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COMPARISON OF THE ELASTIC MODULUS OF ELASTOMER CLAY NANOCOMPOSITES PREDICTED BY VARIOUS MECHANICAL MODELS

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Abstract—Nanoclays are considered as an ideal filler for polymer materials owing to their versatility, low cost, high aspect ratio, large surface area, cross-linking behavior and cation exchange capacity. When compared with conventional composites, clay/polymer nanocomposites exhibit enhanced diffusional barrier, fire retardant, ultraviolet resistant and mechanical properties. The elastic modulus reflects the ability of a material to resist elastic deformation and is thus an important parameter that characterizes the material mechanical properties. Its accurate prediction plays an important role in material design to tailor a material to suit a given application. A broad variety of analytical as well as numerical work has been performed to investigate the elastic modulus of clay reinforced polymer composites. The present paper carries out a review and comparison between various analytical models reported in the technical literature that take fundamentally different approaches for predicting the elastic modulus, namely, the Guth and modified Guth model, the Halpin-Tsai model and modified Halpin-Tsai model, the model by Ji et al., the Hui-Shia model, and the effective modulus model. Elastic modulus predictions from these models for clay/elastomer composites are contrasted and discussed taking into consideration experimental data from the technical literature.

Keywords-clay/elastomer nanocomposites, modulus of elasticity, analytical modeling

I. INTRODUCTION

Polymer materials are frequently used in technical applications owing to their ease of processing, lightweight, low cost, and easily tailorable properties. The latter can be achieved by addition of suitable fillers into the polymer matrix. Popular filler materials are synthetic or natural inorganic reinforcements that are defined as finely divided particles (micron-sized or nano sized). Typically, reinforcing a polymer aims not only at improving a singular material property but also to synergistically enhance or at least maintain other properties. Examples are improvements in diffusion barrier properties, thermo-mechanical behavior, resistance to flammability, electrical or electronic properties [1,2]. The reinforcing ability of a filler depends on the particle size, structure and surface characteristics. Smaller size fillers such as nano-sized fillers typically impart greater reinforcement effects to a polymer matrix than coarse ones (micro-sized fillers) [3]. Polymer composites reinforced with filler particles that have at least one dimension in the nanometer range are termed 'nano-composites'.

Out of the various available nanofillers, platelet-like particles like graphene, layered double hydroxides and especially clays have received considerable attention by material designers. Clay nanofillers are low-cost, environment friendly and possess high aspect ratio, large surface area and cation exchange capacity [4]. Polymer clay nanocomposites, when compared with their micro counterparts and pure polymer resins, were reported to exhibit increased mechanical and physical properties (e.g., fire retardancy, diffusional barrier and ultraviolet light resistance) [5]. Moreover, owing to higher crosslinking behavior of clay with certain polymers, Arroyo et al. [6] reported that only 10 parts per hundred (phr) of clay in polymer were sufficient to meet the reinforcing effects achieved by 40 phr of carbon black.

The first clay polymer nanocomposite was reported in 1965 by Blumstein [7], but it was actually the work reported in 1993 by the Toyota research group [8,9] that made way for further work in this field. Nanocomposite technology has been extended to multiple polymer systems including thermosets like epoxies and elastomers [10]–[14]. Elastomers, such as rubbers, are amorphous polymers that are highly elastic/viscoelastic in nature. They typically have limited thermal and mechanical properties, which may be improved by the addition of a clay nanofiller [15].

The goal of material design is to develop and tailor a material to obey the requirements for a given application. A basic requirement for a composite is to meet the mechanical demand, with elastic modulus being the most significant parameter besides strength. Research pertaining to a filler material's effect on the composite mechanical properties has to be carried out, e.g. [16], which can be achieved via tensile testing. However, due to the many available filler types with different morphologies, experimental means are cumbersome for material design purposes. Predicting the modulus of elasticity accurately via analytical models with low computational effort is most attractive for material design purposes.

In this paper, fundamentally different approaches for predicting the elastic modulus are considered. These models are: Guth model [17], modified Guth model [18], Halpin-Tsai model [19], [20], modified Halpin-Tsai model [21], [22] effective

modulus model [23], [24], Ji et al. model [25], and Hui-Shia model [26]. Some of these models are universally used for filler modified composites, including those reinforced by fiber-like or rod-like fillers [27]–[29]. Here, predictions were made for rubber/clay nanocomposites which are of great industrial importance [11]. The ability of these models to accurately predict the elastic moduli is evaluated by comparison with data for two different rubber/clay composites – nitrile butadiene rubber (NBR)-clay and carboxylated acrylonitrile butadiene rubber (CNBR)-clay, with the experimental data reported from the technical literature.

II. Theoretical Background

The considered modeling approaches are fundamentally different for predicting the elastic modulus of a composite. The Guth model and modified Guth model invoke Einstein's theory of viscosity for suspensions of colloidal particles in a continuous medium, in order to predict other properties for solid media. The notion is that colloidal particles perturb the medium leading to increased energy dissipation and therefore a change in the medium's properties. As such, the model is independent of the filler properties. The Guth model [17], proposed in 1938 for predicting the elastic modulus of a composite, E, is given by:

$$E = E_{\mathrm{m}}(1 + 2.5\emptyset + 14.1\emptyset^2) \tag{1}$$

where E_{m} is the elastic modulus of the matrix, and $\emptyset$ is the volume fraction of the filler particles. Guth ascertained good agreement of predictions for 'GR-S' rubber for $\emptyset < 0.1$.

Later, in 1945, Guth proposed the modified Guth model by considering that chains consisting of spherical fillers are similar to rod-like filler particles embedded in a continuous matrix [18]. The elastic modulus of the composite is given as:

$$E = E_{\mathrm{m}}\,[1 + 0.67\alpha\emptyset + 1.62(\alpha\emptyset)^2] \tag{2}$$

where α is the shape factor, which is the ratio of particle length to width. This model takes into account an accelerated stiffening mechanism of the composite with increasing filler loading.

In the year 1969, Halpin and Tsai proposed a semi-empirical model for predicting the elastic modulus of unidirectional composites as a function of aspect ratio and filler volume fraction. This model was later expanded for composites with discontinuous non-intercalated nanoparticle fillers of different geometries – rods, disks and spheres [27]. The tensile modulus of a composite, with parallel aligned short platelets, according to the Halpin-Tsai model (H-T model) is proposed as:

$$E = E_{\mathrm{m}}\left[\frac{(1 + \xi\eta\emptyset)}{(1 - \eta\emptyset)}\right] \tag{3}$$

where ξ is a reinforcing factor, which considers the shape efficiency of the fillers depending on the filler geometry, packing geometry and loading conditions. For rod-shaped particles (fibers), ξ is considered as $2(l/d)$, and for disk-like platelets as $2(l/t)$, whereby l, d and t are the length, diameter and thickness of the dispersed filler. In Eq.(3), η is a characteristic model parameter which depends on the degree of inhomogeneity and the filler shape, defined as follows:

$$\eta = \left[\frac{\left(\frac{E_{\mathrm{f}}}{E_{\mathrm{m}}} - 1\right)}{\left(\frac{E_{\mathrm{f}}}{E_{\mathrm{m}}} + \xi\right)}\right] \tag{4}$$

where E_{f} is the elastic modulus of the filler.

It is important to understand that the H-T model for high aspect ratio particles approaches to the well-known rule of mixture, i.e., the superior limit, whereas for diminishing aspect ratios (spherical filler particles) the model regresses to the inverse rule of mixture for a composite, i.e., the inferior limit.

The H-T model in Eq.(3) was further modified by Lewis and Nielsen [21], [22]. The modified H-T Model is represented as:

$$E = E_{\mathrm{m}}\left[\frac{(1 + \xi\eta\emptyset)}{(1 - \varphi\eta\emptyset)}\right] \tag{5}$$

$$\varphi = 1 + \emptyset\left[\frac{(1 - \emptyset_{\mathrm{m}})}{(\emptyset_{\mathrm{m}})^2}\right] \tag{6}$$

where φ is contingent on the maximum volumetric packing fraction of the filler, $\emptyset_{\mathrm{m}}$, which is the ratio of the true volume of the filler and the apparent volume occupied by the filler.

The effective modulus model assumes random filler dispersion and orientation in the matrix. Essentially based on laminate theory, the effective modulus can be computed for reinforced composite with fiber-like fillers and platelet fillers using Eqs.(7) and (8), respectively.

$$E^{\mathrm{Fiber}} = 0.184E_{\mathrm{L}} + 0.816E_{\mathrm{T}} \tag{7}$$

$$E^{\mathrm{Platelet}} = 0.49E_{\mathrm{L}} + 0.51E_{\mathrm{T}} \tag{8}$$

where E_{L} and E_{T} are the modulus of a composite in the direction parallel and perpendicular to the major axis of filler, respectively. E_{L} and E_{T} can be predicted by the Halpin-Tsai equations [30], [31]:

$$E_{\mathrm{L}} = E_{\mathrm{m}}\left(\frac{1 + \xi\eta_{\mathrm{L}}\emptyset}{1 - \eta_{\mathrm{L}}\emptyset}\right) \tag{9}$$

$$E_{\mathrm{T}} = E_{\mathrm{m}}\left(\frac{1 + 2\eta_{\mathrm{T}}\emptyset}{1 - \eta_{\mathrm{T}}\emptyset}\right) \tag{10}$$

$$\eta_{\mathrm{L}} = (E_{\mathrm{f}} / E_{\mathrm{m}} - 1) / (E_{\mathrm{f}} / E_{\mathrm{m}} + \xi) \tag{11}$$

$$\eta_{\mathrm{T}} = (E_{\mathrm{f}} / E_{\mathrm{m}} - 1) / (E_{\mathrm{f}} / E_{\mathrm{m}} + 2) \tag{12}$$

For evaluating the elastic modulus of nanocomposites with randomly dispersed fillers in a polymer matrix, Ji et al. developed a three-phase model based on Takayangi's two-phase model [32]. The model by Ji et al. is a combination of a parallel-series model that considers the contributions of matrix, filler and an interphase that sits adjacent to the matrix and filler. The interfacial contribution plays an important role in the stress-

transfer phenomenon. Assuming that platelet-like fillers are randomly oriented and distributed uniformly in the matrix, the resulting elastic modulus is given as:

$$\frac{E}{E_{\mathrm{m}}} = \left[(1-\alpha) + \frac{(\alpha-\beta)}{(1-\alpha)+\alpha(h-1)/\ln(h)} + \frac{(\beta)}{(1-\alpha)+\frac{(\alpha-\beta)(h+1)}{2}/(E_{\mathrm{f}}/E_{\mathrm{m}})\beta} \right]^{-1} \quad (13)$$

$$\alpha = \sqrt{[2(\tau/t)+1]\emptyset} \quad (14)$$

$$\beta = \sqrt{\emptyset} \quad (15)$$

where τ is the interphase thickness and h is the stiffness ratio (ratio of interphase modulus to that of matrix). Characterizing the stiffness ratio, h, is a difficult task, and thus $h = 12$ is assumed in the present study, similar to other work [25][33]–[35]. τ/t is obtained via curve fitting.

A closed form expression was proposed by Hui and Shia to predict the elastic modulus of composites comprising of unidirectional aligned platelets assuming perfect interfacial binding between the platelet shaped filler and the polymer matrix [26]. The elastic modulus prediction by the Hui-Shia model is given as:

$$\frac{E}{E_{\mathrm{m}}} = \frac{1}{1-\frac{\emptyset}{4}\left(\frac{1}{\xi}+\frac{3}{\xi+\Lambda}\right)} \quad (16)$$

$$\xi = \emptyset + \left(\frac{E_{\mathrm{m}}}{E_{\mathrm{f}}-E_{\mathrm{m}}}\right) + 3(1-\emptyset)\left[\frac{(1-g)\alpha^2 - g/2}{\alpha^2-1}\right] \quad (17)$$

$$g = \frac{\pi}{2}\alpha \quad (18)$$

$$\Lambda = (1-\emptyset)\left[\frac{3(\alpha^2+0.25)g - 2\alpha^2}{\alpha^2-1}\right] \quad (19)$$

where α is the inverse aspect ratio of the filler, i.e., $\alpha = t/l$.

III. EXPERIMENTAL

Experimental data for rubber clay nanocomposites were taken from the works by Wu and co-workers [11]–[14], [36]. To provide some context, a synopsis of the methods for preparing the rubber clay nanocomposites followed by the characterization techniques is given in this section.

A. Materials

Wu et al. [12], [14] used clay (Na+-montmorillonite) with cation exchange capacity of about 93 milliequivalent/100 g, and nitrile butadiene rubber (NBR) latex (solid content: 45%) [12] and carboxylated acrylonitrile butadiene (CNBR) latex (solid content: 40%) [14].

B. Preparation of rubber/clay nanocomposites

A latex compounding method [36] was used by Wu et al. [12], [14] for obtaining the rubber/clay nanocomposites. The rubber latex was mixed with a clay aqueous suspension (3% by weight). The mixture was stirred for 30 minutes at a stirring rate of 600 revolution per minute. Later, the mixture was coagulated in an electrolyte solution containing 1% by weight calcium chloride aqueous solution and then washed with water and dried in oven at 80°C for 18 hours. The vulcanizing chemicals and other additives were mixed into the nano-compound using a two-roll mill. Lastly, vulcanization was carried out in a standard mold. In this manner, two sets of rubber clay nanocomposites were made, NBR-clay nanocomposites and CNBR-clay nanocomposites.

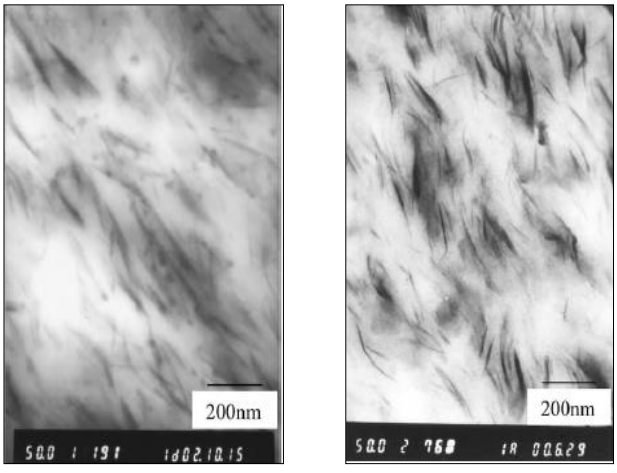
C. Characterisation techniques

Wu et al. determined the tensile modulus of rubber clay nanocomposite samples (80 mm x 10 mm x 2 mm and gauge length 50 mm) by clamping them vertically under tensile load [11]. In addition, transmission electron microscopy (TEM) images from ultrathin sections of rubber-clay nanocomposites were captured [13].

IV. RESULTS AND DISCUSSION

A. Characterization of clay filler composites

First, an understanding of the composite morphological is established from TEM images. Figure 1(a) and (b) depict micrographs containing 20 phr clay for NBR-clay and CNBR-clay nanocomposites, respectively, taken from the work of Wu et al. [13]. Dark lines represent sections of thin platelets of layered silica, and as reported by Wu et al. [11], the thickness of each clay layer bundle is between 4-10 nm. It can be observed that the rubber phase separates clay particles into either individual layers or silicate aggregates, indicating a partially exfoliated structure, which was described as a combination of an exfoliated and intercalated structure [13]. It appears that the silica layers have preferential orientation in the rubber matrix.



(a) (b)

Figure 1. TEM micrographs of (a) NBR-clay nanocomposite and (b) CNBR-clay nanocomposite [11].

B. Comparison of experimental data and theoretical models

The aspect ratio (α), as reported in [11], for the NR-clay nanocomposite is 27.0 and for CNBR-clay nanocomposite is 31.7. Further, the tensile modulus of clay platelets was taken as 170 GPa [11], [28], [37]. The elastic moduli for the NBR and CNBR matrix are 1.66 MPa [11], [38] and 2.12 MPa [11], [38], respectively. The experimental data for the elastic modulus varying with filler volume fractions was taken from [11]. The value of ϕ_m as proposed in [11] is 0.16 for the NBR-clay nanocomposite and 0.15 for the CNBR-clay nanocomposite.

Graphs containing experimental modulus data were plotted along with theoretical modulus values as a function of filler volume fraction, for the NBR-clay nanocomposite and CNBR-clay nanocomposite, as shown in Fig.2 and Fig.3, respectively. It is evident from the experimental data that the elastic moduli increase in a non-linear fashion with clay content. Notably, trends and congruence of the predictions with the experimental data vary substantially for the various models as well as with respect to the range of filler loading. None of the models predicts the experimental data accurately over the full range of filler loadings. More detailed observations for the various models are given in the following.

Guth model: This model deviates significantly from the experimental data. Difference in the predictions with respect to the experimental data may be due to the particle morphology, e.g., the aspect ratio of the nanoclay layers, which is not considered in this model. In addition, model assumptions may be inappropriate, such as a uniform participle dispersion and complete bonding between particles and matrix. Moreover, a major assumption of the Guth model is that filler particles are sufficiently rigid, such that their elastic modulus is much larger than that of the matrix ($E_{filler}/E_m >> 1$), with the result that the matrix is sustaining the bulk of elastic deformation [39]. But this may not be the case with the clay particles, which are flexible and bendable and thus tend to store a certain amount of deformation energy [28]. Consequently, the filler's contribution to storing deformation energy may be considerable, thus invalidating the assumptions made for Guth model. Considering that the Guth model has been shown to closely predict the modulus for elastomers containing small amounts of spherical carbon black [40], the observed poor fit for clay particles is seen to stem from an incompatible filler morphology.

Modified Guth model: This model describes a progressive increasing on modulus similar to the experimental data, yet it tends to significantly overestimate the rubber clay nanocomposite modulus. Similar results have been seen in [28], [29], [41]. The modified Guth model assumes filler particles to be randomly orientated in the nanocomposite matrix. As exhibited by the TEM images in Figure 1, fillers are not arranged randomly and possess a certain level of alignment, which may explain the model's failure to closely predict the experimental data. Notably, in the work done by Praveen et al. [28], it was reported that the modulus values produced by the modified Guth model for SBR-clay nanocomposite are in good agreement for highly exfoliated or highly aggregated composite morphologies whereas the model diverged for intercalated structures of the filler. Hence, large deviations of the predicted values from the experimental values observed in the present study may also stem from an intercalated composite, i.e., non-exfoliated, and non-aggregated structure of the clay fillers, as indicated by the TEM micrograph observations in Figure 1.

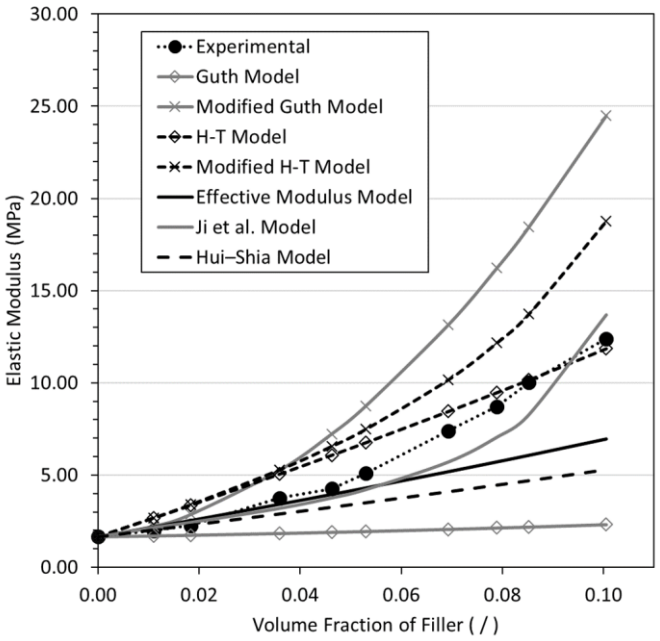


Figure 2. Comparison of elastic modulus values between experimental results and theoretical predictions offered byvarious models for NBR-clay nanocomposite.

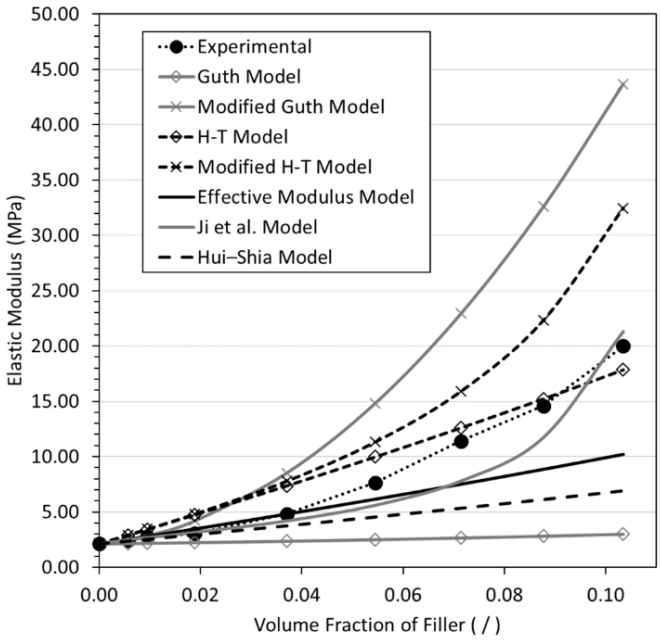


Figure 3. Comparison of elastic modulus values between experimental results and theoretical predictions offered by various models for CNBR-clay nanocomposite.

Halpin-Tsai model: The H-T model is one of the most widely used models in the context of modulus predictions, owing to its typical good agreement with experimental data over a range of filler volume fractions, which has been shown by various studies in the technical literature [37], [42], [51], [52], [43]–[50]. As mentioned earlier, the H-T model assumes a composite system in which the filler reinforcements are fully dispersed and aligned in the loading direction, with perfect interfacial adhesion to the matrix. In the present study, predictions are below the experimental values up to about 9 vol.% of nanoclay, at which point a crossover between the predicted and experimental curves occurs for both material systems. A possible reason for the underprediction up to the crossover point may be the presence of filler aggregations or clusters (as seen in the TEM micrographs in Figure 1) and/or due to imperfect adhesion between filler and matrix. It should be noted that an increase in rubber crystallinity induced by the addition of nanoclay fillers may also lead to an increase in composite modulus [47]. Beyond the crossover point, the H-T model overpredicts the composite modulus. This divergence may be due to the formation of larger nanoclay agglomerations, which effectively create larger size reinforcements. This would impart a decrease in filler-matrix surface area and lead to the reduction of the elastic modulus. Moreover, deviations of predictions from the experimental data may be due to the H-T model's assumption that fillers are straight and similar in length with uniform stress transfer along their length. However, the clay particles exhibit a certain amount of curvature, and hence, the high modulus predicted by the model does not translate into the actual materials [48]–[50].

Modified Halpin-Tsai model: This model produces interesting results wherein the trend of predicted curves is qualitatively similar to the experimental data, yet it overpredicts the experimental results to a significant extent. The modified H-T model is dependent on the maximum volume fraction of the filler, $\emptyset_m$, which is the ratio of true filler volume fraction and apparent volume occupied by the filler, as explained in Section II. The model assumes that the apparent volume of the filler is linked with the dispersion of the filler, with large apparent values indicating better filler dispersion. Since in the present study, the predicted values are similar in trend to the experimental results for all volume fractions, a possible conclusion is that there is adequate dispersion of the reinforcement phase in the nanocomposite. The reasons for moduli being overpredicted with respect to the experimental data may be due to other factors, such as the model's inability to consider the true morphology of the reinforcement phase.

Effective modulus model: For both the NBR and CNBR nanocomposites, the effective modulus model yields reasonable predictions of the experimental data up to about 5 vol.% nanoclay loading. For higher filler loadings, the model underpredicts the experimental data, for the following possible reasons. As shown in the TEM images in Figure 1 the nanoclay fillers may have a prevailing alignment inside the NBR and CNBR nanocomposites. This is in contrast to the assumption of the model of randomly orientated fillers in the matrix. Also, since this model and its parameters are defined indiscriminately of filler size, it is unclear if the model adequately considers nano-size effect of the filler in the matrix, for instance, the enhancement of mechanical properties due to the large surface areas generated by nano-fillers [53].

Ji et al. model: This semi-empirical model (based on a curve fitting method) considers the presence of an interphase between matrix and filler particles. The Ji et al. model assumes full exfoliation, uniform dispersion and random orientation of isotropic clay fillers with no filler interactions [36][33]. The three fitting parameters for the Ji et al. model are the thickness of the filler (t_c), the thickness of the interface (τ) and the stiffness ratio (h). This model has been found to be one of the most versatile models for predicting the elastic modulus of nanocomposites [33], [35], [54]. Interestingly, compared to the other models, the Jie et al. model remained reasonably close to the experimental data for large parts of considered filler loading range, presumably due to the parameters adjustment to fit the experimental data. The largest difference to the experimental values is 32% at 7 vol% filler loading. Nevertheless, this model still does not predict the experimental data comprehensively, which may be due to one or more of the following aspects. The model does not differentiate between two-dimensional and three-dimensional reinforcements [54]; Imperfect bonding that may be present between matrix and nanofillers is not considered; the nanoclay filler morphology is not explicitly reflected [55]; and most importantly, Ji et al. [36] did not present a particular process for determining the values of the fitting parameters.

Hui-Shia model: Finally, predictions from the Hui-Shia model only agree reasonably with the experimental data for low filler loadings (about 2 vol.%) for the NBR and CNBR nanocomposites. Notably, the model fails to capture the non-linear rise of the elastic modulus with increasing filler loading. This is congruent with other works [41], [56]. The reason for this behavior may be attributed to greater interaction between the matrix and the nanoclay at lower filler loading whereas nanoclay agglomerations increase at higher filler loadings, causing reduced adhesion between the matrix and the nanoclay [41]. Moreover, the Hui-Shia model assumes the filler particles to be aligned, however, while some alignment effects may be present as per the TEM images in Figure 1, the actual composite morphology may not sufficiently support this assumption.

V. CONCLUSIONS

In the present study a comparison between various analytical models for the elastic modulus prediction of filler modified polymer composites was performed, including the Guth and modified Guth model, the Halpin-Tsai model and modified Halpin-Tsai model, the effective modulus model, the model by Ji et al., and the Hui-Shia model. Elastic modulus predictions from these models for nanoclay/rubber composites were contrasted and discussed in light of experimental data obtained from the technical literature.

None of the models investigated in this study was able to predict the experimental data accurately over the full range of considered filler loadings (up to 10 vol%). While the experimental data exhibits a progressive increase in modulus with rising filler loading, only some of the models reflect this trend appropriately, namely the modified Guth model, the modified Halpin-Tsai model, and the model by Ji et al. While

the latter model was found to offer the closest prediction of the experimental data, the largest deviation was still over 30%.

The reason for the generally poor fit of model predictions to the experimental results is seen to lie primarily in the difficulty of capturing the complex morphology that is inherent to platelet-type filler modified polymer composites. Characteristics such filler intercalation, agglomeration, matrix adhesion, alignment, waviness and orientation, to name a few, play an important role for the actual reinforcement effect, which is further complicated by changes to these characteristics with rising filler loading. Consequently, it appears inevitable for a particular composite to be comprehensively characterized through experiments, and model parameters be carefully determined, in order to achieve accurate and reliable modulus predictions. In the context of material design where extensive experimental work is onerous given the many possible material configurations, these present findings motivate further research to produce alternative modeling approaches, for example, high-fidelity numerical modeling based on finite element analysis. The latter may be computationally expensive, but on the other hand, may yield comprehensive modeling solutions that become more accessible with ever increasing computational capacity.

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