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An Improved Model for Estimation of Mechanical Properties of Polymer-Clay Nano-Composites

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Abstract

Polymer-clay nanocomposites are more popular in many industries and applications due to improved mechanical and gas barrier properties over pure polymers and classical polymer-based composites. The mechanism by which clay platelets, with thicknesses in the nanometer range, as opposed to the hundred-nanometer range in the other two dimensions, introduce the mechanical and other properties improvement can be attributed to their high efficiency in creating discontinuities to flows through the bulk matrix polymer material. However, the extent of this improvement depends on the success of separation or achieving full exfoliation of the clay platelets through the bulk matrix. Since such full exfoliation is not achievable experimentally, the aspect ratio of the filler particles is not a simple value that mathematical models employ to describe mechanical properties. In this work, a modification is proposed to improve such models by using relationships utilizing different concentrations of varying filler platelets thicknesses. The improvements in elastic tensile modulus are discussed with consideration of the effect of clay platelet inclusions geometry as depicted through the proposed modification to considered models to capture the effect of nano-platelets on the properties of the composite.

Keywords: polymer-clay composites, polymer nanocomposites, mechanical properties. nano-clay platelets, polymer processing, elastic modulus, aspect ratio

1. Introduction

Polymer-clay nanocomposites represent a new emerging class of materials that is gaining wider applications due to the improved properties and advantages they have over pure polymers and classical polymer-based composites. Polymers in general have good electrical and thermal resistance in addition to low weight and ease of fabrication. Nevertheless, they have poor mechanical properties in terms of low modulus and strength, and also noticeable permeability to fluids. That is why polymer-based composites are used to improve mechanical properties. But conventional polymer-based composites still face challenge in some applications since the improvement in mechanical properties is dependent on the volume fraction of the filler constituent, whether a particle or fiber; since the addition of the filler will notably decrease the ductility and elongation. At a high level of volume fractions, which is needed to attain the improved mechanical properties, the loss in ductility and other favorable properties outweighs the improvement in the strength. Using nanofillers to produce polymer-based nanocomposites offers better strength and gas barrier properties at very low volume fraction of the nanofiller, thereby reducing unfavorable degradation of other properties.

Development of polymer-based composites aims to overcome the relatively low tensile properties of polymers in order to use them in high-strength requirement environments, in which metals are traditionally used. Polymer-based composites used in these applications are usually plastic resins reinforced with continuous fibers; using particular manufacturing processes to maximize properties in fibers direction. While pristine polymers are processed by conventional methods such as extrusion and molding techniques, the fiber-based composite are not suitable for such processing methods. Therefore, their applications remained limited (Pinnavaia & Beall, 2000). As an alternative approach, short-ligament based composites were introduced so that techniques like injection-molding can be used to produce them in various forms in mass production operations. The same is true for polymer composites with platelets or particles such as mica and clay. With high ratio of surface area to volume, mechanical properties are noticeably improved. However, other properties like ductility and impact strength, are compromised (Gianellis, 1996; Lichtenhan, Otonari, & Carr, 1995).

The effect of size reduction of the fillers from the micrometer range to the nanometer range can produce the anticipated strength improvements at much lower volume content of the composite. This means that the effect on other properties will be minimized. Other advantages include improvements in chemical and physical properties like diffusion of gases (sometimes referred to as permeability), water adsorption, and heat-distortion temperature (Gianellis, 1996). This is due to the fact that once we have a larger exposed surface area (in the nano-composite) for interaction between the filler particles and the matrix (as opposed to the micro-composite) for the same volume content, more favorable interactions will occur between the two.

Polymer-clay nanocomposites (PCNC) may be produced by a chemical process which uses an aqueous solution for polymerization. They may also be produced by physical mixture using melt intercalation, in which clay platelets with nano-size thickness are introduced in a polymer matrix and a blending process occurs for the melting polymer. This process utilizes a double-extruder which is commonly used plastics industry.

Nanocomposite materials are distinguished from conventional composites when the filler phase has one or more of the dimensions of its particles in the order of magnitude of nanometer ($=10^{-9}$m). For a single nano-range dimension with the other two in the micro-range, the filler shape is like a sheet or a platelet, and the composite is usually referred to as polymer-layered nanocomposites. Polymer-clay nanocomposites (PCNC), which belong to this class, are polymer composites with nano-size clay and layered silicates particles as the filler. They have wide interest for research, as clay is abundantly available and the relevant chemistry is well understood. Improvements in the performance of these composites include modulus and strength enhancements, in addition to other properties such as better diffusivity and decreased flammability (Utracki & Kamal, 2002). Table 1 shows classification of polymer nanocomposites according to geometrical shape of the filler phase, the characteristic dimension and the ratio of surface area to volume for each class.

Table 1. Some Aspects of Nanocomposites

Dimensions at nanoscale	Shape	Characteristic dimensions	Type	Surface area to volume [m^{-1}]
Three	Spherical	Radius (r)	Iso-dimensional particles	3/r
Two	Cylindrical	Radius (r), Length (l)	Nanofibers or whiskers: continuous	2/r
			Nanofibers or whiskers: short l ~ 10 r	4.2/r
One	Plate	Thickness (t)	Sheet-shaped filler	2/t

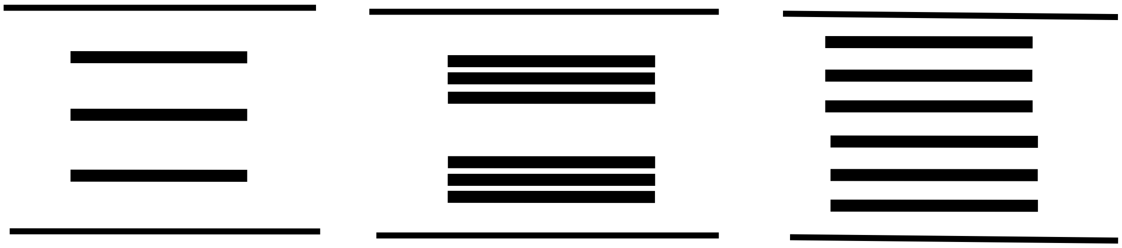
When the clay platelets disperse (with ideal exfoliation) within the polymer medium, and single silicate layers (of nano size thickness) interact with the surrounding matrix, the rheological and phenomenological behavior of the material changes even at very low volume fractions, which are too small to cause any effect through the traditional composite law, since the filler portion is too low to bear any loading as part of the composite. Superior mechanical properties for polymer-based composites with nano-clay platelets were reported for various polymers. For example, polyamides had a 14% improvement in tensile strength and 26% in flexural strength and modulus for PA-6 based PCNC with 2% of Organoclay (Bharadwaj, 2001). For polypropylene, an improvement of up to of up to 30% in tensile modulus but without significant change in tensile stress was reported (Pinnavaia & Beall, 2000; Utracki & Kamal, 2002; Xu, Zheng, Song & Shangguan, 2004). A strong improvement in tensile stress was found for polystyrene, with almost double the value (Utracki & Kamal, 2002) for good intercalation of nanofillers. Also, good improvements in tensile strength and modulus were reported for Nylon-6, with 50% improvement and double values, respectively (Gianellis, 1996; Utracki & Kamal, 2002). Apart from some compromise in elongation other properties were also improved in the clay-filler nanocomposite. Table 2 shows samples of some common thermoplastic-clay nanocomposites with relative improvements in selected mechanical properties, as per literature.

Table 2. Some examples of mechanical properties improvements in nanocomposites

Composite	**E**	**S_y**	**S_u**	**K_{IC}***	**E_S****
PP, MMT clay 4, 8%	54%	15%			50%
Nylon 6; S-clay MMT, 7%	100%				
Polyamid-6; Nanomer I.30TC 10%	100%	12%		80%	
Naylon 6, clay 2% by in-situ polymerization;		-22%			
PP, clay 3% by melt processing			90%		

* *Fracture toughness,* ***Storage Modulus.*

In this work, we consider the role of geometry of clay platelets in improving mechanical properties of polymer-clay nanocomposites. The mathematical models developed to characterize tensile modulus of a composite with features representing the PCNC are considered. These models, like the Halpin and Tsai theory and the Mori–Tanaka Average Stress Theory, use property values like aspect ratio to account for the distinct geometrical effect. The aspect ratio is a function of the geometry of the filler, and is determined by dividing the long dimension on the short one. Since these models assume consistency of geometry of the filler, the ratio is assigned a single value, and a representative volume element (or unit) is assumed (RVE). However, it is very well known that in actual preparation of polymer clay nanocomposites, such uniformity of filler particles within the polymer matrix is far from the truth. Moreover, the desired result of full dispersion of single clay-layer platelets in the surrounding medium is not usually achieved when preparing these composites. Usually, there are three possibilities: full dispersion (single-layer platelets), stacking of platelets, or partial separation which is called intercalation. These are depicted schematically in Figure 1. One approach is to use an average value of for the aspect ratio of these particles. While this may sound reasonable, it effectively nullifies the strengthening effect of the filler as it overlooks the superior performance of the fully exfoliated particles which constitute a certain portion of the total volume fraction of the filler.



(a) Exfoliated (b) Stacked (c) Intercalated

Figure 1. Three idealized distinct shapes of clay platelets dispersion within polymer matrix

The attempt is made here to overcome this approximation by introducing a simple modification whereby the contribution of each type of particle based on geometry is accounted for and the resultant is obtained by superposition of all contributions. The models for averaging the tensile modulus for composite are first discussed. Then, a proposed modification to the averaging approach is introduced for cases of single occurrence of phase shapes, and for multiple occurrences of phase shapes. After that, the models are applied for various cases of filler volume fraction and different geometries as defined by aspect ratio, and the results are presented.

2. Models for Mechanical Behavior of Polymer-Clay Nanocomposites

The traditional approach to identify mechanical properties of composite materials is based on properties of the pristine components and the morphology of the composite. This approach assumes independence of properties between the matrix and the filler in shaping the final composite properties. Theories for prediction of composite performance provide measures for contribution of different variables like the elastic modulus and volume fraction of both components. Also, the aspect ratio of the strengthening filler and its effect on the overall anisotropy due to orientation if it is not symmetric. The approach used here will derive from previous work on gas barrier properties (Al-Abduljabbar, 2014; Al-Abduljabbar, 2017). To this end, we will confine analysis to the tensile modulus, although the concept can be extended to other properties.

For the case of polymers enhanced with clay nanoplatelets, the aspect ratio is a very important factor especially when high levels of exfoliation are attained. Halpin-Tsai theory for stiffness of unidirectional composites highlights the importance of aspect ratio (Fornes, 2003), and provides a good model to depict the modulus estimation for PCNC. It presents a simplified analytic expression for the tensile modulus that can be used for different geometries of the added phase. The normalized elastic modulus of the composite is given by

$$\underline{E} = \frac{1 + \zeta\eta\phi_f}{1 - \eta\phi_f}, \tag{1}$$

where $\underline{E}$ is the composite normalized elastic modulus $\underline{E} = E/E_m$, E is the elastic modulus of the composite, E_m is the elastic modulus of the matrix, and ζ is a geometry-dependent shape factor, ϕ_f is the volume fraction of filler. The parameter η is dependent on the properties of the two phases and the geometry:

$$\eta = \frac{\frac{E_f}{E_m} - 1}{\frac{E_f}{E_m} + \zeta}, \tag{2}$$

where the subscripts f and m refer to the filler and matrix, respectively. For a filler of length a and thickness b, a suggested value for $\zeta = 2(a/b)$ for the longitudinal modulus E_{11} based on numerical solutions of Ashton, Halpin & Petit (1969), which highlights dependence on aspect ratio. On the other hand, the transverse modulus E_{22} is independent from the aspect ratio with an approximate value of $\zeta = 2$. For short cylindrical fibers and rectangular platelets, the reported values of the shape factor were $\zeta = (l/t)$ and $\zeta = (w/t)$ for elastic moduli E_{11} and E_{22}, respectively. The dimensions $l, w\ and\ t$ are the length, width and thickness of the platelet, respectively. The Halpin-Tsai relations will reduce to either two extreme simplified cases of rule of mixtures on inverse rule of mixtures for the extreme limits of $\zeta \to \infty$ and $\zeta \to 0$, respectively as follows:

$$\frac{1}{E} = \frac{\phi_f}{E_f} + \frac{(1 - \phi_f)}{E_m}, \tag{3}$$

$$E = E_f\phi_f + (1 - \phi_f)E_m. \tag{4}$$

The numerator of last term in Equation 3 and coefficient of E_m in Equation 4 are essentially ϕ_m, since $\phi_f + \phi_m = 1$. The Halpin-Tsai theory and other models like the Mori-Tanaka theory, model the behavior by using a single specific value for different properties values like the aspect ratio used in Equation 1. For disk-shaped platelets, it is represented as (d/t) where d is the diameter of the disk and t is the thickness; and for rectangular platelets it is represented as (l/t) where l is the length of the platelet. This use of one representative value is usually employed to facilitate the use of such relations although it is well known that the aspect ratio is dependent on the extent of exfoliation of clay platelets in the surrounding polymer medium. However, the determination of extent of such exfoliation is important to assign realistic values. As shown by Fornes (2003), this process is very involved and requires complex set of experimental and measurement techniques. Moreover, the process of exfoliation is not consistent or uniform. So, in actuality, a range of aspect ratios of different thicknesses exists within the polymer nano-clay composite, as the clay platelets disperse within the pristine polymer.

When dealing with this challenge, one approach is to employ an averaging process by considering the clay particles and deciding the number of platelets in each particle. In the above-mentioned thorough study of Fornes, a reliable value of 1.47 layers of clay was found. However, such approximation does not reflect the actual behavior of the composite. Single-platelet particles will definitely have different aspect ratios. One of the most important features that account for contribution of the filler to the strength of the composite is the large contact area between the surface of the platelet and the matrix. For example, if there are five particles fully exfoliated with single platelets, they will occupy a volume less than a particle with five stacked or intercalated platelets. That also means an aspect ratio of around five times than in the second case. Moreover, in the first case, the interface surfaces will be five times more. Both factors will greatly affect the bonding and interaction between the matrix and fillers, and subsequently the tensile properties. Therefore, there is a need to provide better approximation of the contribution of the filler platelets to the overall tensile behavior of the composite. This is the focus of the next section.

3. A Modified Model to Account for Varying Platelet Thickness

The basic model to capture the tensile properties of PCNC assumes that the particles of the filler phase have ideally uniform thickness. In this case, a single layer of clay platelet is the unit considered for the model, indicating full exfoliation (dispersion) of the clay nanoparticles platelets within the surrounding polymer. It is well established from experimental studies that full exfoliation is not possible and only partial dispersion is present resulting in a mixed state of exfoliation and intercalation is present. Therefore, a better representation of the material is to include both phases the single-layer platelets (exfoliation) and multi-layer platelets (intercalation) in the model used to represent the composite behavior. As indicated in the previous section, models based on averaging the thicknesses do not necessarily capture the essence of the behavior. In order to achieve this goal, we introduce a modification to the models to include a multi-phase system of fillers, each of which has a distinct thickness, and all of them contribute to the overall mechanical properties of the composite, each one based on its relative volume fraction. The overall performance is obtained using the principle of superposition. As mentioned earlier, the analysis will be built for the elastic modulus.

We first consider the simplest case of a composite consisting of a polymer matrix with the filler particles composed of the three distinct possibilities of particle formation as shown in Figure 1. In this case, the thickness of the particles in the exfoliated case (Figure1-a) is constant because it represents the thickness platelet. It is further assumed that the particles in (Figure1-b) and (Figure1-c) have uniform thickness. So, the filler will be composed of a number of particles consisting of: (a) single platelets, which will be denoted n_a; (b) a number of particles consisting of sets of stacked platelets which will be denoted n_b; and (c) a number of particles consisting of sets of intercalated platelets which will be denoted n_c. The volume fraction of each type, and eventually of the whole filler, will depend on the thickness of particles in each type. The total volume fraction of the filler (φ_f) is determined as the sum of the volume fraction of the three types, as follows.

$$\varphi_f = \varphi_{fa} + \varphi_{fb} + \varphi_{fc}. \tag{5}$$

Then, the expression for the elastic modulus of the composite, which is obtained using the upper bound for the rule of mixture relationship given by Equation 4, can be generalized to include fillers of different geometries, as follows

$$E = E_{fa}\phi_{fa} + E_{fb}\phi_{fb} + E_{fc}\phi_{fc} + (1 - \phi_f)E_m. \tag{6}$$

In the general case, it is most expected that there will be particles from type (b) which represent stacked platelets and type (c) which represent intercalated platelets. Such particles will have varying number of platelets, or different thicknesses. Therefore, the relationship representing the total filler volume fraction given by Equation 5 has to be generalized as follows:

$$\varphi_f = \varphi_{fa} + \sum\varphi_{fbi} + \sum\varphi_{fcj}, \qquad i = 1 \dots m,\ j = 1 \dots l, \tag{7}$$

where m and l represent the total number of platelets in particles of types (b) and (c) respectively, and φ_{fbi} and φ_{fcj} denote the volume fractions for of these platelets in the two types. Analogously, using the same approach, the expression for the elastic modulus of the composite using the rule of mixture can be generalized to include multiple fillers of different geometries:

$$E = E_{fa}\phi_{fa} + \sum E_{fbi}\varphi_{fbi} + \sum E_{fcj}\varphi_{fcj} + (1 - \phi_f)E_m, \tag{8}$$

where E_{fbi} and E_{fci} denote the elastic moduli of different platelets in particles of types (b) and (c) respectively.

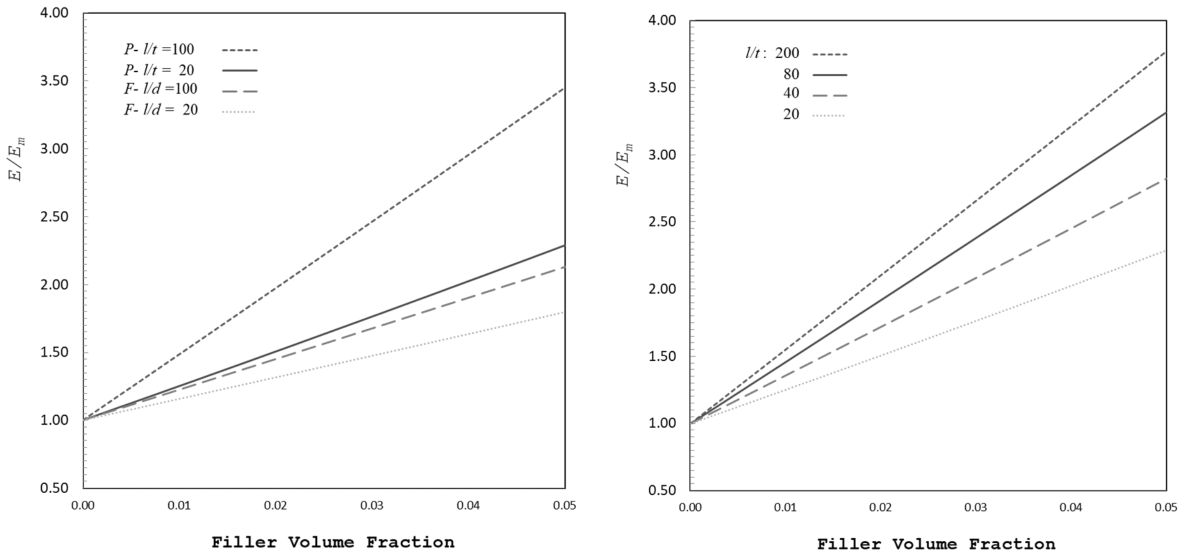
4. Results

In this section we consider the application of the proposed modification on the model which was introduced in the previous section on different cases. For the scope of this work, only the simple case of consistent thickness of each type of the fillers is assumed. This case is represented by Equations 5 and 6. Although this case is an idealization, it captures the trend of the functions proposed. Moreover, the exhaustive experimental work of Fornes (2003) showed that such case covers most of the distribution of fillers in the matrix. We write Equation 6 in a normalized form by dividing it over E_m:

$$\underline{E} = \underline{E}_{fa}\phi_{fa} + \underline{E}_{fb}\phi_{fb} + \underline{E}_{fc}\phi_{fc} + (1 - \phi_f), \tag{9}$$

where $\underline{E} = E/E_m$ and $\underline{E}_{fi} = E_{fi}/E_m$, for $i = a, b$ and c.

The values for the elastic modulus for composites with different filler concentrations, types and aspect ratios are investigated according to the relationships developed based on the approach discussed earlier, to explore the effects of different factors affecting tensile properties of the nano-composite. The composite elastic modulus dependence on the volume fraction for two reference cases are presented in Figure 2. As illustrated in the works reviewed in the introduction, and summarized in Table 2, the effect of nanofillers are very noticeable at very low concentrations. Accordingly, the figures of the dependence of the elastic modulus on the filler content are plotted for values up to 5% volume fraction.

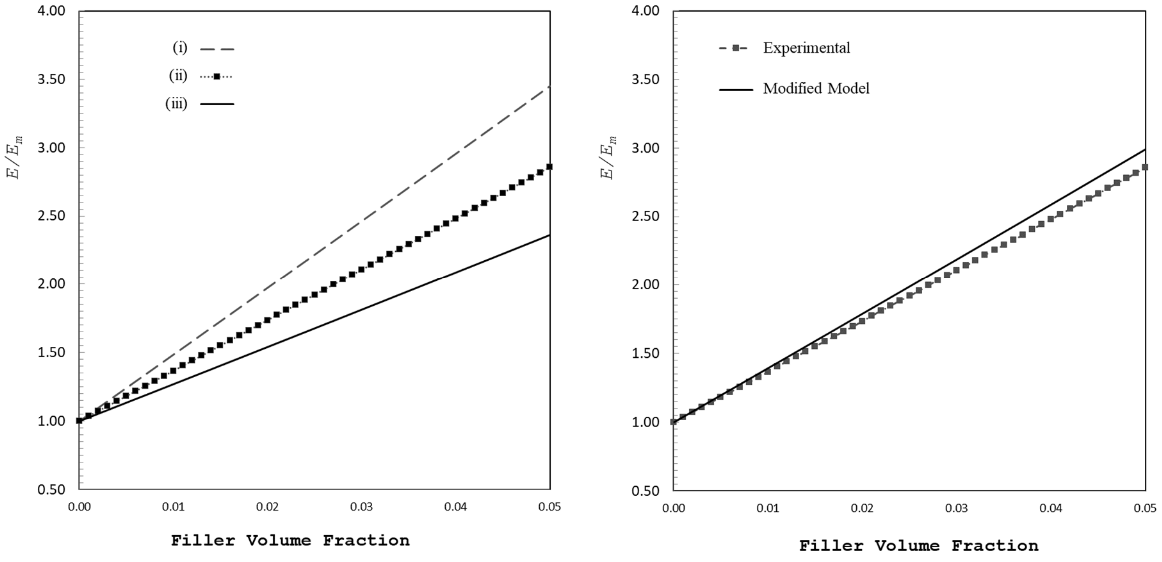


(a) (b)

Figure 2. Plots of the elastic modulus for the two cases as a function of clay volume fraction for different values of aspect ratios

The first graph (a) shows the results for two types of nanocomposites, mainly glass-fiber reinforced type, and clay nanoplatelets. They are plotted for two different values of aspect ratios of the filler nanoparticles as shown in the Figure 2-(a). The figure shows plots of the elastic modulus for the two cases as a function of clay volume fraction for different values of aspect ratios (for the clay platelets *l/t* = 100 and 20; and for the glass fibers *l/d* = 100 and 20, where *d* is the fiber diameter). The graphs confirm results obtained by Fornes (2003). Figure 2-(b), depicts the plots of elastic modulus perfectly exfoliated platelets for gradually increasing aspect ratios with values: 20, 40, 80 and 200. The aim is to span the usual range of used aspect ratios. It is evident that as the aspect ratio increases the rate of change (the slope) of the normalized elastic modulus decreases.

Figure 3 shows the results of using the model, compared with the experimental results from the work of Fornes (2003). In Figure 3-(a), the first curve, (i), is for the perfect case of aspect ratio of 100, the second curve, (ii), is for experimental results for an average number of platelets n=1.37 with aspect ratio, AR= 57 and average modulus 150 GPa. As for the third curve (iii), it is for the case for n=4, AR=10, E=105. Average values for moduli are taken from figure 15 in Fornes (2003) base on experimental work. The solution proposed by Equation 7 is plotted in Figure 3-(b) as the dotted line compared with the experimental reference used in Figure 3-(a) curve b. As shown in the figure, the value of tensile elastic modulus is slightly higher than the reference because a better account of the inherent strength of the exfoliated platelets is possible. As can be seen from the two plots, the proposed modified model is closer to the experimental results than using direct averaging of the aspect ratios.



(a) (b)

Figure 3. (a) Comparison between values obtained from the current analysis vs those of Fornes (2003); (i) The case for AR= 100, (ii) Fornes experimental results for n=1.37, AR= 57 and E=150 GPa; (iii) calculations based on n=4, AR=10, E=105. (b) The modified modulus result (dashed line) compared to experimental

5. Conclusion

A simple modification was used to illustrate a better procedure to account for tensile properties of polymer clay nanocomposites. Demonstration is made for the elastic modulus. The model is based on accounting for the contribution of each type of clay platelets formation within the polymer. Other properties could also be addressed by the same concept. The use of a more generalized tool as presented by Equation 8, where multiple phases of clay particles with different levels of intercalation, in addition to exfoliation can be accounted for to obtain a better description of the behavior of the nanocomposite. This, however, necessitate experimental data to use as input for the model, which is an interesting research direction to pursue.

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