phi_f < 0.02$. Therefore, the conductivity improves by high filler concentration and low percolation threshold, while only low filler concentration can significantly decrease the conductivity. These results are sensible, because these parameters efficiently manipulate the dimensions of conductive networks.

A high content of conductive nanoparticles in nanocomposites produces the large networks, which can mainly transfer the electrons and cause the conductivity. However, a low filler concentration creates the small networks, which cannot induce a high conductivity. Moreover, a high filler concentration reduces the tunneling distance in the nanocomposites,^{46,47} because a large number of nanoparticles produce small inter-particle distance. In addition, a low percolation threshold enhances the percentages of CNT in the conductive networks (eqn (16)). In other words, a poor percolation level contributes a large number of CNT in the networks. However, a high percolation threshold causes the small

conductive networks in nanocomposites limiting the conductivity. According to these evidences, the developed model displays the correct outputs at different values of filler concentration and percolation threshold.

Fig. 5 shows the variation of conductivity at dissimilar levels of “ σ_f ” and “ f ” parameters. The maximum value of conductivity as 0.18 S m^{-1} is observed at $\sigma_f > 10^5 \text{ S m}^{-1}$ and $f = 0.7$, while the conductivity of nanocomposite cannot improve at $f < 0.2$. As a result, the medium and high levels of CNT conductivity as well as the high percentages of CNT in the networks can mainly improve the conductivity, but a small fraction of CNT in the networks decreases it. In fact, the percentage of CNT in the conductive networks dominantly controls the conductivity of nanocomposites and the CNT conductivity plays a negligible role.

Although the conductivity of nanocomposites directly depends on the filler conductivity (eqn (24)), but the high filler conductivity enlarges the “ L_c ” term (eqn (1)) assuming imperfect interfacial conductivity. In other words, a high level of CNT conductivity increases the required length of CNT for efficient conductivity transferring. Actually, the high filler conductivity is limitedly transferred to polymer matrix in the case of

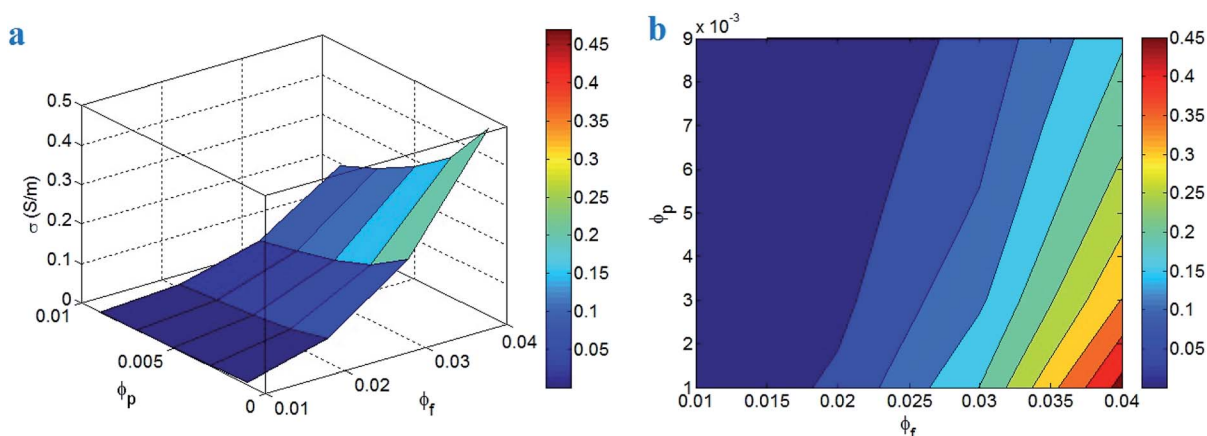


Fig. 4 Expression of conductivity at different values of filler concentration and percolation threshold by (a) 3D and (b) contour designs.



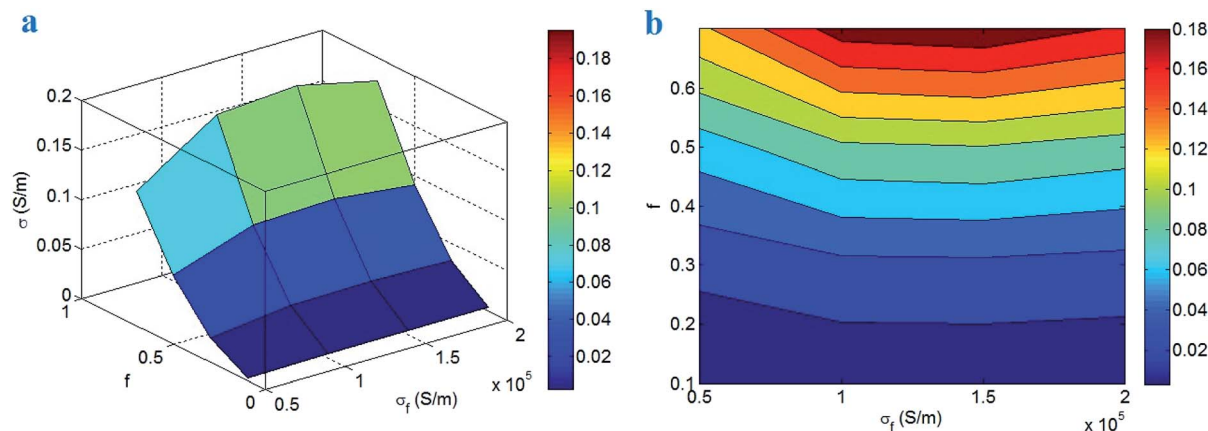


Fig. 5 Impacts of " σ_f " and " f " parameters on the conductivity of nanocomposites by (a) 3D and (b) contour illustrations.

incomplete interfacial adhesion, which weakens the conductivity of nanocomposites. Accordingly, the filler conductivity insignificantly governs the conductivity, due to the dissimilar roles of this parameter in conductivity transferring and conductivity of networks. However, the conductivity of nanocomposites significantly improves when the big networks are established in the nanocomposites. The networks can provide the charge transportation in nanocomposites and there is a direct correlation between charge transportation and network size.^{48,49} Therefore, the large networks (high f) can effectively transfer the electrons and improve the conductivity. Based on these explanations, the developed model properly exhibits the roles of " σ_f " and " f " parameters in the conductivity of PCNT.

Fig. 6 displays the calculations of conductivity at different values of " R " and " t " parameters. The most desirable conductivity of 0.022 S m^{-1} is achieved by $R = 5 \text{ nm}$ and $t > 16 \text{ nm}$, while the conductivity diminishes to 0 at $R > 20 \text{ nm}$. Therefore, the conductivity improves by thin CNT and thick interphase, but only thick CNT can deteriorate the conductivity of nanocomposites. These results indicate that the sizes of CNT and interphase layer surrounding CNT meaningfully govern the conductivity of nanocomposites.

The thin CNT reduce the level of " L_c " in nanocomposites. It means that thin CNT produce an efficient conductivity transferring between nanoparticles and polymer matrix, which increases the effective filler concentration and effective length. Furthermore, thin CNT drop the percolation threshold. The desirable levels of effective filler concentration, effective length and percolation threshold grow the percentages of CNT in the networks. So, thin CNT can be easily networked in nanocomposites, which improve the conductivity of nanocomposites. Additionally, thick interphase decreases the percolation threshold, because the interphase regions contribute to the conductive networks. As a result, thick interphase increases the dimensions of conductive networks in nanocomposites raising the conductivity. The previous articles also found the direct role of interphase thickness in the percolation threshold.^{26,50} Conclusively, both " R " and " t " parameters logically control the conductivity of nanocomposites, which validate the developed model.

3.2 Evaluation of predictions by experimental data

The predictions of the developed equations can be compared with the experimental results. The experimental results of

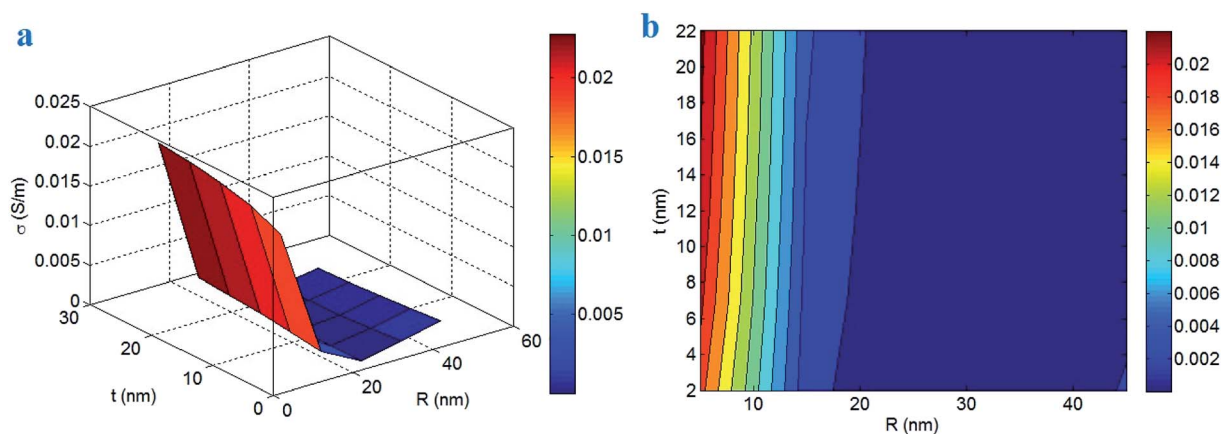


Fig. 6 Illustration of the roles of " R " and " t " parameters in the conductivity of nanocomposites by (a) 3D and (b) contour designs.

percolation threshold and conductivity for four samples including epoxy/single walled CNT (SWCNT) ($R = 1$ nm, $l \approx 2$ μm , $u = 1.6$ and $\phi_p = 0.0003$)⁵¹, polycarbonate (PC)/acrylonitrile butadiene styrene (ABS)/multi walled CNT (MWCNT) ($R = 5$ nm, $l \approx 1.5$ μm , $u = 1.2$ and $\phi_p = 0.002$)⁴⁷, poly (vinyl chloride) (PVC)/MWCNT ($R = 8$ nm, $l \approx 16$ μm , $u = 1.2$ and $\phi_p = 0.0005$)⁵² and epoxy/MWCNT ($R = 8$ nm, $l \approx 30$ μm , $u = 1.2$ and $\phi_p = 0.0002$)⁵³ are considered. The values of percolation threshold are compared with eqn (22) to calculate the interphase thickness and interfacial conductivity. The interfacial conductivity changes the " L_c " ($\sigma_f = 10^5$ S m^{-1}) and the effective length of CNT. Eqn (22) presents the different pairs for " t " and " k ", but we reported the average values for these parameters. In fact, we calculated the different values of these parameters for the samples by eqn (22) and reported the average levels. The average values of (t , k) are calculated as (10, 700), (5, 250), (7, 200) and (2, 280) (nm, S m^{-1}) for epoxy/SWCNT, PC/ABS/MWCNT, PVC/MWCNT and epoxy/MWCNT samples, respectively. Generally, these results demonstrate the proper expression of percolation threshold as a function of filler dimensions, interphase thickness and interfacial conductivity. These outputs also show the formation of different interphase regions in the studied samples. The thickest and the thinnest interphase is observed

in epoxy/SWCNT and epoxy/MWCNT samples, respectively. Also, the samples display the different levels for interfacial conductivity depending on the characteristics of interfacial interaction between polymer matrix and nanoparticles. The highest and the lowest levels of interfacial conductivity are obtained for epoxy/SWCNT and PVC/MWCNT nanocomposites, respectively.

The calculations of all parameters are considered in the developed model to predict the conductivity of samples at different filler concentrations. Fig. 7 reveals the experimental and theoretical levels of conductivity in epoxy/SWCNT, PC/ABS/MWCNT, PVC/MWCNT and epoxy/MWCNT samples. The predictions show desirable agreement with the experimental results, which approve the developed model. In other words, the calculations of conductivity at different filler concentrations are consistent with the experimental measurements. Therefore, the developed model supposing interfacial conductivity can properly calculate the conductivity of nanocomposites.

The values of " d " as tunneling distance are also obtained as 1.3, 0.5, 1.1 and 1 nm for epoxy/SWCNT, PC/ABS/MWCNT, PVC/MWCNT and epoxy/MWCNT nanocomposites, respectively. The shortest and the largest tunneling distance is observed in PC/ABS/MWCNT and epoxy/SWCNT samples, correspondingly.

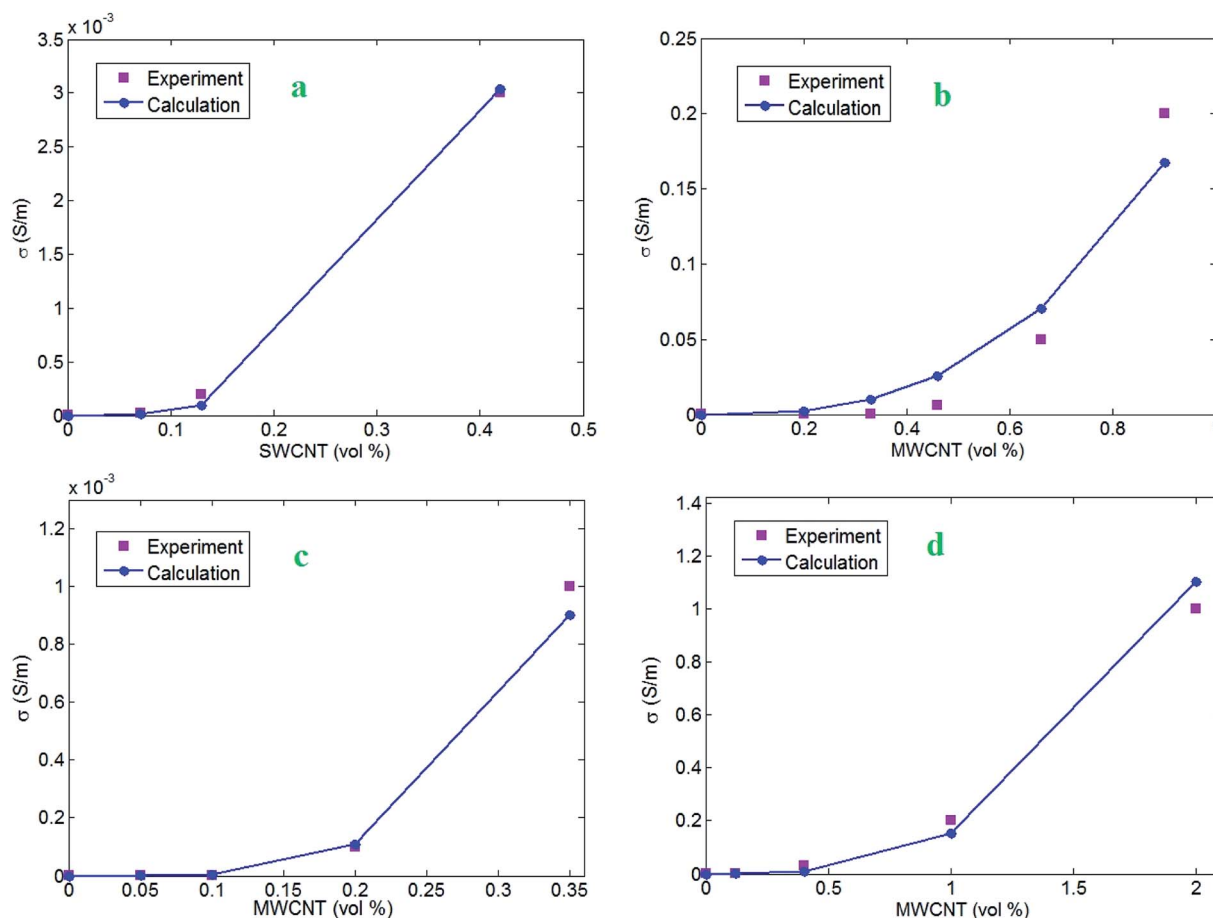


Fig. 7 Experimental data of conductivity and the calculations of developed model for (a) epoxy/SWCNT,⁵¹ (b) PC/ABS/MWCNT,⁴⁷ (c) PVC/MWCNT⁵² and (d) epoxy/MWCNT⁵³ samples.



However, these results show a negligible variation in the tunneling distance of reported samples. Conclusively, the developed model can properly calculate the conductivity of nanocomposites assuming the effective parameters for CNT networks, interphase and tunneling regions.

4 Conclusions

A simple model was developed to predict the conductivity of PCNT by CNT dimensions, CNT conductivity, waviness, interphase thickness, interfacial conductivity and tunneling distance. 3D and contour plots expressed the roles of all parameters in the conductivity of PCNT. Also, the experimental results of percolation threshold and conductivity of several samples were compared to the predictions to validate the developed equations. CNT concentration, CNT length, the percentage of CNT in the networks, interfacial conductivity and interphase thickness directly affect the conductivity of nanocomposites. So, the high levels of these parameters are necessary to improve the conductivity. However, thin CNT, low waviness, poor percolation threshold and short tunneling distance can increase the conductivity of PCNT, but the conductivity mainly decreases or an insulated nanocomposite is observed by the high levels of these factors. Additionally, the different levels of CNT conductivity negligibly change the conductivity of PCNT, because it adversely affects the effective length and effective concentration of CNT as well as the conductivity of filler networks. The predictions show desirable agreement with the experimental results of percolation threshold and conductivity. Therefore, the developed equations supposing the interfacial conductivity can appropriately calculate the percolation threshold and conductivity in PCNT.

Nomenclature

σ_f	CNT conductivity
D	CNT diameter
R	CNT radius
k	Interfacial conductivity
σ	Normal conductivity
$\bar{\sigma}$	Average normal conductivity
l	CNT length
l_{eff}	Effective length of CNT
ϕ_{eff}	Effective CNT concentration
ϕ_f	Volume fraction of CNT
l_{eq}	Equivalent length
u	Waviness parameter
f	The percentage of networked CNT
ϕ_p	Percolation threshold of CNT
ϕ_N	The volume fraction of networked CNT
V	CNT volume
V_{ex}	Excluded volume of CNT
t	Interphase thickness
σ_0	The conductivity of polymer matrix
d	Tunneling distance between adjacent CNT
z	Tunneling parameter

Conflicts of interest

There are no conflicts to declare.

References

- 1 Y. Hu, P. Tang, L. Li, J. Yang, X. Jian and Y. Bin, High absorption shielding material of poly (phthalazinone etherketone)/multiwall carbon nanotube composite films with sandwich configurations, *RSC Adv.*, 2019, **9**, 18758–18766.
- 2 K. Silakaew and P. Thongbai, Significantly improved dielectric properties of multiwall carbon nanotube-BaTiO₃/PVDF polymer composites by tuning the particle size of the ceramic filler, *RSC Adv.*, 2019, **9**, 23498–23507.
- 3 R. Ma, G. Mu, H. Zhang, J. Liu, Y. Gao, X. Zhao and L. Zhang, Percolation analysis of the electrical conductive network in a polymer nanocomposite by nanorod functionalization, *RSC Adv.*, 2019, **9**, 36324–36333.
- 4 O. Saber, A. Aljaafari, A. Alshoaibi and A. Osama, A low-temperature technique and new strategy for the dual growth of carbon nanotubes and nanorods through the confinement of explosive materials inside a porous structure, *RSC Adv.*, 2019, **9**, 30509–30518.
- 5 Y. Zare and K. Y. Rhee, Expression of normal stress difference and relaxation modulus for ternary nanocomposites containing biodegradable polymers and carbon nanotubes by storage and loss modulus data, *Composites, Part B*, 2019, **158**, 162–168.
- 6 Y. Zare and K. Y. Rhee, Modeling of viscosity and complex modulus for poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes nanocomposites assuming yield stress and network breaking time, *Composites, Part B*, 2019, **156**, 100–107.
- 7 A. Rostami, F. Eskandari, M. Masoomi and M. Nowrouzi, Evolution of Microstructure and Physical Properties of PMMA/MWCNTs Nanocomposites upon the Addition of Organoclay, *Journal of Oil, Gas and Petrochemical Technology*, 2019, accepted.
- 8 A. Rostami and M. I. Moosavi, High-performance thermoplastic polyurethane nanocomposites induced by hybrid application of functionalized graphene and carbon nanotubes, *J. Appl. Polym. Sci.*, 2019, 48520.
- 9 Y. Zhang, K. Y. Rhee and S.-J. Park, Nanodiamond nanocluster-decorated graphene oxide/epoxy nanocomposites with enhanced mechanical behavior and thermal stability, *Composites, Part B*, 2017, **114**, 111–120.
- 10 S. Shi, Y. Chen, J. Jing and L. Yang, Preparation and 3D-printing of highly conductive polylactic acid/carbon nanotube nanocomposites via local enrichment strategy, *RSC Adv.*, 2019, **9**, 29980–29986.
- 11 H. Wang, Z. Li, K. Hong, M. Chen, Z. Qiao, Z. Yuan and Z. Wang, Property improvement of multi-walled carbon nanotubes/polypropylene composites with high filler loading via interfacial modification, *RSC Adv.*, 2019, **9**, 29087–29096.



- 12 Y. Zare, S. P. Park and K. Y. Rhee, Analysis of complex viscosity and shear thinning behavior in poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes biosensor based on Carreau–Yasuda model, *Results Phys.*, 2019, **13**, 102245.
- 13 A. H. Z. Kalkhoran, O. Vahidi and S. M. Naghib, A new mathematical approach to predict the actual drug release from hydrogels, *Eur. J. Pharm. Sci.*, 2018, **111**, 303–310.
- 14 S. M. Naghib, E. Parnian, H. Keshvari, E. Omidinia and M. Eshghan-Malek, Synthesis, characterization and electrochemical evaluation of polyvinylalcohol/graphene oxide/silver nanocomposites for glucose biosensing application, *Int. J. Electrochem. Sci.*, 2018, **13**, 1013–1026.
- 15 Y. Zhang and S.-J. Park, Influence of the nanoscaled hybrid based on nanodiamond@ graphene oxide architecture on the rheological and thermo-physical performances of carboxylated-polymeric composites, *Composites, Part A*, 2018, **112**, 356–364.
- 16 A. Roy, S. Dhibar, S. Kundu and S. Malik, Covalently linked benzimidazole-containing reduced graphene oxide/polyaniline nanocomposites as electrode materials, *RSC Adv.*, 2019, **9**, 24646–24653.
- 17 J. Bhadra, A. Popelka, A. Abdulkareem, Z. Ahmad, F. Touati and N. Al-Thani, Fabrication of polyaniline–graphene/polystyrene nanocomposites for flexible gas sensors, *RSC Adv.*, 2019, **9**, 12496–12506.
- 18 S. K. Krishnan, E. Singh, P. Singh, M. Meyyappan and H. S. Nalwa, A review on graphene-based nanocomposites for electrochemical and fluorescent biosensors, *RSC Adv.*, 2019, **9**, 8778–8881.
- 19 R. Salahandish, A. Ghaffarinejad, S. M. Naghib, A. Niyazi, K. Majidzadeh-A, M. Janmaleki and A. Sanati-Nezhad, Sandwich-structured nanoparticles-grafted functionalized graphene based 3D nanocomposites for high-performance biosensors to detect ascorbic acid biomolecule, *Sci. Rep.*, 2019, **9**, 1226.
- 20 E. Askari and S. M. Naghib, A novel approach to facile synthesis and biosensing of the protein-regulated graphene, *Int. J. Electrochem. Sci.*, 2018, **13**, 886–897.
- 21 Y. Zare and K. Y. Rhee, Simplification and development of McLachlan model for electrical conductivity of polymer carbon nanotubes nanocomposites assuming the networking of interphase regions, *Composites, Part B*, 2019, **156**, 64–71.
- 22 Y. Zare and K. Rhee, Evaluation and Development of Expanded Equations Based on Takayanagi Model for Tensile Modulus of Polymer Nanocomposites Assuming the Formation of Percolating Networks, *Phys. Mesomech.*, 2018, **21**, 351–357.
- 23 F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer and K. I. Winey, Nanotube networks in polymer nanocomposites: rheology and electrical conductivity, *Macromolecules*, 2004, **37**, 9048–9055.
- 24 C. Li, E. T. Thostenson and T.-W. Chou, Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube-based composites, *Appl. Phys. Lett.*, 2007, **91**, 223114.
- 25 S. Kim, Y. Zare, H. Garmabi and K. Y. Rhee, Variations of tunneling properties in poly (lactic acid)(PLA)/poly (ethylene oxide)(PEO)/carbon nanotubes (CNT) nanocomposites during hydrolytic degradation, *Sens. Actuators, A*, 2018, **274**, 28–36.
- 26 R. Razavi, Y. Zare and K. Y. Rhee, The roles of interphase and filler dimensions in the properties of tunneling spaces between CNT in polymer nanocomposites, *Polym. Compos.*, 2019, **40**, 801–810.
- 27 M. Mohiuddin and S. V. Hoa, Estimation of contact resistance and its effect on electrical conductivity of CNT/PEEK composites, *Compos. Sci. Technol.*, 2013, **79**, 42–48.
- 28 C. J. Lee, R. Salehiyan, D. S. Ham, S. K. Cho, S.-J. Lee, K. J. Kim, Y. Yoo, K. Hyun, J. H. Lee and W. J. Choi, Influence of carbon nanotubes localization and transfer on electrical conductivity in PA66/(PS/PPE)/CNTs nanocomposites, *Polymer*, 2016, **84**, 198–208.
- 29 Y. Zare and K. Y. Rhee, Development of a conventional model to predict the electrical conductivity of polymer/carbon nanotubes nanocomposites by interphase, waviness and contact effects, *Composites, Part A*, 2017, **100**, 305–312.
- 30 T. Takeda, Y. Shindo, Y. Kuronuma and F. Narita, Modeling and characterization of the electrical conductivity of carbon nanotube-based polymer composites, *Polymer*, 2011, **52**, 3852–3856.
- 31 C. Feng and L. Jiang, Micromechanics modeling of the electrical conductivity of carbon nanotube (CNT)–polymer nanocomposites, *Composites, Part A*, 2013, **47**, 143–149.
- 32 W. Peng, S. Rhim, Y. Zare and K. Y. Rhee, Effect of “Z” factor for strength of interphase layers on the tensile strength of polymer nanocomposites, *Polym. Compos.*, 2019, **40**, 1117–1122.
- 33 Y. Zare and K. Y. Rhee, Evaluation of the Tensile Strength in Carbon Nanotube-Reinforced Nanocomposites Using the Expanded Takayanagi Model, *JOM*, 2019, 1–9.
- 34 D. N. Bikiaris, A. Vassiliou, E. Pavlidou and G. P. Karayannidis, Compatibilisation effect of PP-g-MA copolymer on iPP/SiO₂ nanocomposites prepared by melt mixing, *Eur. Polym. J.*, 2005, **41**, 1965–1978.
- 35 Z. M. Ishak, W. Chow and T. Takeichi, Compatibilizing effect of SEBS-g-MA on the mechanical properties of different types of OMMT filled polyamide 6/polypropylene nanocomposites, *Composites, Part A*, 2008, **39**, 1802–1814.
- 36 Y. Zare and K. Y. Rhee, Effects of interphase regions and filler networks on the viscosity of PLA/PEO/carbon nanotubes biosensor, *Polym. Compos.*, 2019, **40**, 4135–4141.
- 37 D. Shia, C. Hui, S. Burnside and E. Giannelis, An interface model for the prediction of Young's modulus of layered silicate-elastomer nanocomposites, *Polym. Compos.*, 1998, **19**, 608–617.
- 38 Y. Zare, K. Y. Rhee and S.-J. Park, A modeling methodology to investigate the effect of interfacial adhesion on the yield strength of MMT reinforced nanocomposites, *J. Ind. Eng. Chem.*, 2019, **69**, 331–337.
- 39 Y. Zare, K. Y. Rhee and S.-J. Park, A developed equation for electrical conductivity of polymer carbon nanotubes (CNT)



- nanocomposites based on Halpin-Tsai model, *Results Phys.*, 2019, 102406.
- 40 L. Berhan and A. Sastry, Modeling percolation in high-aspect-ratio fiber systems. I. Soft-core *versus* hard-core models, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2007, 75, 041120.
 - 41 Y. Zare, S. Rhim, H. Garmabi and K. Y. Rhee, A simple model for constant storage modulus of poly (lactic acid)/poly (ethylene oxide)/carbon nanotubes nanocomposites at low frequencies assuming the properties of interphase regions and networks, *J. Mech. Behav. Biomed. Mater.*, 2018, 80, 164–170.
 - 42 Y. Zare and K. Y. Rhee, Tensile strength prediction of carbon nanotube reinforced composites by expansion of cross-orthogonal skeleton structure, *Composites, Part B*, 2019, 161, 601–607.
 - 43 R. Qiao and L. C. Brinson, Simulation of interphase percolation and gradients in polymer nanocomposites, *Compos. Sci. Technol.*, 2009, 69, 491–499.
 - 44 F. Deng and Q.-S. Zheng, An analytical model of effective electrical conductivity of carbon nanotube composites, *Appl. Phys. Lett.*, 2008, 92, 071902.
 - 45 Y. Zare, K. Y. Rhee and S.-J. Park, Modeling the roles of carbon nanotubes and interphase dimensions in the conductivity of nanocomposites, *Results Phys.*, 2019, 15, 102562.
 - 46 S. Maiti, S. Suin, N. K. Shrivastava and B. Khatua, Low percolation threshold in polycarbonate/multiwalled carbon nanotubes nanocomposites through melt blending with poly (butylene terephthalate), *J. Appl. Polym. Sci.*, 2013, 130, 543–553.
 - 47 S. Maiti, N. K. Shrivastava and B. Khatua, Reduction of percolation threshold through double percolation in melt-blended polycarbonate/acrylonitrile butadiene styrene/multiwall carbon nanotubes elastomer nanocomposites, *Polym. Compos.*, 2013, 34, 570–579.
 - 48 F. Dalmas, R. Dendievel, L. Chazeau, J.-Y. Cavaillé and C. Gauthier, Carbon nanotube-filled polymer composites. Numerical simulation of electrical conductivity in three-dimensional entangled fibrous networks, *Acta Mater.*, 2006, 54, 2923–2931.
 - 49 M. H. Al-Saleh, Influence of conductive network structure on the EMI shielding and electrical percolation of carbon nanotube/polymer nanocomposites, *Synth. Met.*, 2015, 205, 78–84.
 - 50 Y. Zare and K. Y. Rhee, Significances of interphase conductivity and tunneling resistance on the conductivity of carbon nanotubes nanocomposites, *Polym. Compos.*, in press.
 - 51 F. H. Gojny, M. H. Wichmann, B. Fiedler, I. A. Kinloch, W. Bauhofer, A. H. Windle and K. Schulte, Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites, *Polymer*, 2006, 47, 2036–2045.
 - 52 Y. Mamunya, A. Boudenne, N. Lebovka, L. Ibos, Y. Candau and M. Lisunova, Electrical and thermophysical behaviour of PVC-MWCNT nanocomposites, *Compos. Sci. Technol.*, 2008, 68, 1981–1988.
 - 53 Y. J. Kim, T. S. Shin, H. Do Choi, J. H. Kwon, Y.-C. Chung and H. G. Yoon, Electrical conductivity of chemically modified multiwalled carbon nanotube/epoxy composites, *Carbon*, 2005, 43, 23–30.

