

Accurate model for computing dielectric constant of dielectric nanocomposites

M. Ezzat · N. A. Sabiha · M. Izzularab

Received: 4 January 2013 / Accepted: 4 February 2013 / Published online: 27 February 2013
© The Author(s) 2013. This article is published with open access at Springerlink.com

Abstract In this paper, an accurate model for computing dielectric constant of dielectric nanocomposites is presented. The effect of interaction zone between the nanofiller and the resin material is calculated and taken into consideration in the developed model for polymer and ceramic resins. Also, the effect of filler volume fraction, filler dielectric constant and particle shape is studied through the proposed model. Finally, the validity of the proposed model for evaluating the dielectric constant of a uniform composite system of discrete particles dispersed within a matrix is achieved by comparison with experimental results. The proposed model shows simplicity and gives accurate results as compared to the other theoretical models.

Keywords Dielectric constant · Interaction zone · Nanocomposites

Introduction

Nanotechnology caused a breakthrough in material science, engineering and of course industrial applications. The use of this technology in enhancing electrical (Zhao and He 2006; Kim et al. 2009; Chen and Chen 2009), mechanical (Tan and Yang 1998; Awaji et al. 2009) and thermal properties (Momen and Farzanah 2011; Cherney 2005) of dielectrics has found a great interest from researchers and scientists. As the use of this technology with dielectrics is recent, there are several challenges facing researchers working in this area. Exact evaluation of the effective

dielectric constant of nanofilled composites is one of these challenges. Therefore, the exact evaluation of the effective dielectric constant of nanofilled composites is of high concern in material science and engineering fields. Many theoretical approaches were suggested for the computation of the effective dielectric constant of nanofilled composites such as Maxwell–Garnett, Bottcher, power-law (PL) and the interphase power-law (IPL) models (Yoon et al. 2003; Karkkainen et al. 2000; Birchak et al. 1974; Nelson and Bartley 1998; Nelson 1983; Priou 1992; Nelson and You 1990; Nelson 2001; Gershon et al. 2001; Brosseau et al. 2001).

In this paper, a simple and accurate model is presented. The effect of interaction between the nanofiller and the resin material is computed for polymer and ceramic resins and taken into consideration. The effect of filler loading, filler dielectric constant and particle shape is investigated through the proposed model. Also, the proposed model is experimentally verified using a wide range of published results for different base materials and nanofillers. Finally, the results obtained from the proposed model are compared to other theoretical models to show the validity of the proposed model.

Models for effective dielectric constant calculation

There are different models for computing the effective dielectric constant of dielectric nanocomposites. These models are summarized in this section.

Maxwell–Garnett (MG) model

In this model, the effective dielectric constant of the composite (ϵ_c) can be computed using Eq. (1). This model

M. Ezzat (✉) · N. A. Sabiha · M. Izzularab
Faculty of Engineering, Minoufiya University,
Shebin El-Kom 32511, Egypt
e-mail: en.ezzat@yahoo.com

is based on a mean field approximation of a single spherical inclusion surrounded by a continuous matrix of polymer (Yoon et al. 2003).

$$\varepsilon_c = \varepsilon_2 \frac{\varepsilon_1(1 + 2\varphi_1) - 2\varepsilon_2(\varphi_1 - 1)}{\varepsilon_2(2 + \varphi_1) + \varepsilon_1(1 - \varphi_1)}, \quad (1)$$

where ε_1 and ε_2 are the filler and matrix dielectric constants, respectively. φ_1 is the filler volume fraction. The use of MG model with the nanofilled dielectrics did not give accurate results as it did not take the effect of interaction zone between the nanofiller and the base material into consideration. Also, it did not take the effect of particle shape and orientation into account.

Bottcher Mixture (BM) model

Another mean field theory, known as the Bottcher model, treats the binary mixture as being composed of repeated unit cells composed of the matrix phase with spherical inclusions in the center. According to this model, the effective dielectric constant of the composite (ε_c) can be calculated using Eq. (2).

$$\varphi_1 \frac{\varepsilon_1 - \varepsilon_c}{\varepsilon_1 + 2\varepsilon_c} + (1 - \varphi_1) \frac{\varepsilon_2 - \varepsilon_c}{\varepsilon_2 + 2\varepsilon_c} = 0. \quad (2)$$

Similar to MG model, BM model did not give accurate results for the same reasons mentioned in MG model. To increase the accuracy, the effect of particle shape and orientation should be taken into consideration. So, the PL model was developed to cover this point.

Power-law model

Power-law model relationships have been used in computing the effective dielectric constant of composite systems (Karkkainen et al. 2000; Birchak et al. 1974; Nelson and Bartley 1998; Nelson 1983, 2001; Priou 1992; Nelson and You 1990; Gershon et al. 2001; Brosseau et al. 2001). According to PL model, the effective dielectric constant of a composite (ε_c) can be calculated using Eq. (3).

$$\varepsilon_c^\beta = \varphi_1 \varepsilon_1^\beta + (1 - \varphi_1) \varepsilon_2^\beta, \quad (3)$$

where β is a dimensionless parameter depending on the shape and orientation of the filler and can be computed from Eq. (4) (Todd et al. 2005).

$$\beta = 1 - 2 \left[\frac{1}{1 + 1.6(a : b) + 0.4(a : b)^2} \right], \quad (4)$$

where a and b are the axial dimensions of the particle. When $a = b$ this means a spherical particle. At this condition $\beta = 1/3$.

More generally, for a composite comprised m number of mixtures, the PL model can be rewritten as:

$$\varepsilon_c^\beta = \sum_1^m \varphi_i \varepsilon_i^\beta, \quad (5)$$

where φ_i and ε_i are the volume fraction and the dielectric constant of each constituent material, respectively. The accuracy of this model was found to be higher than the two above-mentioned models due to the inclusion of particle shape and orientation. However, this model is not accurate as the interaction between the nanoparticulate and the base material was not taken into consideration. This defect was taken into account in the so-called IPL model.

Interphase power-law model

According to this model, the effective dielectric constant of a composite (ε_c) can be calculated as (Todd et al. 2005):

$$\varepsilon_c^\beta = \varphi_1 \varepsilon_1^\beta + \varphi_2 \varepsilon_3^\beta + (1 - \varphi_1 - \varphi_2) \varepsilon_2^\beta, \quad (6)$$

where ε_3 and φ_2 are the interphase dielectric constant and the interphase volume fraction, respectively. The interphase volume fraction depends on the filler volume fraction as shown in Fig. 1 and can be computed from Eq. (7) (Todd et al. 2005).

$$\varphi_2 = k \varphi_1 \frac{1 - \varphi_1}{1 + k \varphi_1}, \quad (7)$$

where k is a factor depending on the interphase thickness. The increase in k means larger thickness and vice versa.

From Fig. 1, the interphase volume fraction increases from zero, at no filler, to maximum at a certain filler

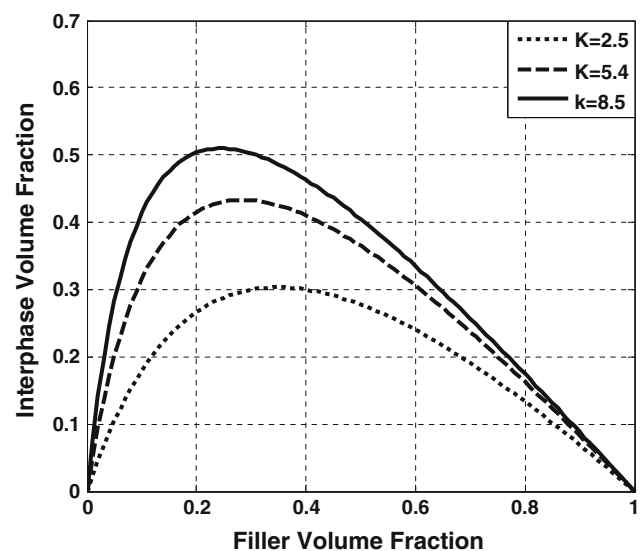
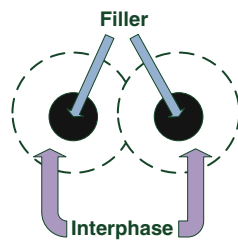


Fig. 1 Effect of filler volume fraction on the interphase volume fraction

Fig. 2 Overlap of interphase zones



volume fraction then decreases until it reaches zero again at unity filler volume fraction. The reason of this variation comes from the overlap of interphase zones as shown in Fig. 2.

According to the investigations of Todd et al. (Todd et al. 2005), the accuracy of this model was found to be higher than the all above-mentioned models but in fact, they did not introduce any method for how the interphase dielectric constant (ϵ_3) can be determined for nanocomposite materials.

Up to now, there is no introduced technique to predict the interphase dielectric constant. So, the proposed model is presented in the current paper to compute the effective dielectric constant of nanocomposites with prediction of interphase dielectric constant.

Proposed model

Polymer-dispersant interfaces have been proved by many researchers (Ozmusul and Picu 2002; Qu and Wong 2002; Vo and Shi 2002; Todd and Shi 2002; Vo et al. 2001). PL, Maxwell–Garnett and Bottcher models do not take into account the effect of these regions which increase the error between calculated and experimental results. To reduce the error between the calculated and the experimental results, the effect of interphase regions should be taken into account.

But the question here, how can this effect be taken into account? Consider a single nanoparticle is dispersed into a matrix as shown in Fig. 3. This nanoparticle consists of atoms and molecules and may take several shapes. The most common shape is the spherical shape, but in fact, the shape may deviate from this shape. But it is still treated as a spherical one for simplicity. From Fig. 3, a narrow region around the nanoparticle arises. In this region, the orientation of matrix molecules may be changed so that air voids may be formed. Also, this region may contain some molecules of the non-uniform nanoparticulate. So that, the interphase region may be treated as three materials they are, matrix or resin material, air and filler molecules. Mathematically, the interphase dielectric constant can be expressed as:

$$\epsilon_3^\beta = \epsilon_2^\beta + \varphi_a(1 - \epsilon_2^\beta) + \varphi_f(\epsilon_1^\beta - \epsilon_2^\beta), \quad (8)$$

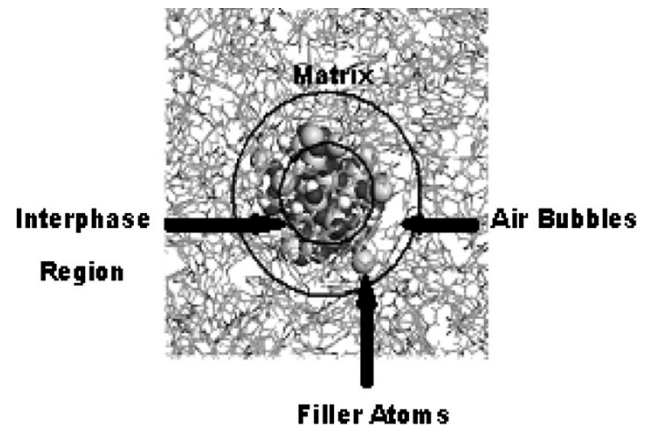


Fig. 3 Nanoparticulate dispersed in a resin

where φ_a and φ_f are the air volume fraction and the filler fraction in the interphase zone, respectively.

For polymers, especially those of large molecules, formation of air voids in the interphase region is dominant as compared to the filler molecules so that, the interphase region can be assumed to consist of resin material and air bubbles. So, the interphase dielectric constant can be assumed to be function of resin and air dielectric constants only, and the interphase dielectric constant can be computed from:

$$\epsilon_3^\beta = \epsilon_2^\beta + \varphi_a(1 - \epsilon_2^\beta). \quad (9)$$

For ceramic and polymers of smaller molecules, formation of air voids in the interphase region can be neglected as compared to the filler molecules so that, the interphase region can be assumed to consist of resin material and filler molecules. So, the interphase dielectric constant can be assumed to be function of resin and filler dielectric constants only, and the interphase dielectric constant can be computed from:

$$\epsilon_3^\beta = \epsilon_2^\beta + \varphi_f(\epsilon_1^\beta - \epsilon_2^\beta). \quad (10)$$

According to this interpretation, the variation of interphase term ($\varphi_2 \epsilon_3$) with filler volume fraction is assumed to be as shown in Fig. 4. Also, the effective dielectric constant of a composite can be calculated from Eq. (11).

$$\epsilon_c^\beta = \varphi_1 \epsilon_1^\beta + (1 - \varphi_1) \epsilon_2^\beta + \varphi'(\epsilon^\beta - \epsilon_2^\beta), \quad (11)$$

where ϵ is the dielectric constant of air (≈ 1) for polymers of large molecules or ϵ is the dielectric constant of the filler for ceramics and polymers of smaller molecules. φ' can be computed from:

$$\varphi' = \varphi_1 \frac{1 - \varphi_1}{1 + \varphi_1}. \quad (12)$$

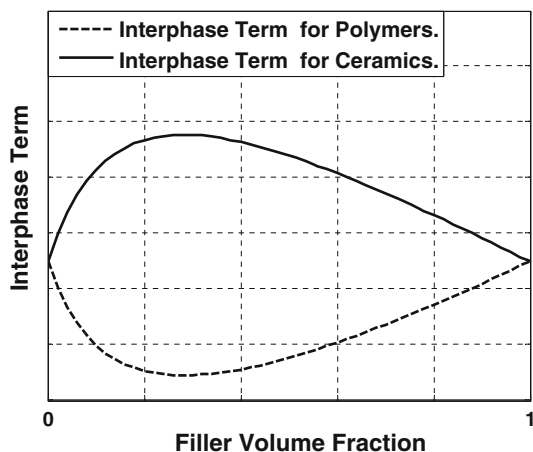


Fig. 4 Variation of dielectric constant term of interphase region

Note For ceramics or polymers of smaller molecules, if the dielectric constant of the matrix is greater than the dielectric constant of the filler then ϵ_1 and ϵ_2 must be reversed in the last term of Eq. (11).

By looking at all the pre-mentioned models, MG and BM models did not take into account either the effect of interphase zone or the effect of particle shape and orientation. PL model gives a better accuracy than MG and BM models as it takes into account the effect of particle shape and orientation although it did not take into account the effect of interphase zones. IPL model gives a better accuracy than MG, BM and PL models as it takes into account the effect of interphase zones, and particle shape and orientation, but IPL model did not introduce a technique for how the interphase permittivity can be determined. So, the attempt, in this paper, is to present a model to compute the dielectric constant of a nanocomposite with high accuracy taking into account all the pre-mentioned effects with computing the interphase dielectric constant as shown from (8).

Model estimations

Using the proposed model, the effect of filler volume fraction, filler dielectric constant and particle shape is presented in this section.

Effect of filler volume fraction

Due to the effect of interaction between filler particulates and the resin material, the proposed model predicts a distinct non-linearity in the effective dielectric constant as a function of filler volume fraction. This non-linearity may come from the non-linear change of interphase volume fraction. The non-linear change of dielectric constant starts from the dielectric constant of the resin at zero volume fraction until it reaches to filler dielectric constant at unity

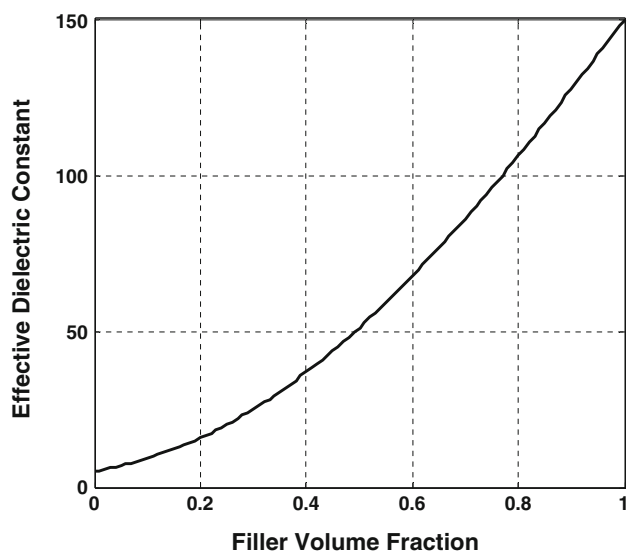


Fig. 5 Variation of dielectric constant for polymer filled nanoparticle with filler volume fraction

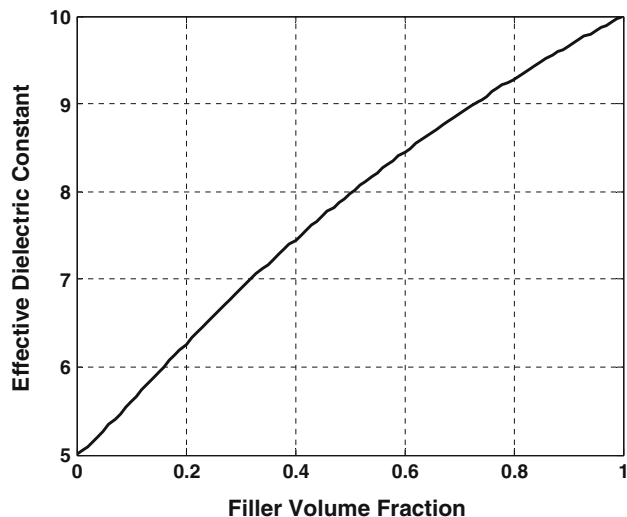


Fig. 6 Variation of dielectric constant for ceramic filled nanoparticle with filler volume fraction

volume fraction. For ceramic resins, the slope of variation may be higher than polymer resins. Figures 5 and 6 show the variation of effective dielectric constant with the filler volume fraction for polymer and ceramic resins, respectively. From these figures, it can be seen that the variation is non-linear and the slope of variation for ceramic resins is higher than polymer resins as predicted before.

Effect of filler dielectric constant

Figure 7 shows the effective dielectric constant variation as a function of filler volume fraction at different values of filler dielectric constants. From this figure, it can be seen that the effective dielectric constant of the composite has a

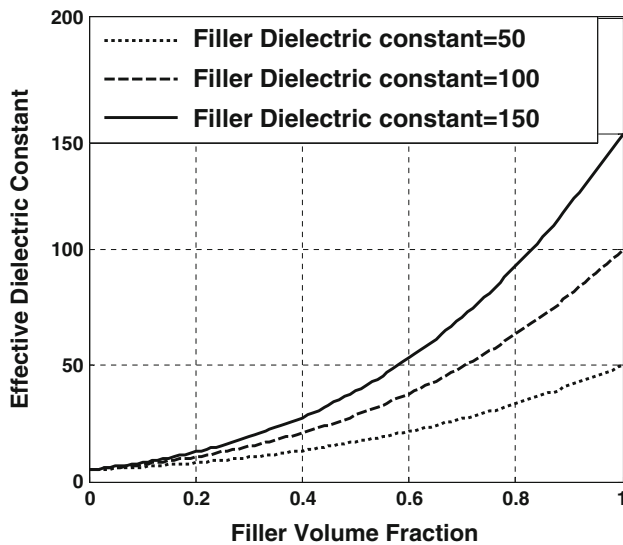


Fig. 7 Effect of filler dielectric constant on the effective dielectric constant

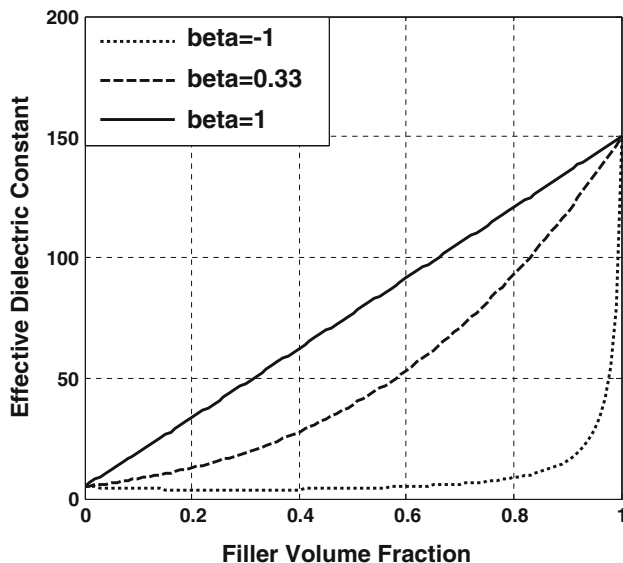


Fig. 8 Effect of particle shape on the effective dielectric constant

large value at large values of filler dielectric constant at the same volume fraction. This means that a filler of large dielectric constant should be used when a composite of large dielectric constant is desired and vice versa. Again, the change of dielectric constant with the filler volume fraction is non-linear as discussed before.

Effect of particle shape and orientation

Figure 8 shows the effect of particle shape and orientation which taken in the proposed model. The dimensionless parameter β in the modified model represents this action. It is expected that the effective dielectric constant is large when β is equal to 1 as it means thin films in parallel, but

when β equal to -1 the composite dielectric constant has its minimum value at the same loading as it means thin films in series. With other particle shapes, the composite dielectric constant lies in between.

Experimental validation

The Proposed model is verified using several reported experimental sets of data. One such data set was published by Gershon et al. (2001) which reported the complex permittivity of copper oxide (CuO) filled alumina composites analyzed at 2.66 GHz. This set of data was also used by Todd and Shi (2004) to verify their proposed model which is called the IPL model.

This set of experimental data is used in this paper to verify the proposed model. Figure 9 shows the validation using this set of experimental data. From this figure, the proposed model gives high accuracy and good fitting to the experimental data.

Another two sets of experimental data published in (Vo and Shi 2002; Eftekhari et al. 1994; Bae et al. 2000) are evaluated using the proposed model and used in the current paper to verify the accuracy of the proposed model as illustrated in Figs. 10 and 11. From these figures, the accuracy of the proposed model is high. This high accuracy comes as the effect of interphase zones and particle shape are taken into consideration.

Also, another two sets of experimental data are used to verify the proposed model. One set of these data was published by Todd et al. (2005). In his research, the barium titanate was used as a nanofiller and the TMPTA polymer

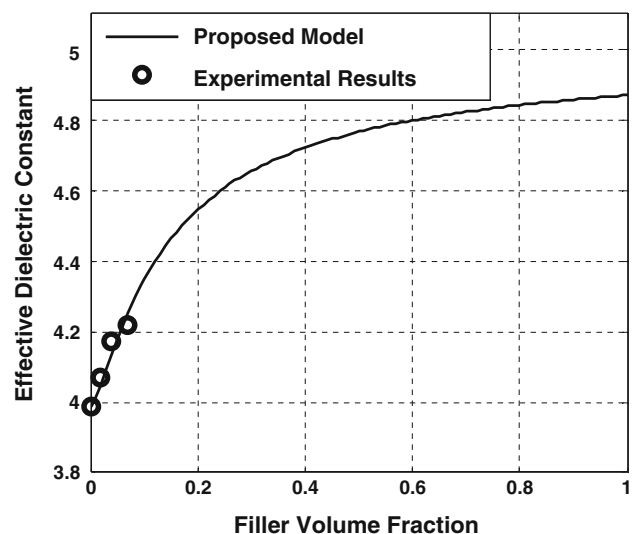


Fig. 9 Effective composite dielectric constant as a function of filler volume fraction of CuO filled alumina composite and model evaluation—experimental data (Gershon et al. 2001)

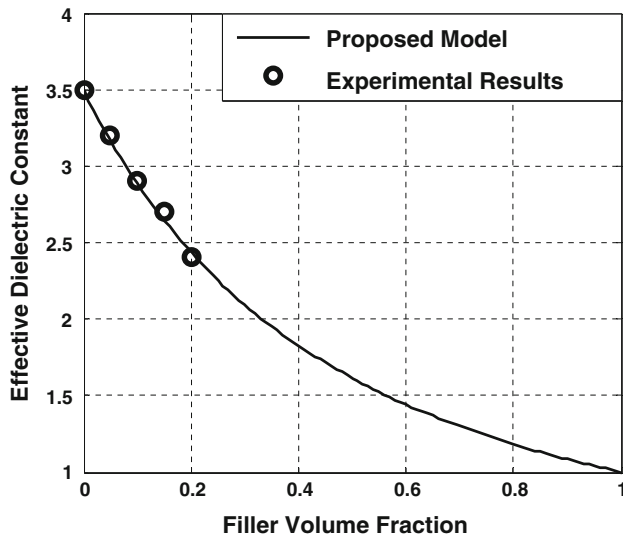


Fig. 10 Effective composite dielectric constant as a function of filler volume fraction and model evaluation—experimental data (Eftekhari et al. 1994)

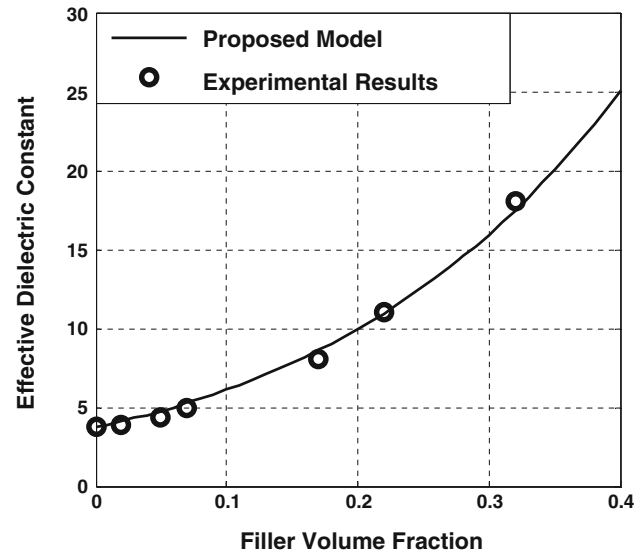


Fig. 12 Effective composite dielectric constant as a function of filler volume fraction of BaTiO₃ filled TMPTA composite and model evaluation—experimental data (Todd et al. 2005)

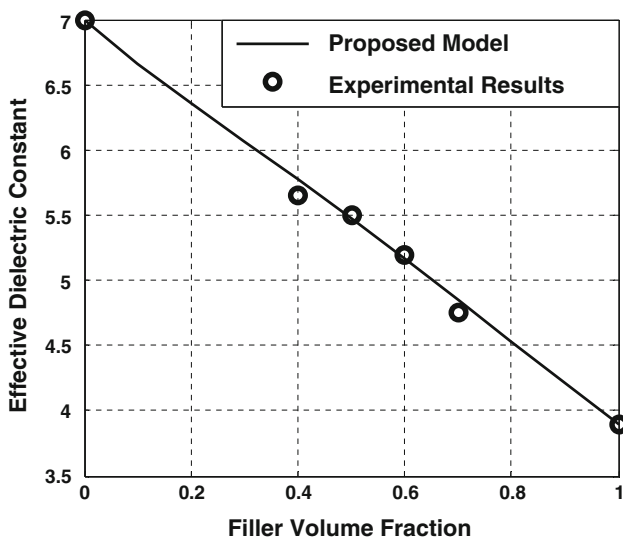


Fig. 11 Effective composite dielectric constant as a function of filler volume fraction and model evaluation—experimental data (Bae et al. 2000)

as a resin material. Figure 12 shows this set of experimental data and the evaluation of the proposed model. The other set of experimental data was published by Deka and Nidhi (2005). In this research, the dielectric constant of alumina filled polystyrene was reported at 9.68 GHz. This set of experimental data is used for evaluation of the proposed model as illustrated in Fig. 13.

From all the above results, it can be concluded that the introduced model has a high accuracy for computing the dielectric constant of nanocomposites. This model takes the effect of both interaction zone and the effect of particle shape into consideration. The interphase dielectric constant is predicted unlike the IPL model which assumes it.

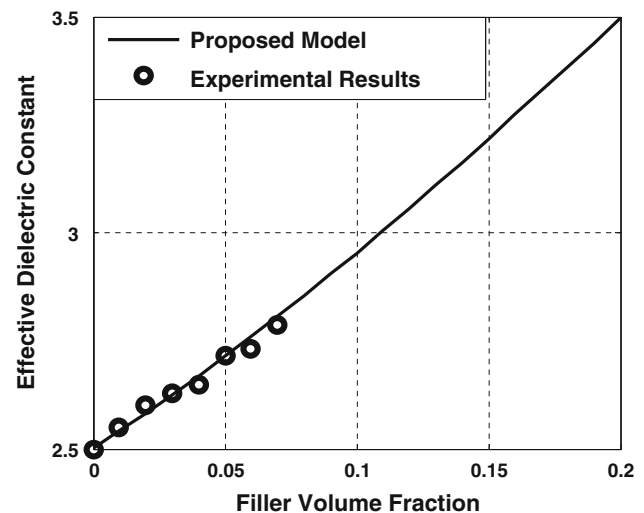


Fig. 13 Effective composite dielectric constant as a function of filler volume fraction of alumina filled polystyrene and model evaluation—experimental data (Deka and Nidhi 2005)

Comparison with other theoretical models

This section presents a comparison between the proposed model and other theoretical models. It is well known that BM model gives results with no large difference as compared to MG model. Also, the IPL model assumes the interphase dielectric constant (ϵ_3) to give a good fitting to experimental results. So, MG and PL models only are chosen in this comparison. Figures 14 and 15 show this comparison. As seen from these figures, the proposed model gives the best fitting to experimental data which ensures the ability to use this model for computing the dielectric constant of nanocomposites.

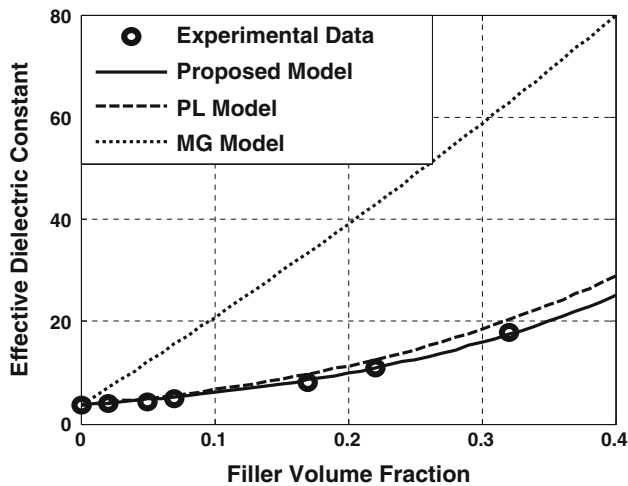


Fig. 14 Comparison between the proposed model and other theoretical models (MG and PL), effective composite dielectric constant as a function of filler volume fraction of alumina filled polystyrene and model evaluation—experimental data (Deka and Nidhi 2005)

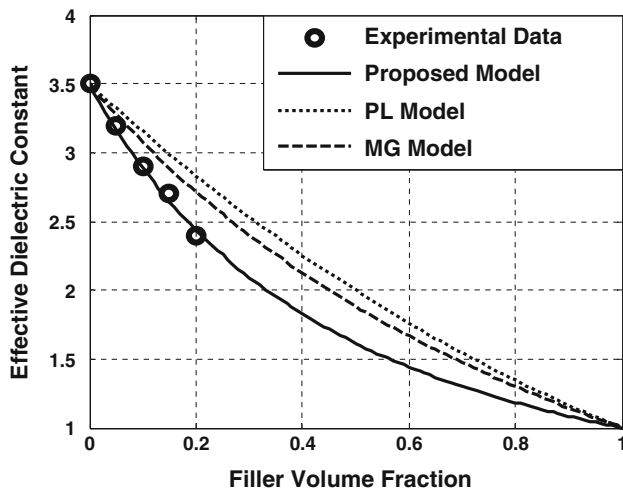


Fig. 15 Comparison between the proposed model and other theoretical models (MG and PL), effective composite dielectric constant as a function of filler volume fraction of alumina filled polystyrene and model evaluation—experimental data (Deka and Nidhi 2005)

Conclusion

A proposed model for computing the dielectric constant of nanocomposites has been presented. The effect of filler volume fraction, filler dielectric constant and particle shape has been studied through the proposed model. A non-linear change has been detected due to the non-linear change of the interphase volume fraction with the filler volume fraction. Experimental validation of the proposed model has been carried out and has shown a good accuracy of the model. Finally, the proposed model has shown a good accuracy as compared to other theoretical models which

ensures the ability of using this model in dielectric constant computation of nanofilled composites.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Awaji H, Nishimura Y, Choi SM, Takahashi Y, Goto T, Hashimoto S (2009) Toughening mechanism and frontal process zone size of ceramics. *J Ceram Soc Japan* 117:623–629
- Bae JW, Kim W, Cho SH, Lee SH (2000) The properties of AlN-filler epoxy molding compounds by the effects of filler size distribution. *J Mater Sci* 35:5907–5913
- Birchak JR, Gardner LG, Hipp JW, Victor JM (1974) High dielectric constant microwave probes for sensing soil moisture. *Proc IEEE* 62:93–98
- Brosseau C, Queffelec P, Talbot P (2001) Microwave characterization of filled polymers. *J Appl Phys* 89(8):4532–4540
- Chen L, Chen GH (2009) Relaxation behavior study of silicone rubber crosslinked network under static and dynamic compression by electric response. *Polymer Compos* 30:101–106
- Cherney EA (2005) Silicone rubber dielectrics modified by inorganic fillers for outdoor high voltage insulation applications. *IEEE Trans Dielectr Electr Insul* 12:1108–1115
- Deka JR, Nidhi SB (2005) Micro characterization of alumina filled polystyrene composite. [http://www.ursi.org/Proceedings/ProcGA05/pdf/D04.6\(0652\).pdf](http://www.ursi.org/Proceedings/ProcGA05/pdf/D04.6(0652).pdf)
- Eftekhari A, Clair AK, Stoakly DM, Sprinkle DR, Singh JJ (1994) Microstructural characterization of thin polyimide films by positron lifetime spectroscopy. In: *Polymers for microelectronics*, vol 537, pp 535–545
- Gershon D, Calame JP, Birnboim A (2001) Complex permittivity measurements and mixing laws of alumina composites. *J Appl Phys* 89(12):8110–8116
- Karkkainen KK, Sihvola AH, Nikoskinen KI (2000) Effective permittivity of mixtures: numerical validation by the FDTD method. *IEEE Trans Geosci Remote Sens* 38(3):1303–1308
- Kim P, Doss NM, Tillotson JP, Hotchkiss PJ, Pan MJ, Marder SR, Li JY, Calame JP, Perry JW (2009) High energy density nanocomposites based on surface-modified BaTiO₃ and ferroelectric polymer. *Am Chem Soc Nano* 3:2581–2592
- Momen G, Farzanah M (2011) Survey of micro/nano filler use to improve silicone rubber for outdoor insulators. *Rev Adv Mater Sci* 27:1–13
- Nelson SO (1983) Observations on the density dependence of dielectric properties of particulate materials. *J Microw Power* 18(2):143–152
- Nelson SO (2001) Measurement and calculation of powdered mixture permittivities. *IEEE Trans Inst Meas* 50(5):1066–1070
- Nelson SO, Bartley PG Jr (1998) Open-ended coaxial-line permittivity measurements on pulverized materials. *IEEE Trans Inst Meas* 47(1):133–137
- Nelson SO, You TS (1990) Relationships between microwave permittivities of solid and pulverized plastics. *J Phys D Appl Phys* 23:346–353
- Ozmusul MS, Picu RC (2002) Elastic moduli of particulate composites with graded filler-matrix interfaces. *Polymer Compos* 23(1):110–119
- Priou A (ed) (1992) *Dielectric properties of heterogeneous materials*, vol 6. Elsevier Press, New York

- Qu J, Wong CP (2002) Effective elastic modulus of underfill material for flip-chip applications. *IEEE Trans Compon Packag Technol* 25(1):53–55
- Tan H, Yang W (1998) Toughening mechanisms of nano-composite ceramics. *Mech Mater* 30:111–123
- Todd M, Shi FG (2002) Validation of a novel dielectric constant simulation model. *Microelectron J* 33:627–632
- Todd M, Shi F (2004) Dielectric characteristics of complex composite systems containing interphase regions. In: 9th International symposium on advanced packing materials, pp 112–117
- Todd MG, Shi FG (2005) Complex permittivity composite systems: a comprehensive interphase approach. *IEEE Trans Dielectr Electr Insul* 12:601–611
- Vo H, Shi FG (2002) Towards model-based engineering of optoelectronic packaging materials: dielectric constant modeling. *Microelectron J* 33(5):409–415
- Vo H, Todd M, Shi F, Shapiro A, Edwards M (2001) Towards model-based engineering of underfill materials: CTE modeling. *Microelectron J* 32:331–338
- Yoon DH, Zhang J, Lee BI (2003) Dielectric constant and mixing model of barium titanate composite thick films. *Mater Res Bull* 38:765–772
- Zhao KS, He KJ (2006) Dielectric relaxation of suspensions of nanoscale particles surrounded by a thick electric double layer. *Phys Rev B* 74:205319–205319-10