Analysis of Tensile Modulus of PP/Nanoclay/$CaCO_3$ Ternary Nanocomposite Using Composite Theories

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ABSTRACT: The tensile modulus of PP/nanoclay/$CaCO_3$ hybrid ternary nanocomposite was analyzed using composite models. Rule of mixtures, inverse rule of mixtures, modified rule of mixtures (MROM), Guth, Paul, Counto, Hirsch, Halpin–Tsai, Takayanagi, and Kerner–Nielsen models were developed for three-phase system containing two nanofillers. Among the studied models, inverse rule of mixtures, Hirsch, Halpin–Tsai, and Kerner–Nielsen models calculated the tensile modulus of PP/nanoclay/$CaCO_3$ ternary nanocomposite successfully compared with others. Furthermore, the Kerner–Nielsen model was simplified to predict the tensile modulus by volume fractions of nanofillers. Also, Takayanagi model was modified for the current ternary system. The developed Takayanagi model can predict the tensile modulus using Young's modulus and volume fractions of matrix and nanofillers. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2309–2319, 2012

Key words: analysis of tensile modulus; PP/nanoclay/$CaCO_3$ nanocomposite

INTRODUCTION

Polymeric nanocomposites, developed in 1980's,[1] are multiphase materials which show superior mechanical, flammability, and permeability properties at very low nanofiller contents.[2,3] Their applications in thermoplastic and thermoset polymers are well established due to the more adhesion improvement between matrix and filler. In the last 2 decades, extensive studies have been carried out in micromechanics and macromechanics of nanocomposites[4–10] in which the structure of nanocomposite, such as the dispersion of nanofiller in the matrix, and the properties of nanocomposites as a uniform texture are studied, respectively. Despite the large volume of studies, no clear relationship has been introduced between structure, processing and properties of the nanocomposites so far. To verify the effects of various material and processing variables on the structure and properties of nanocomposite, large number of experiments are required leading to much cost and time. Therefore, further development and optimization of nanocomposite behavior has been a major challenge in the scientific communities.

Recently, the modeling of nanocomposite behavior has been seriously considered for optimizing the desired properties. The models can provide the substantial information that eases the prediction of the nanocomposite behavior. The mechanical properties of nanocomposites have attracted much interest because of the excellent potential of nanocomposites in this area.[11–14] Therefore, the analysis of tensile modulus has involved much attention in the literature.[15–20]

Many models have been introduced for predicting the tensile modulus of binary nanocomposites. Wu et al. added a modulus reduction factor (MRF) to Halpin–Tsai, modified Halpin–Tsai and Guth models to predict the tensile modulus of rubber/clay nanocomposites.[18] Kalaitzidou et al. also compared the Halpin–Tsai and Tandon-Weng theories for various PP nanocomposites. They indicated that a good fitting was found for low nanofiller content but these models overestimated the modulus as the filler content increased.[19] Sisakht et al. applied the conventional composite models to calculate the tensile modulus as a first approximation or initial estimation in the PA66/$CaCO_3$ nanocomposite.[2] They pointed out that the experimental data are higher than the theoretical results.

Although a large number of researchers analyze the tensile modulus in the binary nanocomposites, this subject for ternary nanocomposites containing two nanofillers has not been investigated so far. Expectedly, the reinforcing effects of two nanofillers affect the overall performances of ternary nanocomposite especially mechanical properties.[21–23] Chen et al. have shown that PP/nanoclay/$CaCO_3$ ternary nanocomposite presented better tensile modulus compared with the binary PP/nanoclay and PP/$CaCO_3$ nanocomposites.[23]

In the recent works, researchers have shown that more parameters affect the tensile modulus of

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nanocomposites, such as the crystalline morphology of matrix, level of filler dispersion, the interaction between two fillers, matrix-filler interface, nanoclay orientation, and the aspect ratio of filler.[22–33] However, taking into account of all these parameters simultaneously in one model causes a very complex case.

In this work, various known composite models were developed to predict the tensile modulus of PP/nanoclay/$CaCO_3$ ternary nanocomposite. Furthermore, the modification of Kerner–Nielsen and Takayanagi models were carried out to introduce the simplest model for calculating the tensile modulus of the current system. Obviously, more investigation is needed in this area in future to study the effect of more parameters for developing other theories.

BACKGROUND

The simplest models for predicting the tensile modulus in a two-phase system are "parallel" and "series" models introduced by Broutman and Krock in 1967.[34] In the "parallel" or "rule of mixtures" model, represented in eq. (1), the equal strain is assumed in the matrix and filler phases[35–37]:

$$E = E_m\ \phi_m + E_f\phi_f \tag{1}$$

where E_m and E_f are the Young's modulus of matrix and filler, respectively and ϕ_m and ϕ_f are the volume fraction of the matrix and filler in that order. Generally, rule of mixture expresses the upper limit of the tensile modulus. The models are developed for the PP/nanoclay/$CaCO_3$ ternary nanocomposite in the current research. So, by adding another filler phase, rule of mixtures is developed to eq. (2):

$$E = E_m\phi_m + E_{f1}\phi_{f1} + E_{f2}\phi_{f2} \tag{2}$$

where subscript 1 and 2 denote the name of fillers. In this study, 1 and 2 indicate to nanoclay and $CaCO_3$ phases, respectively.

When assuming uniform stress in the matrix and filler phases, the "series" or "inverse rule of mixtures" model is obtained as presented in eq. (3):

$$\frac{1}{E} = \frac{\phi_m}{E_m} + \frac{\phi_f}{E_f} \tag{3}$$

For a three-phase system, the inverse rule of mixtures is presented in eq. (4):

$$\frac{1}{E} = \frac{\phi_m}{E_m} + \frac{\phi_{f1}}{E_{f1}} + \frac{\phi_{f2}}{E_{f2}} \tag{4}$$

The parallel and series models were later modified to achieve improvement in the prediction accuracy.

Guth and Gold (1938) used an approach of the Smallwood–Einstein equation and considered the interaction between filler particles.[38–40] The Guth model is shown in eq. (5):

$$E = E_m(1 + 2.5\phi_f + 14.1\phi_f^2) \tag{5}$$

By adding another filler phase, Guth model is developed to eq. (6):

$$E = E_m[1 + 2.5(\phi_{f1} + \phi_{f2}) + 14.1(\phi_{f1} + \phi_{f2})^2] \tag{6}$$

Paul assumed that consistent stress is applied at the matrix-filler boundary.[41] Paul model is given by eqs. (7) and (8):

$$E = E_m\left[\frac{1 + (m-1)\phi_f^{2/3}}{1 + (m-1)(\phi_f^{2/3} - \phi_f)}\right] \tag{7}$$

$$m = E_f/E_m \tag{8}$$

For a three-phase system, Paul model is developed to eqs. (9)–(11):

$$E = E_m\left[\frac{1 + (\frac{m_1+m_2}{2} - 1)(\phi_{f1} + \phi_{f2})^{2/3}}{1 + (\frac{m_1+m_2}{2} - 1)[(\phi_{f1} + \phi_{f2})^{2/3} - (\phi_{f1} + \phi_{f2})]}\right] \tag{9}$$

$$m_1 = E_{f1}/E_m \tag{10}$$

$$m_2 = E_{f2}/E_m \tag{11}$$

Counto assumed perfect adhesion in the matrix-filler interface and suggested the following model.[42] Counto model is presented in eq. (12):

$$\frac{1}{E} = \frac{1 - \phi_f^{1/2}}{E_m} + \frac{1}{(1 - \phi_f^{1/2})/\phi_f^{1/2}E_m + E_f} \tag{12}$$

For two filler phases, Counto model is shown in eq. (13):

$$\frac{1}{E} = \frac{1 - (\phi_{f1} + \phi_{f2})^{1/2}}{E_m} + \frac{1}{[1 - (\phi_{f1} + \phi_{f2})^{1/2}]/(\phi_{f1} + \phi_{f2})^{1/2}E_m + \frac{1}{2}(E_{f1} + E_{f2})} \tag{13}$$

Hirsch combined these two models and presented eq. (14)[43] in which x and (1 – x) represent the relative contributions of composite conforming to the upper and lower limits of modulus, respectively.

$$E = x(E_m\phi_m + E_f\phi_f) + (1-x)\left[\frac{E_f E_m}{E_f\phi_m + E_m\phi_f}\right] \quad (14)$$

For a three-phase system, Hirsch model can be developed to eq. (15):

$$E = x\left[E_m\phi_m + \left(\frac{E_{f1}+E_{f2}}{2}\right)(\phi_{f1}+\phi_{f2})\right] + (1-x)\left[\frac{E_m(E_{f1}+E_{f2})}{(E_{f1}+E_{f2})\phi_m + 2E_m(\phi_{f1}+\phi_{f2})}\right] \quad (15)$$

In 1976, Riley modified the rule of mixtures model by assuming a modulus reduction factor (MRF)[44,45]. Unlike the previous works, Riley took account of other variables for developing parallel and series models. He introduced the aspect ratio of filler and the shear modulus of matrix in MRF. Riley model, referred to as modified rule of mixtures (MROM) is presented in eqs. (16)–(18):

$$E = E_m\phi_m + \mathrm{MRF}\phi_f E_f \quad (16)$$

$$\mathrm{MRF} = 1 - \frac{Ln(u+1)}{u} \quad (17)$$

$$u = \frac{1}{\alpha}\sqrt{\frac{\phi_f G}{E_f\phi_m}} \quad (18)$$

where G is the shear modulus of matrix, α is the aspect ratio of filler defined as $\alpha = w/t$ (w and t are the width and thickness of the dispersed filler, respectively).

For a three-phase composite, the MROM model is developed to eqs. (19)–(21):

$$E = E_m\phi_m + \frac{1}{2}MRF(\phi_{f1}+\phi_{f2})(E_{f1}+E_{f2}) \quad (19)$$

$$\mathrm{MRF} = 1 - \frac{Ln(u+1)}{u} \quad (20)$$

$$u = \frac{2}{\alpha_1+\alpha_2}\sqrt{\frac{2(\phi_{f1}+\phi_{f1})G}{(E_{f1}+E_{f2})\phi_m}} \quad (21)$$

Takayanagi also proposed a model for composites and blends in 1964.[46–48] He considered a combination of series and parallel models as shown in Figure 1(a) and given by eq. (22):

$$E = \left[\frac{\alpha}{(1-\beta)E_m + \beta E_f} + \frac{1-\alpha}{E_f}\right]^{-1} \quad (22)$$

Where α and β illustrate the state of parallel and series coupling in the composite and are a function of volume fraction of the filler presented in eqs. (23) and (24):

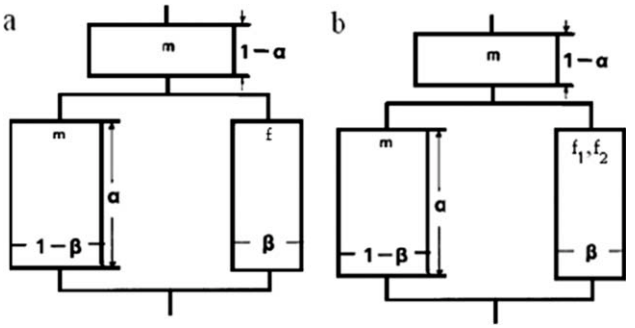

Figure 1 The Takayanagi model for (a) binary and (b) ternary system containing two nanofillers. m and f refer to matrix and filler phases, respectively.

$$\alpha = 5\phi_f/(2+3\phi_f) \quad (23)$$

$$\beta = (2+3\phi_f)/5 \quad (24)$$

For a three-phase system containing two nanofillers, Takayanagi model is developed to Figure 1(b). The Takayanagi model for the current system is presented later in the Development of Takayanagi model section.

Halpin and Tsai introduced a mathematical model.[49–51] The Halpin–Tsai model is represented in eqs. (25)–(47):

$$E = E_m\left(\frac{1+\eta\xi\phi_f}{1-\eta\phi_f}\right) \quad (25)$$

$$\eta = (E_f/E_m - 1)/(E_f/E_m + \xi) \quad (26)$$

$$\xi = 2(w/t) \quad (27)$$

For a three-phase system, Halpin–Tsai equation changes to eqs. (28)–(32):

$$E = E_m\left(\frac{1+\eta_1\xi_1\phi_{f1}+\eta_2\xi_2\phi_{f2}}{1-\eta_1\phi_{f1}-\eta_2\phi_{f2}}\right) \quad (28)$$

$$\eta_1 = \frac{E_{f1}/E_m - 1}{E_{f1}/E_m + \xi_1} \quad (29)$$

$$\eta_2 = \frac{E_{f2}/E_m - 1}{E_{f2}/E_m + \xi_2} \quad (30)$$

$$\xi_1 = 2(w_1/t_1) \quad (31)$$

$$\xi_2 = 2(w_2/t_2) \quad (32)$$

Halpin–Tsai model was modified by Kerner and Nielsen in 1990's.[52–54] They eliminated the effect of filler aspect ratio and defined two new parameters: A_f as a function of the Poisson ratio of matrix (υ_m) and ϕ_{max} as the maximum volumetric packing fraction of the filler (true volume of the filler/ apparent volume occupied by the filler).

The Kerner–Nielsen model is represented in eqs. (33)–(36):

TABLE I
The Young's Modulus and Density of PP, Nanoclay, and $CaCO_3$

Material (g/cm^3)	Young's modulus (GPa)	Density
PP	2.17	0.91
Nanoclay	178	1.77
$CaCO_3$	26	2.71

$$E = E_m\left(\frac{1 + A_f B_f \phi_f}{1 - P_f B_f \phi_f}\right) \quad (33)$$

$$A_f = (7 - 5\upsilon_m)/(8 - 10\upsilon_m) \quad (34)$$

$$B_f = (E_f/E_m - 1)/(E_f/E_m + A_f) \quad (35)$$

$$P_f = 1 + \phi_f^2[(1 - \phi_{\max})/\phi_{\max}] \quad (36)$$

For a three-phase system, the Kerner–Nielsen model is developed to eqs. (37)–(41).

$$E = E_m\left(\frac{1 + A_f B_{f1} \phi_{f1} + A_f B_{f2} \phi_{f2}}{1 - P_f B_{f1} \phi_{f1} - P_f B_{f2} \phi_{f2}}\right) \quad (37)$$

$$A_f = (7 - 5\upsilon_m)/(8 - 10\upsilon_m) \quad (38)$$

$$B_{f1} = (E_{f1}/E_m - 1)/(E_{f1}/E_m + A_f) \quad (39)$$

$$B_{f2} = (E_{f2}/E_m - 1)/(E_{f2}/E_m + A_f \quad (40)$$

$$P_f = 1 + (\phi_{f1} + \phi_{f2})^2\left[1 - \left(\frac{\phi_{\max 1} + \phi_{\max 2}}{2}\right)\right] \Bigg/ \left(\frac{\phi_{\max 1} + \phi_{\max 2}}{2}\right) \quad (41)$$

EXPERIMENTAL

PP homopolymer (ZH500, MFI = 10 g/10 min, 230°C, 2.16 kg) was provided from a local manufacturer, Navid Zar Shimi, Iran. The nanoclay (Cloisite 20A) is a natural montmorillonite modified with a quaternary ammonium salt was purchased from the Southern Clay Products. Maleic anhydride grafted PP, PPgMA (PB3150, MFI = 20 g/10 min) with 0.5 wt % of Maleic anhydride was supplied by Crompton Corp. Precipitated $CaCO_3$ (SOCAL312) nanopowder, with an average particle size of 70 nm and coated with an organic layer of Stearic acid was also prepared from Solvay.

First, all materials were dried at 80°C for 10 h in an oven. After dry-mixing of all the materials, melt blending process was carried out in a Brabender DSE 20/40D (D = 25 mm, L/D = 40) co-rotating twin screw extruder in the following operating condition: screw speed of 250 rpm, temperature profile of 210–230°C and constant feeding rate of 3 kg/h. Equal weight content of PPgMA and nanoclay were used in all samples.

Injection molding of samples were performed using a MonoMat 80 injection molding machine at temperatures ranging from 190–220°C from feed zone to nozzle.

The tensile test was carried out according to ASTM D638 with a Z050-Zwick tester with the crosshead speed of 50 mm/min. For each sample, at least five specimens were tested.

The Young's modulus and density of PP, nanoclay, and $CaCO_3$ are shown in Table I according to the presented product's data sheets by companies.

The Poisson ratio of PP matrix obtained by the tensile test is 0.38. The shear modulus was obtained as 0.78 GPa and also, the aspect ratio of 1 was assumed for $CaCO_3$ nanoparticles.

RESULTS AND DISCUSSION

Nanocomposite properties

The morphological properties of prepared samples were investigated using various techniques, such as XRD, AFM, and SEM.[55] The photographs showed intercalated/exfoliated nanoclay layers. Also, $CaCO_3$ nanoparticles were well dispersed and distributed in the PP matrix in the presence of nanoclay particles. The samples were prepared in the high range of 2–20 wt % of $CaCO_3$ for the better analysis of tensile modulus models.

The experimental results of tensile modulus are shown in Table II. In nanoclay contents of 2 and 4 wt %, tensile modulus enhance with increasing of $CaCO_3$ content, but a different trend is observed in nanoclay content of 6 wt %. The tensile modulus of sample No.12 with 6 wt % of nanoclay and 20 wt % of $CaCO_3$ is lower than that of other samples containing the same nanoclay content. Possibly, the low dispersion of nanoparticles in the high contents of nanoparticles leads to the low interface between

TABLE II
The Experimental Data of Tensile Modulus

Sample No.	Nanoclay wt %	$CaCO_3$ wt %	Tensile modulus (GPa)
1	2	2	2.41 ± 0.15
2	2	8	2.49 ± 0.08
3	2	14	2.57 ± 0.13
4	2	20	2.7 ± 0.05
5	4	2	2.48 ± 0.16
6	4	8	2.57 ± 0.12
7	4	14	2.65 ± 0.05
8	4	20	2.95 ± 0.13
9	6	2	2.6 ± 0.17
10	6	8	2.71 ± 0.11
11	6	14	2.92 ± 0.13
12	6	20	2.52 ± 0.08

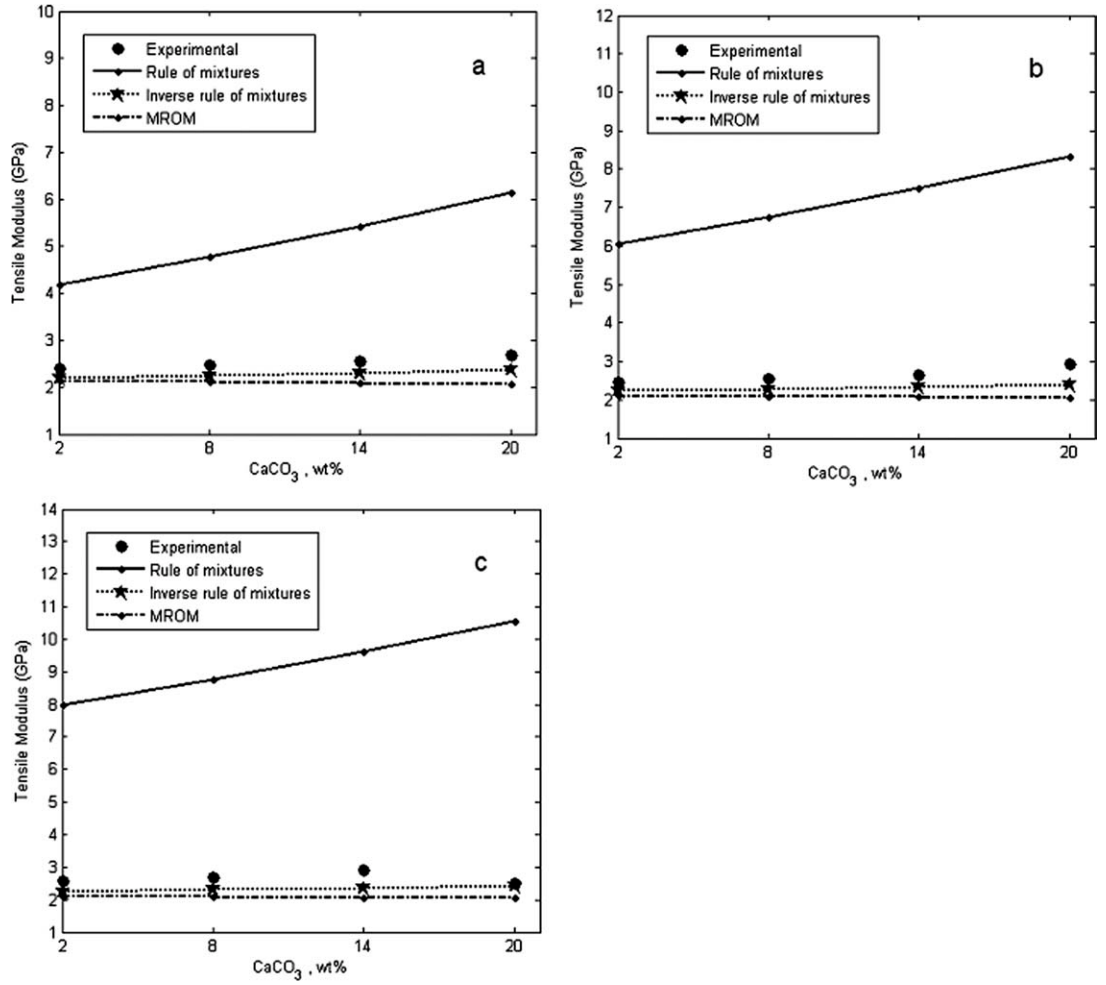

Figure 2 Experimental tensile modulus data and theoretical predictions by rule of mixtures, inverse rule of mixtures, and MROM models in nanoclay contents of (a) 2 wt %, (b) 4 wt %, and (c) 6 wt %.

nanofillers and PP matrix. However, the agglomeration and segregation of nanoparticles were not observed in all samples. In the present ternary nanocomposite, modified nanoparticles have been used to persuade more interaction and adhesion between PP chains and nanoparticles. It created much lower agglomerates for higher nanofiller contents. In addition, high melt viscosity induced by low MFI of PP and optimized processing parameters obtained empirically (screw speed of 250 rpm, feeding rate of 3 kg/h and temperature profile of 210–230°C) caused high mechanical shear stress on the melt mixing that could broke up the filler agglomerations. It is worth noting that obtained photographs also confirm this evidences.[55]

Moreover, the crystallization behavior of PP was affected by nanoparticles in the present ternary nanocomposite.[55] The findings indicated that increasing of nanoclay content from 2 wt % to 6 wt % decrease the crystallization temperature and crystallinity degree due to the restriction of PP chains; whereas increasing of $CaCO_3$ content from 8 wt % to 20 wt % increased the crystallization temperature but had a slight effect on the crystallinity content. Also, the α-crystal of PP was formed much more than β-phase in the current prepared ternary nanocomposite.

Application of composite theories

All of the developed composite models for a ternary system are applied for PP/nanoclay/$CaCO_3$ ternary nanocomposite. Figure 2 shows the experimental data and theoretical tensile modulus by rule of mixtures, inverse rule of mixtures, and MROM models. These models predict the tensile modulus using Young's modulus and the volume fractions of matrix and nanofillers. Among these models, rule of mixtures presents the upper bound of the tensile modulus, whereas it shows a clear disparity with the experimental results. It is worth noting that the enhancement of nanoclay increases the differences. The over-predictions of rule of mixtures are most probably due to the high Young's modulus of

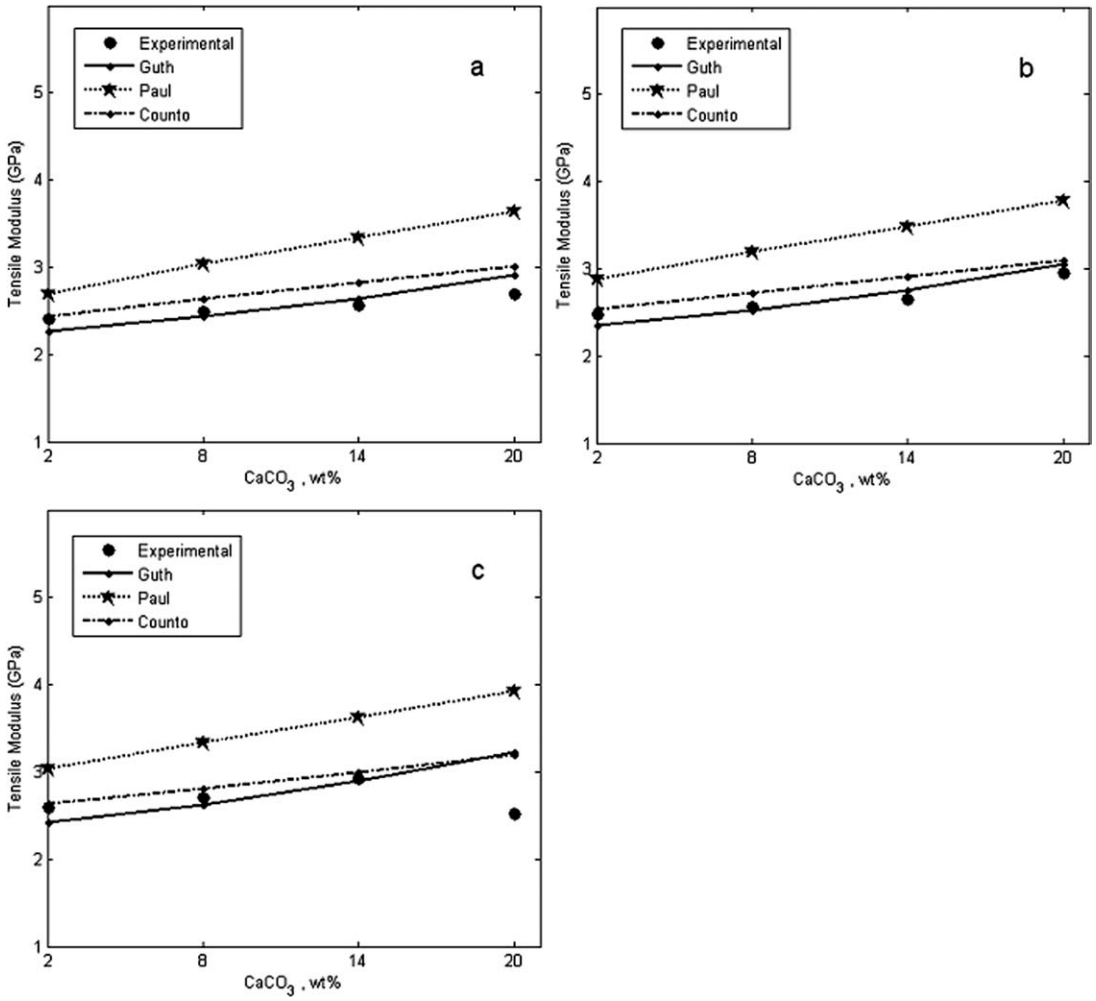

Figure 3 Experimental data and predicted tensile modulus by Guth, Paul, and Counto models in nanoclay contents of (a) 2 wt %, (b) 4 wt %, and (c) 6 wt %.

nanofillers. The predicted data by inverse rule of mixtures are well fitted to the experimental results. Also, the predictions of inverse rule of mixtures and MROM are lower than the experimental data in all samples. Among the all studied models, MROM predict the lowest values for the present ternary nanocomposite.

In MROM model, Riley considered the effect of filler aspect ratio (α) for binary systems.[44,45] However, α has a different effect in a ternary system, whereas the aspect ratio of nanoclay layers in a long range of 5–1000 has very slight influence on the calculated tensile modulus. Therefore, the predicted data by MROM presented in Figure 2 is independent of the aspect ratio. In another study on the PA6/clay nanocomposite,[45] MROM was fitted to the experimental data successfully for various nanoclay types in the nanoclay aspect ratio of 7–130.

Figure 3 shows the experimental tensile modulus and the predicted data using Guth, Paul and Counto models. Obviously, the predicted modulus by Paul is higher than Counto and Guth predictions. The predicted data by Guth is well fitted to the experimental results compared with Paul and Counto. Also, Counto can predict the tensile modulus better than Paul.

The theoretical data by Hirsch model is illustrated in Figure 4. The experimental data are fitted to the theoretical predictions in low value of x about 0.05 indicating that the tensile modulus of PP/nanoclay/$CaCO_3$ ternary nanocomposite conforms to the inverse rule of mixtures model more than rule of mixtures. According to these findings, low value of x shows that the addition of nanoclay and $CaCO_3$ nanofillers to PP can not improve the tensile modulus of ternary nanocomposite expectedly when compared with PP/nanoclay and PP/$CaCO_3$ binary nanocomposites.[23]

The theoretical tensile modulus by Halpin–Tsai model is shown in Figure 5. In the current ternary nanocomposite, the predicted results are fitted to the experimental data in low aspect ratio ($\alpha = 2$). As seen, only the predicted data for sample containing 6 wt % of nanoclay and 20 wt % of $CaCO_3$ show

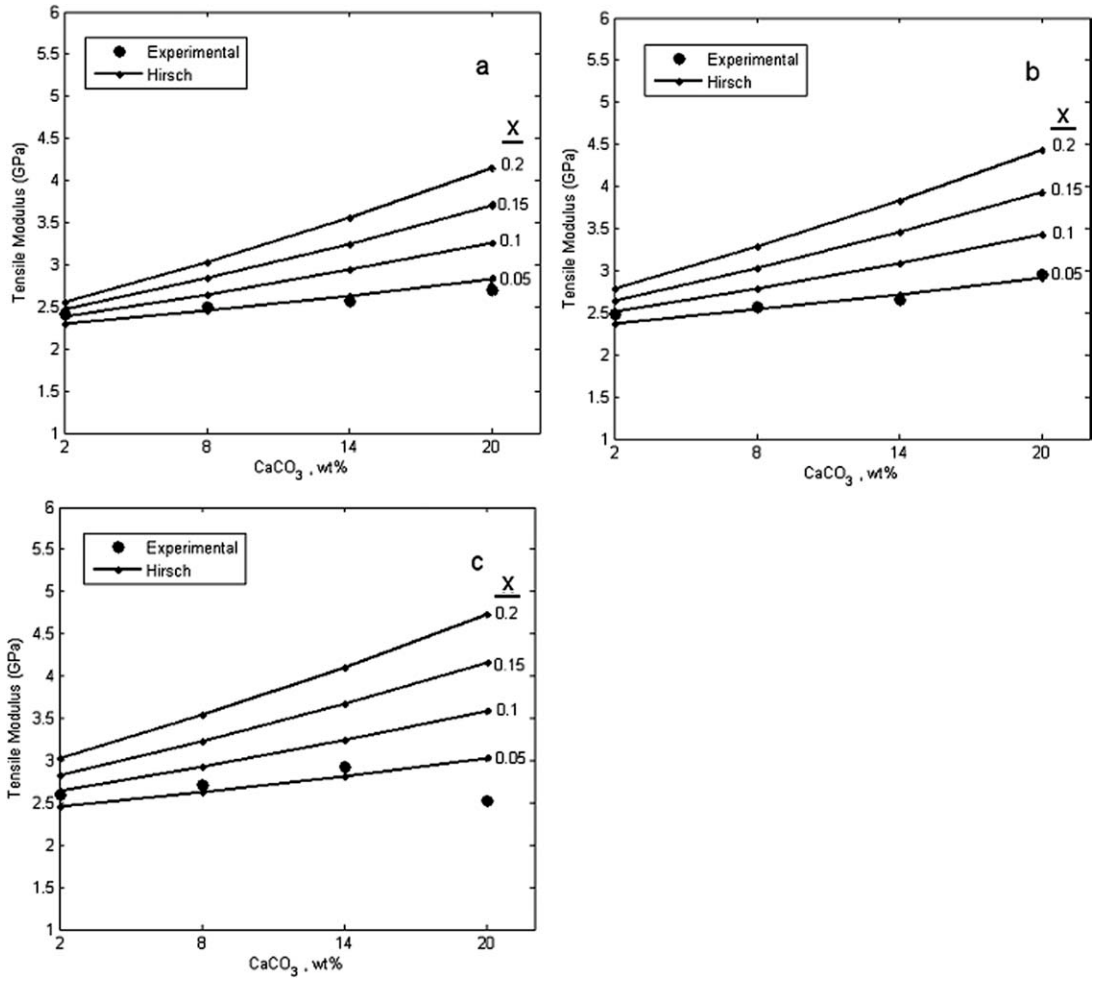

Figure 4 Experimental tensile modulus and theoretical data by Hirsch model in nanoclay contents of (a) 2 wt %, (b) 4 wt %, and (c) 6 wt %. x shows the relative contribution of composite conforming to the rule of mixtures model.

some difference. According to the Halpin–Tsai predictions in Figure 5, increasing of nanoclay aspect ratio from 2 to 30 enhances the tensile modulus. In the present PP/nanoclay/$CaCO_3$ nanocomposite, the presence of $CaCO_3$ nanoparticles increases the melt viscosity resulting in much higher shear stress. It may be suggested that the high shear stress break up the nanoclay layers leading to lower effective aspect ratio. Therefore, the low aspect ratio fitted to the Halpin–Tsai model can be expected. To verify this claim, more investigation on the ternary system is required to measure the aspect ratio of nanoclay layers.

Furthermore, in several studies, Halpin–Tsai has over-predicted the tensile modulus of binary nanocomposites compared with the experimental results.[2,19,56] The over-prediction of Halpin–Tsai model in the binary systems could be related to the lower contribution of the plate-like nanoclay (two dimensional filler) and the spherical $CaCO_3$ (three dimensional filler) to tensile modulus compared to the fiber-like (one dimensional filler).[57]

Modification of Kerner–Nielsen model

As indicated before in the Background section, Kerner and Nielsen modified the Halpin–Tsai model and considered two parameters: A_f, a function of the Poisson ratio of matrix and ϕ_{max}, the maximum volumetric packing fraction of the filler.[52–54] Figure 6 shows the theoretical tensile modulus by Kerner–Nielsen. In the present ternary system, it is found that the ϕ_{max} values from 0.05 to 0.95 for both nanoclay and $CaCO_3$ do not affect the predicted data. As a result, the presented data by Kerner–Nielsen are independent of ϕ_{max}. The calculated predictions are well fitted to the experimental data for various nanoclay and $CaCO_3$ contents.

Some evidences show that this model can be simplified and modified for application in the present ternary nanocomposite.

As seen in eqs. (38)–(40), A_f is a function of Poisson ratio of matrix (υ_m) and B_{f1} and B_{f2} are functions of both A_f and "E_f/E_m." The Young's modulus of nanoclay and $CaCO_3$ is much higher than the tensile modulus of matrix. Therefore, (E_f/E_m) is very high:

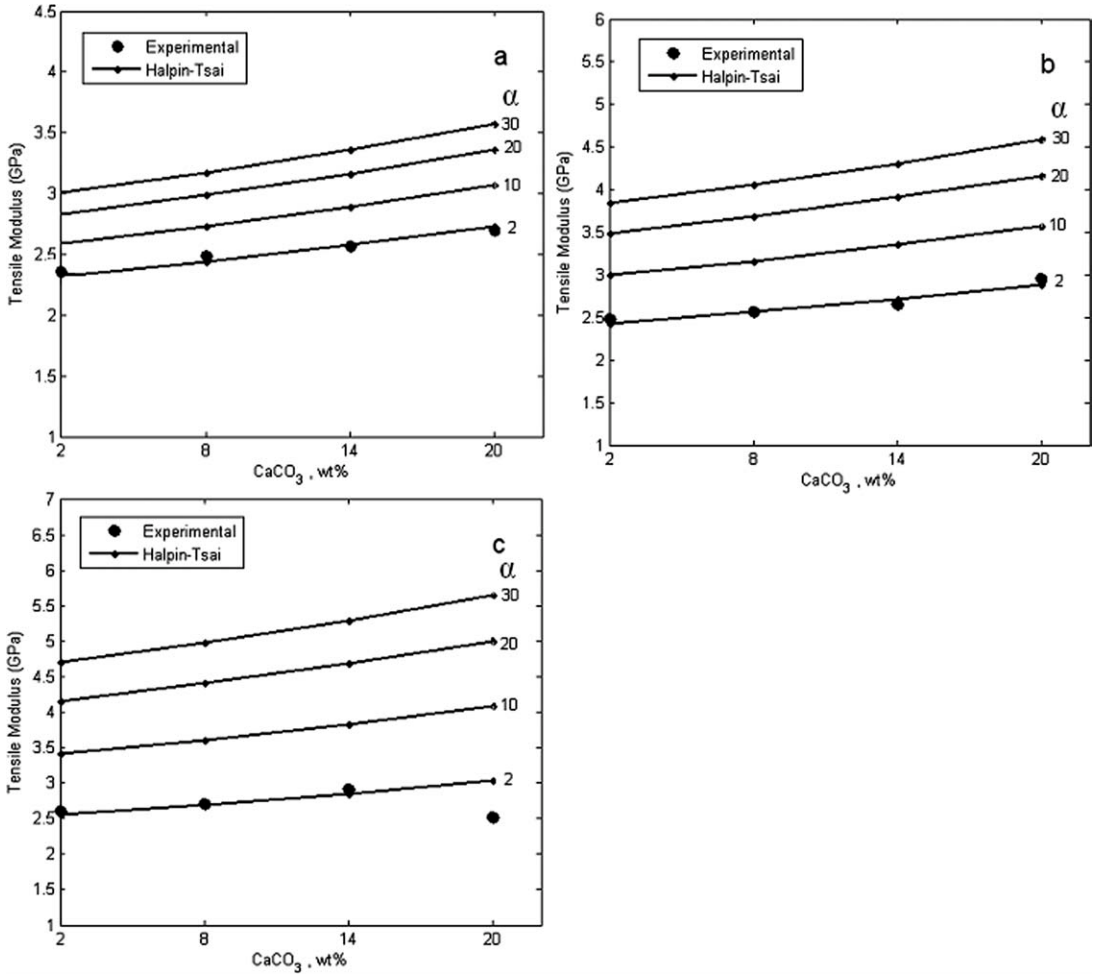

Figure 5 Experimental tensile modulus data and theoretical predictions by Halpin–Tsai in nanoclay contents of (a) 2 wt %, (b) 4 wt %, and (c) 6 wt %. α is the aspect ratio of nanoclay.

for nanoclay, $E_{f1}/E_m = 178/2 = 89$ and for $CaCO_3$, $E_{f2}/E_m = 26/2 = 13$. In addition, the Poisson ratio (υ_m) of polymers is in the range of 0.33–0.5. The influence of different Poisson ratio (υ_m) on A_f and then on B_{f1} and B_{f2} are shown in Table III. The variations of B_{f1} and B_{f2} are insignificant indicating that these variables can be eliminated from the Kerner–Nielsen model for ternary system.

Moreover, in eq. (41), the parameters ϕ_{max1} and ϕ_{max2} can get any values between 0 and 1. However, in the current ternary system, ϕ_{max1} and ϕ_{max2} in the range of 0 to 1 have a slight effect on the predicted results, as indicated before. The variations of P_f as defined in eq. (41) at different ϕ_{max1}, ϕ_{max2} and nanofiller contents are shown in Table IV. It is observed that the effects of ϕ_{max1} and ϕ_{max2} in the wide range (from 0.05 to 0.95) and also different nanofiller contents (2–6 wt % for nanoclay and 2–20 wt % for $CaCO_3$) on P_f are negligible. Therefore, ϕ_{max1}, ϕ_{max2} and P_f values do not influence the tensile modulus calculations by Kerner–Nielsen model that can be eliminated from eq. (37).

After assuming A_f, B_{f1}, B_{f2}, P_f as 1, the simplified Kerner–Nielsen model was fitted to the experimental results using trial and error method. The modified Kerner–Nielsen equation for predicting the tensile modulus of prepared ternary nanocomposite can be presented in eq. (42):

$$E = E_m \left[\frac{1 + 2(\phi_{f1} + \phi_{f2})}{1 - (\phi_{f1} + \phi_{f2})} \right] \tag{42}$$

The predictions of Modified Kerner–Nielsen are also observed in Figure 6. The suggested model has a significant fitness with the experimental results. As shown, the calculated data by Kerner–Nielsen and Modified Kerner–Nielsen models are similarly. The Modified Kerner–Nielsen can predict the tensile modulus of ternary nanocomposite using the volume fractions of nanofillers and the matrix modulus.

Development of Takayanagi model

Takayanagi model is a combination of parallel and series models.[46–48] The α and β equations have been

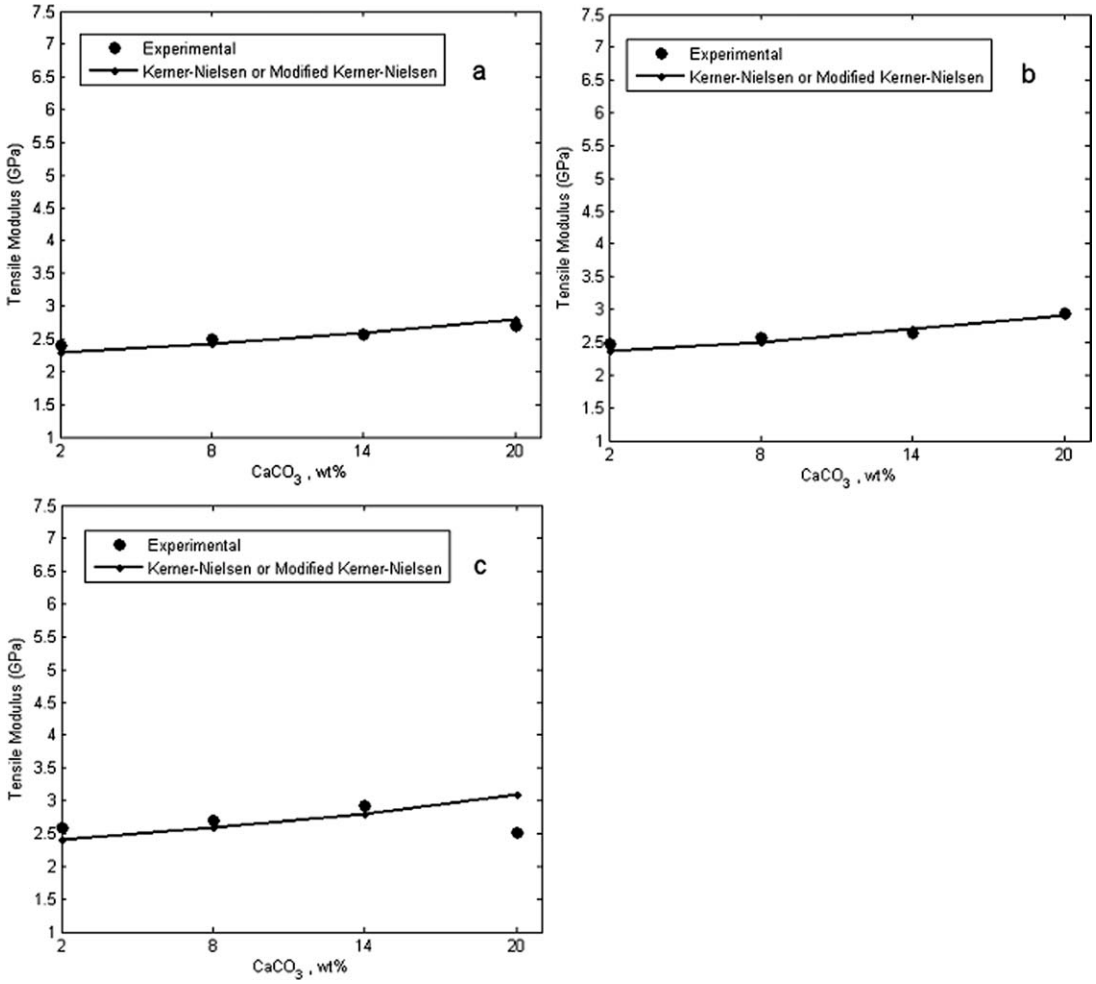

Figure 6 Experimental data and predicted tensile modulus by Kerner–Nielsen and modified Kerner–Nielsen models in nanoclay contents of (a) 2 wt %, (b) 4 wt %, and (c) 6 wt %.

suggested for spherically dispersed particles in the matrix,[46] but for different shapes of filler, such as nanoclay layers, no equation for α and β has been proposed. In the presence of two fillers, such as the present ternary system, Takayanagi model can be presented in Figure 1(b) and eq. (43). In this model, two nanofillers are considered as one-filler phase.

The developed α and β equations for the ternary system is shown in eqs. (44), (45). The calculated data by Takayanagi model is shown in Table V. The predicted data are too higher than the experimental results. So, this forms of α and β equations are not appropriate for the present ternary system. Therefore, mathematical operations (trial and error method) were applied to fit the experimental results to the Takayanagi model. The modified α and β (α_m and β_m) as functions of filler volume fractions for different shapes of fillers were suggested in eqs. (46), (47).

TABLE III
The Variation of A_f, B_{f_1}, and B_{f_2} for Different Poisson Ratio (υ_m)

υ_m	A_f	B_{f_1}	B_{f_2}
0.33	1.1383	0.9743	0.8370
0.4	1.2500	0.9730	0.8300
0.45	1.3571	0.9717	0.8233
0.5	1.5000	0.9701	0.8146

TABLE IV
The Variation of P_f in Different ϕ_{max} and Nanofiller Contents

Nanoclay wt %	$CaCO_3$ wt %	$\phi_{max\ 1}$	$\phi_{max\ 2}$	P_f
2	2	0.05	0.05	1.9999
2	2	0.05	0.95	1.9999
2	2	0.95	0.95	1.9999
2	20	0.05	0.05	1.9980
2	20	0.05	0.95	1.9980
2	20	0.95	0.95	1.9980
6	2	0.05	0.05	1.9996
6	2	0.05	0.95	1.9996
6	2	0.95	0.95	1.9996
6	20	0.05	0.05	1.9966
6	20	0.05	0.95	1.9966
6	20	0.95	0.95	1.9966

TABLE V
The Predicted Tensile Modulus Data by Takayanagi Model

Sample No.	Nanoclay wt %	$CaCO_3$ wt %	Tensile modulus (GPa)
1	2	2	300
2	2	8	231.2
3	2	14	189.9
4	2	20	162.6
5	4	2	261.1
6	4	8	208.8
7	4	14	175.6
8	4	20	152.9
9	6	2	232.1
10	6	8	191.2
11	6	14	164
12	6	20	144.8

$$E = \left[\frac{\alpha}{(1-\beta)E_m + \frac{1}{2}\beta(E_{f1}+E_{f2})} + \frac{1-\alpha}{\frac{1}{2}(E_{f1}+E_{f2})}\right]^{-1} \quad (43)$$

$$\alpha = 5(\phi_{f1}+\phi_{f2})/[2+3(\phi_{f1}+\phi_{f2})] \quad (44)$$

$$\beta = [2+3(\phi_{f1}+\phi_{f2})]/5 \quad (45)$$

$$\alpha_m = 90(\phi_{f1}+\phi_{f2})/[1+60(\phi_{f1}+\phi_{f2})] \quad (46)$$

$$\beta_m = [1+(\phi_{f1}+\phi_{f2})]/100 \quad (47)$$

Figure 7 illustrates the theoretical values of tensile modulus by the developed Takayanagi model. The presented model can predict the modulus much better than the initial Takayanagi model.

CONCLUSIONS

The tensile modulus of PP/nanoclay/$CaCO_3$ ternary nanocomposite was analyzed using different composite models developed for ternary system. Among the studied models, the rule of mixtures suggests the upper values of tensile modulus while the MROM equation under-predicts most. The aspect ratio of nanoclay does not affect the predicted tensile

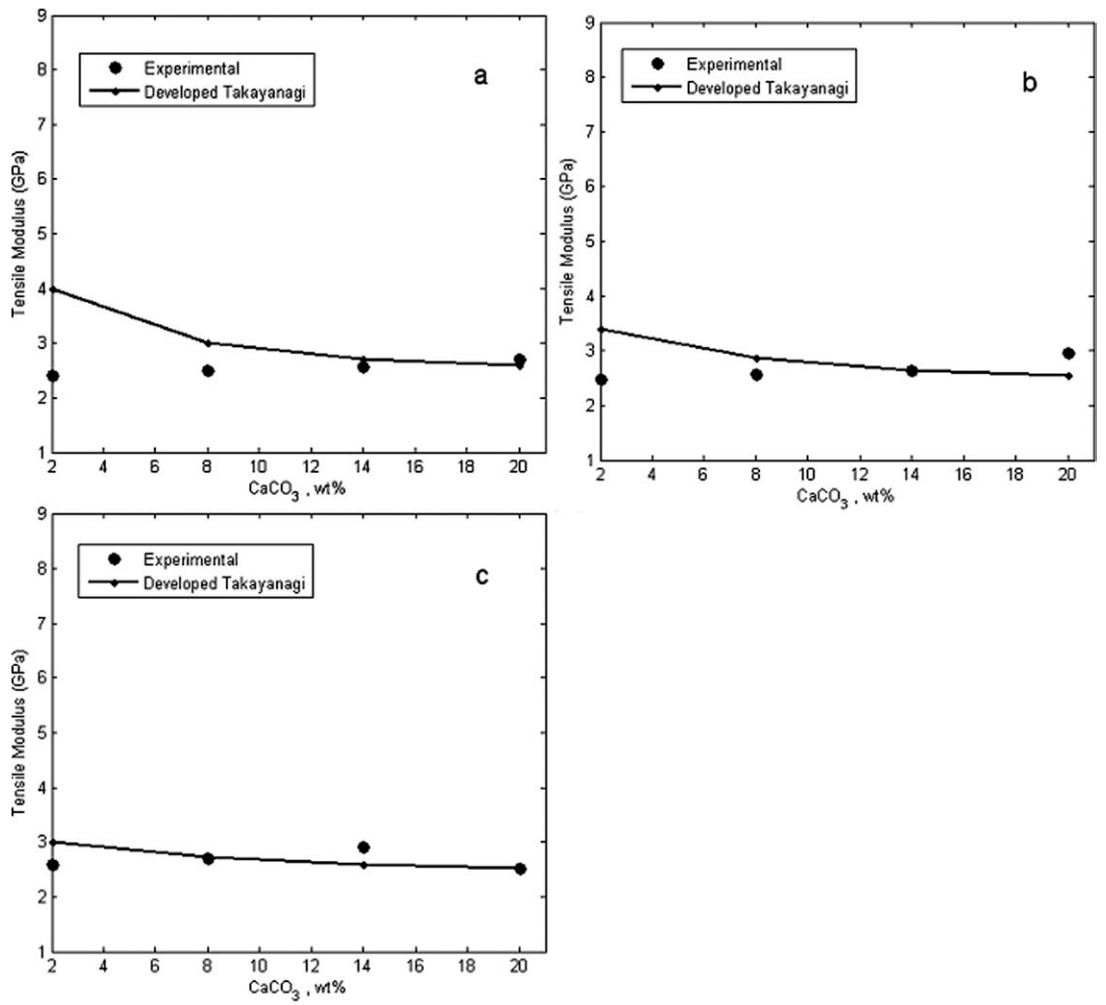

Figure 7 Experimental tensile modulus data and predicted values by developed Takayanagi model in nanoclay contents of (a) 2 wt %, (b) 4 wt %, and (c) 6 wt %.

modulus data in MROM model. The Hirsch model can predict the tensile modulus of the ternary nanocomposite at x value of 0.05. The theoretical predictions of Halpin–Tsai are fitted to the experimental results in very low aspect ratio ($\alpha = 2$). It may be suggested that $CaCO_3$ nanoparticles increase the shear stress in the melt mixing process of nanocomposite reducing the aspect ratio of nanoclay layers.

Additionally, Kerner–Nielsen model was modified to calculate the tensile modulus of PP/nanoclay/$CaCO_3$ ternary nanocomposite. The proposed Kerner–Nielsen equation can calculate the tensile modulus more accurately only by the volume fractions of nanofillers. Moreover, Takayanagi model was developed and the equations of α and β were suggested for various types of nanofillers to predict the tensile modulus of the present ternary system. The proposed Takayanagi model calculated the tensile modulus, successfully.

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