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Modeling of Stiffening and Strengthening in Nano-Layered Silicate/Epoxy

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A B S T R A C T

The aim of this paper is to investigate adhesion property between nano-layered filler and the polymer matrix using a combination of experimental and micromechanical models as well as the changes in yield strength and stiffness of a layered silicate-filled epoxy nanocomposite. The results indicate that addition of intercalated layered silicate particles increased Young's modulus and yield strength of the epoxy resin, although the increases in stiffness and yield strength are modest, 30% and 4%, respectively. In addition, experimental results were compared with predictive stiffening and strengthening models. The rule of mixtures provides an upper bound for the modulus in these materials, while the Halpin-Tsai model provides a lower bound at low filler contents. The strengthening model used suggests the possibility of presence of a relatively modest adhesion between the intercalated layered silicate and epoxy resin rather than weak adhesion in the intercalated systems.

1. INTRODUCTION

First investigations on layered-silicates/epoxy nanocomposites were published in 1994 [1-3]. The focus of these studies was on achieving delaminated silicate layers in an epoxy resin and evaluating effective parameters on this phenomenon [2]. Since that time, extensive studies have been performed to process nanocomposites and understand the responsible mechanism for delamination, and characterize the mechanical, thermal, and other properties of layered silicate-epoxy nanocomposites [4-11]. Wang and Pinnavaia [2] investigated the effect of matrix ductility and alkyl ammonium chain length on mechanical properties of exfoliated silicate-epoxy nanocomposites. It should be mentioned that delamination occurred inside the layered silicate aggregates and aggregated particulates in few-micron size remained in the epoxy matrix. These researchers found that the delamination-polymerization temperature depended on the heating rate and the nature of organo-functional groups used to modify the compatibility between silicate layers and epoxy [2]. In another work, it was shown that reinforcement of the layered silicate-epoxy depended on both the silicate content and the matrix ductility [1]. The moderately higher tensile strength and modulus of the exfoliated nanocomposite based on relatively high-glass transition temperature (high-T_g) epoxy were compared to the neat epoxy [1], while the ten-fold increase in the modulus was achieved by addition of 15 wt% silicate layers into the low-T_g epoxy. Furthermore, the nanocomposite based on a rubbery epoxy showed much larger strain at break compared to the nanocomposite based on a glassy epoxy. At the same time, Messersmith and Giannelis [3] reported a 58% improvement in the storage modulus of an epoxy in glassy state. These researchers observed 450% storage modulus increase in rubbery state along with the broadening and slight increase in T_g by addition of only 15 wt% delaminated layered silicates with the *d*-spacing in the range of 10 nm [3]. The stiffening effect was more than when the conventional layered silicate in micron-size was used [3]. Fornes and Paul [12] showed the importance of aspect ratio for nano-layered silicate/polyamide 6 (PA6).

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Beside experimental efforts, some papers have been dedicated to predict the effect of nano-layered fillers in stiffening of polymers using estimating models developed for predicting modulus of particulate composites [12-15]. Fornes and Paul [12] and Ahmed and Jones [13] have provided an overview of such models. In all the models reviewed, linear elastic behavior is assumed for matrix and filler as well as perfect adhesion, uniform dispersion and aspect ratio. Effects such as particle size, agglomeration, particles interactions, interface strength, and interphase are neglected. The feasibility of extending these micromechanical models to nano-layered silicate-filled polymers has been evaluated [12, 16-20] and in most cases relatively good predictions have been achieved. In addition, recently some attempts have been concentrated on developing modifications on stiffening models [17-20] considering the complex structure and morphology of silicate platelets. Brief descriptions for each of these predictive models are given below.

Rule of mixtures

The simple rule of mixtures can be derived from an iso-strain model and usually used to predict the stiffness of continuous fiber composites. When fillers are unidirectionally aligned parallel to the direction of loading, where E_f and E_m are moduli of filler and matrix, respectively and φ_f is the volume fraction of filler:

$$E_{II} = \varphi_f E_f + (1 - \varphi_f) E_m \tag{1}$$

When fillers are unidirectionally aligned perpendicular to the direction of loading, the following Equation (4) can be derived from an iso-stress model:

$$\frac{1}{E_\perp} = \frac{\varphi_f}{E_f} + \frac{(1 - \varphi_f)}{E_m} \tag{2}$$

When plate-like fillers are randomly dispersed in the matrix the modulus can be predicted using the laminate approximation proposed by Van Es et al. [21]:

$$E_r = 0.49 E_{II} + 0.51 E_\perp \tag{3}$$

Halpin-Tsai model

The Halpin-Tsai model is a well-known micromechanical model to estimate the stiffness of unidirectional composites, which covers a variety of reinforcement geometries via applying the aspect ratio effect.

$$\frac{E}{E_m} = \frac{1 + \zeta \eta \varphi_f}{1 - \eta \varphi_f} \tag{4}$$

$$\eta = \frac{\dfrac{E_f}{E_m} - 1}{\dfrac{E_f}{E_m} + \zeta} \tag{5}$$

when fillers are unidirectionally aligned parallel to the direction of loading:

$$\zeta = \frac{2w}{t}$$

when fillers are unidirectionally aligned perpendicular to the direction of loading:

$$\zeta = 2$$

where w and t are the width (or length) and thickness of the platelets, respectively and ζ is the shape factor dependent on the filler geometric parameters and loading direction. Note (w/t) is the aspect ratio of platelet filler.

Some decades ago, Brown [22] mentioned that any variable which increases the modulus should also increase the yield strength of a glassy polymer. He suggested a linear relationship between yield strength and Young's modulus in a range of 1/60-1/30 such as lower and upper boundaries for almost all glassy polymers. Therefore, it is interesting to evaluate the yield behavior of the intercalated layered silicate-filled epoxies. The studies by Ahmed and Jones [13] and Liang and Li [21] provide overviews on strengthening models for particulate composites. Compared to the stiffening, much less work has been done to assess whether composites strengthening models can predict the strength of polymer nanocomposites [23-25]. Szazdi et al. [24, 25] have tried to model the strengthening effect of nano-fillers in polypropylene (PP) based nanocomposites. However, there is a lack on modeling of yield behavior and strengthening effect in layered-silicate epoxy based nanocomposites. Therefore, considering this gap in the literature and high importance of epoxy resins in industry, the aim of this research is to predict the strengthening effect of layered silicate in an epoxy system as well as its stiffening effect based on micromechanical models. Furthermore, the adhesion property between nano-layered filler and the polymer matrix is assessed.

2. MATERIALS AND METHODS

The epoxy resin used in this study was a diglycidyl ether of bisphenol A (DGEBA), EPON 828, from Hexion Specialty Chemicals. Piperidne from Sigma-Aldrich was chosen as the curing agent. The organophilic smectic montmorillonite (MMT) layered silicate with the cation exchange capacity (CEC) of 110 meq/100 g from Zhejiang Fenghong Clay with the trade name of NANOLIN DK1 was used in this study while its concentration was varied systematically up to 15 wt%.

For preparation of nanocomposites, layered silicate powder was mixed with the appropriate amount of epoxy at 80 °C using a Heidolph RZR2102 mechanical stirrer at 600 rpm for 2 hrs. Then, 5 parts curing agent

per hundred parts resin (phr) was injected gently into the liquid suspension and mixed for 15 min at the same temperature. Vacuum was then applied while stirring continued for another 15 min to degas the mixture. Next, the mixture was cast into a preheated aluminum mold and cured at 120 °C for 16 hrs.

The nano-filler dispersion in the epoxy matrix was investigated using wide angle X-ray diffraction (WAXD). A Philips PRO Xpert with Cu-K_α radiation was used in this experiment.

Dispersion of layered silicates in the epoxy matrix was investigated by a transmission electron microscope (TEM). Samples were cut using a Leica Ultracut UCT ultra-microtome and examined using a Philips CM200, field emission gun (FEG) TEM at an accelerating voltage of 200 kV.

Tensile tests were performed on type-I specimens (ASTM D638 Standard) at a cross-head speed of 5 mm min^{-1}, using a screw-driven Hounsfield H10KS testing frame.

The compressive behavior of the layered silicates-filled epoxies and the neat epoxy were evaluated in accordance with the ASTM D695 test method using a Hounsfield H10KS universal frame at a crosshead speed of 1.5 mm min^{-1}.

3. RESULTS AND DISCUSSION

3. 1. Morphology   The XRD patterns of pure organo-layered silicate and the epoxy compounds made are shown in Figure 1. As seen, the original organo-layered silicate has a sharp peak at 4.2º. According to the Bragg's law, this peak corresponds to the (001) plane at *d*-spacing of 2.12 nm. As seen in Figure 1, introduction of layered silicate into the epoxy shifts this peak to about 2.6º (≈ 3.5 nm) and reduces the intensity of the peak. However, the intensity increases with the layered silicate loading (Figure 1). The XRD patterns indicate the intercalation of layered silicates in the epoxy matrix and successful penetration of the silicate galleries with pre-polymer. Figure 1, also, illustrates another peak at nearly 5.15° (*d*-spacing of about 1.7 nm) in the layered silicate-filled epoxy systems that indicate the presence of some micro-particles in the composite and that the pre-polymer molecules have not been able to penetrate among some silicate layers. In other words, there is not full intercalation of silicate platelets in the epoxy matrix and the fillers dispersed in the matrix are both microns and nanometers in size.

According to the TEM images shown in Figure 2, the *d*-spacing between neighboring layers are 2-3.5 nm. The average *d*-spacing measured by TEM agrees with the 1.7 and 3.5 nm *d*-spacings measured by XRD.

3. 2. Stiffening Effect   The results of tensile tests are presented in Figure 3. The results show that incorporation of layered silicate into the epoxy resin increased modulus as a linear function of layered silicate content (Figure 3). Layered silicate loading of 15 wt% reinforced the modulus from 2.9 to 3.7 GPa, i.e. a 30% increase. Similar increases in tensile modulus, up to a 30% increase, has been reported for a different intercalated layered silicate-filled epoxy system by Zilg et al. [26]. Zerda and Lesser [27] have reported an increase of elastic modulus of an intercalated nanocomposite as well, although to a lesser extent (max. 14% increase at 12.7 wt% layered silicate loading). The enhancement in modulus is directly attributable to the reinforcement effect provided by the rigid silicate nano-layers. Presence of silicate platelets with higher modulus in the epoxy network can constrain epoxy chains close to the layered silicates. Similarly, Kojima et al. [28] attributed the increase in tensile modulus of layered silicate/polyamide 6 (PA6) to the constrained polymer chains in vicinity of the inorganic phase.

In the current study, the stiffening effects of both fully exfoliated and intercalated silicate are predicted using two of the more popular micromechanical models, the rule of mixtures and Halpin-Tsai. Table 1 summarizes the physical properties of material components placed in these micromechanical models. In the literature, the modulus of layered silicate (montmorillonite: MMT) has been assumed equal to 178 GPa as that of the muscovite, a mica-based silicate with similar structure to MMT [12].
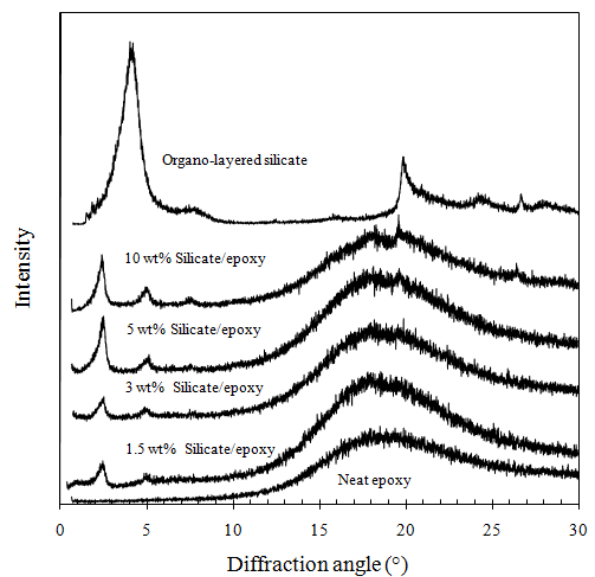

Figure 1. X-ray patterns of pure organo-layered silicate, neat epoxy, and organo-layered silicate-filled epoxies

Predicted values of stiffness are compared with the experimental results in Figure 3.

Assuming a fully exfoliated morphology for silicate nano-platelets and given the rule of mixtures the value of 178 GPa as the modulus of filler predicted a remarkable stiffening effect; about 350% increase in stiffness if platelets unidirectionally aligned and a 175% increase for random dispersion compared to a 30% increase in modulus observed in the experimental results of this study when 15 wt% organo-layered silicates (8.3 vol% organo-layered silicates or 5.8 vol% layered silicates) were added into the epoxy. The Halpin-Tsai model predicted a significant stiffening effect of fully exfoliated layered silicates as well, however, as expected; the prediction level is less than that of the rule of mixtures. Parenthetically speaking, a significant stiffening effect of nano-layered silicates in an epoxy resin is expected due to its high aspect ratio, high modulus of exfoliated silicate platelets and their two-dimensional stiffening potential as well. While in reality, much lower aspect ratio, random dispersion, and effective modulus of tactoids/stacks/individual platelets control the reinforcement effect.
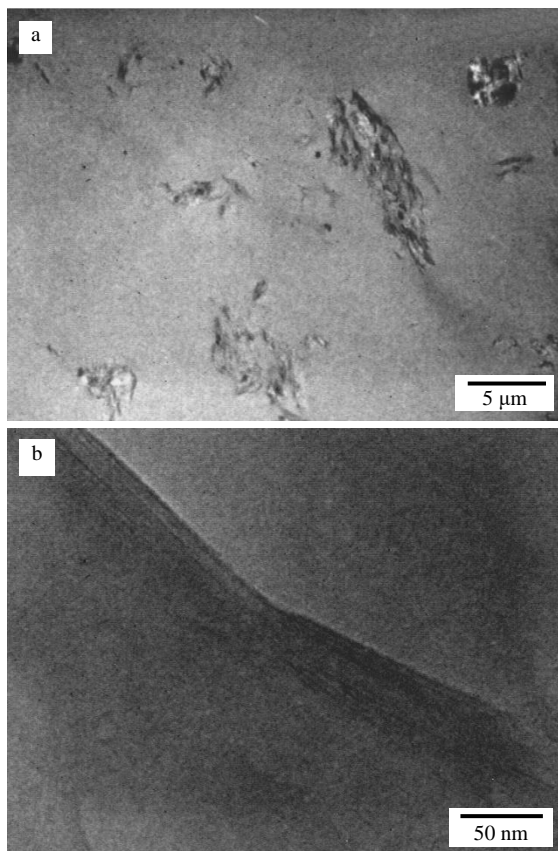
Since in the present investigation, layered silicate-filled epoxies have an intercalated morphology, the modulus of an effective particle is applied. Considering that typically organo-layered silicates contain about 30 wt% surfactant, the effective modulus of intercalated organo-layered silicate (82 GPa) is considered as modulus value of effective particle and volume fraction of organo-layered silicate as volume fraction of filler. Note using the aspect ratio of an effective particle for modulus prediction in these intercalated epoxy systems rather than exfoliated systems due to complexity of organo-layered silicate dispersion states in the polymeric resin (Figure 4).

Inspired from the microscopy studies (optical and electron microscopies shown in Figure 4), Figure 5 schematically illustrates a four-phase model containing organo-layered silicate tactoids, stacks, individual platelets, and epoxy resin.
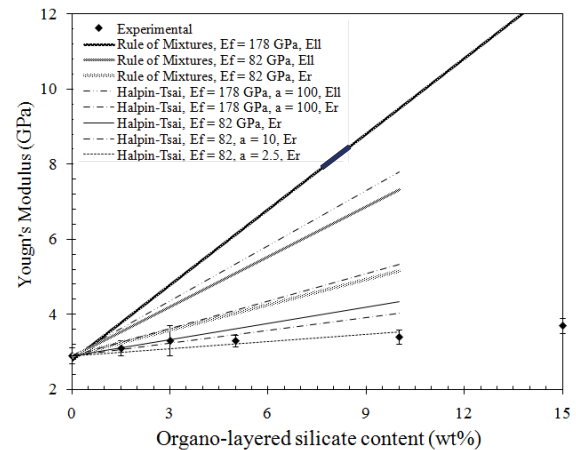

Figure 3. Variation of Young's modulus as a function of organo-layered silicate content in epoxy resin based on experimental results and micromechanical models

TABLE 1. Physical properties of the components of intercalated layered silicate-filled epoxies

Components	Young's Modulus (GPa)	Poisson's Ratio	Density (g/cm³)
Epoxy	2.9	0.35	1.1
Surfactant†	2.9	0.35	1.1
Clay	178‡	0.2	2.8
Effective Particle*	82	0.28	1.8

† The physical properties of surfactant were assumed similar to that of the epoxy resin.
‡ In the literature the modulus of montmorillonite (MMT) layered silicate itself is assumed to be equal to 178 GPa as that of the muscovite, a mica-based layered silicate with similar structure to MMT [12].
* The physical properties of effective particle were calculated from the rule of mixtures by assuming 30 wt% of effective particles are surfactant and epoxy in total.

Figure 2. TEM micrographs of the 5 wt% layered silicate-filled epoxy taken at (a) low magnification, (b) higher magnification. Note the presence of the tactoids at low magnification and wide *d*-spacing between silicate layers at high magnification

When effective particles were randomly dispersed the rule of mixtures, one of the simplest models, not considering the aspect ratio effect, and given the effective modulus value in this model, gave an overestimation on reinforcement ability of intercalated layered silicate. Despite the rule of mixtures which does not apply the aspect ratio effect in predicting stiffness, the Halpin-Tsai model considers the effect of aspect ratio. Given the Halpin-Tsai model the component properties from Table 1, a lower reinforcing effect is predicted than that of the experimental data when the effective aspect ratio is assumed smaller than 10, while the predicted values are close to that of the measured values when the aspect ratio of effective particles is assumed equal to 20 at low filler content. Although assuming the aspect ratio of 20 rendered a very close approximation to the experimental results for modulus at low volume fractions, the microscopy analyses showed that the effective particles have an aspect ratio of smaller than 10.

This suggests underestimations on stiffening effect for intercalated layered silicate at low content filler using the Halpin-Tsai model, although in the literature, a relatively good agreement between predicted and experimental values has been reported [13, 16]. It should be mentioned that the experimental result fitted the Halpin-Tsai model given that the aspect ratio of 2.5 when 10 wt% layered silicates were added into the epoxy.
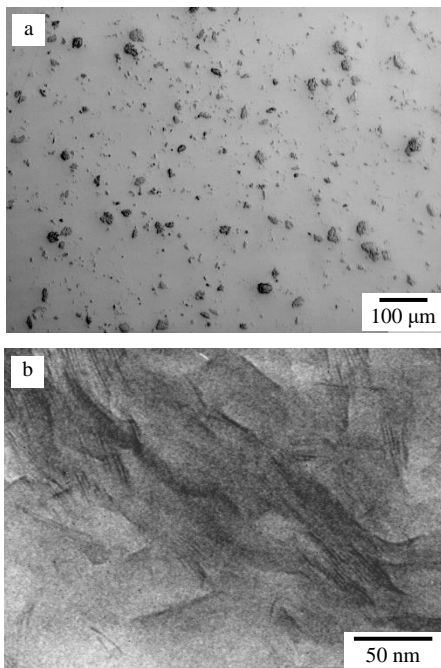
This is in consensus with Fornes and Paul's study [12] focused on the effect of number of layers per stack on stiffening effect of silicate in a polymeric matrix. Based on their estimations, even having two platelets per stack instead of only one, dramatically drops the stiffening efficiency. These researchers explained the importance of aspect ratio due to controlling the effective length of load transfer from a polymeric matrix to the filler [12].

As a summary, it can be concluded that the rule of mixtures provided an upper bound for the modulus in these materials, while the Halpin-Tsai model provided a lower bound at low filler contents.

3. 3. Strengthening Effect   Since tensile strength is strongly influenced by the presence of surface flaws, the influence of organo-layered silicate content on tensile strength was avoided in this study. Instead, the influence of layered silicate content on compressive yield strength of the epoxy resin was studied and is illustrated in Figure 6.
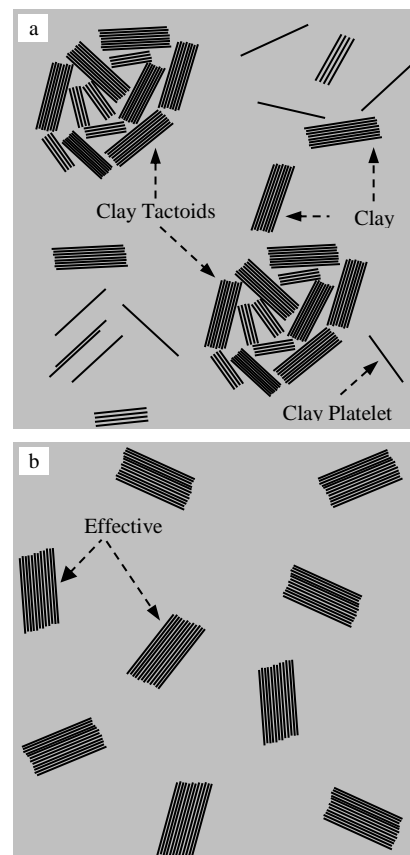
Figure 5. Schematics sketches showing: (a) a four-phase model illustrating complex dispersion states of layered silicate in polymeric/epoxy resin corresponding to the optical and TEM micrographs and (b) effective particles. Note the presence of tactoids, stacks, and exfoliated silicate platelets in matrix suggesting a complex dispersion state for layered silicate in (a)

Figure 4. Dispersion states of layered silicate in an epoxy matrix: (a) an optical micrograph illustrating the presence of organo-layered silicate tactoids (b) a TEM micrograph showing stacks and exfoliated silicate layers in 3 wt% organo-layered silicate-filled epoxy
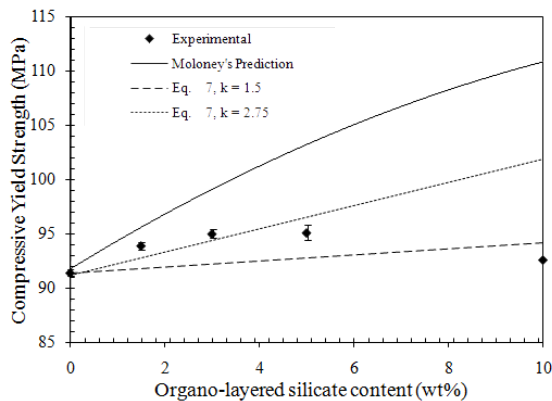
Figure 6. Variation of compressive yield strength as a function of organo-layered silicate content in epoxy resin

Slight increases in compressive yield strength of the nanocomposites were observed (c.a. 4 MPa). Based on Figure 6, addition of 3 wt% organo-layered silicate resulted in only 4% increase in yield strength of the nanocomposite as compared to that of the neat resin. That is, the yield strength of the neat epoxy increased from 91.5 MPa to 95 MPa in 3 wt% intercalated-layered silicate/epoxy. These results are in agreement with Liu et al. [29] who reported little increase (less than 5 MPa) in compressive yield strength of epoxy nanocomposites. The results reported by Pinnavaia et al. [30] showed limited improvement on the compressive behavior for exfoliated nanocomposites in a glassy epoxy matrix as well. However, the intercalated morphology did not demonstrate any measurable difference in either yield strength or compressive modulus [31]. Another group of researchers have also reported that intercalated layered silicate particles were completely ineffective in providing reinforcement to the matrix under compressive strain [32].

Despite the slight increase in yield strength observed in the current research, Akbari and Bagheri's results [33] showed a significant decrease in the compressive yield stress of an epoxy resin from 70 to 53 MPa in an intercalated silicate-filled epoxy. These researchers attributed the easier plastic deformation in their intercalated silicate-filled epoxy systems due to the presence of lower crosslinked and even linear epoxy between silicate layers [33]. This difference could be influenced from type and amount of surfactant on layered silicate, type of epoxy and morphology of dispersed layered silicate in the epoxy resin. Another possible reason for this behavior may be explained by either the interface strength between silicate platelets and the epoxy matrix or the ductility of the interphase outside.

Among several strengthening models, it seems that the following equation is more feasible to use in the current study since the other micromechanical models

need more information to be substituted. This equation was extended by Moloney et al. [34] from the stiffening model proposed by Ishai and Cohen [35] to predict the compressive yield strength of particulate filled epoxies as a function of filler volume fraction. In Mohoney's model, the yield strength was related to the volume fraction of filler as follows [34]:

$$\sigma_{yc} = \frac{\sigma_{ym}}{1 - 1.2\varphi_f^{\frac{2}{3}}} \qquad (6)$$

where σ_{yc} and σ_{ym} are the yield strengths of the composite and the unfilled epoxy, respectively and φ_f is the volume fraction of filler. Based on the Moloney's model, a stronger strengthening effect is expected due to the presence of intercalated layered silicate in the epoxy resin compared to the experimental results (Figure 6). The difference can be obtained from ignoring either interface or interphase effect in the Moloney's model.

Although it is difficult to predict the strengthening effect of nano-layered silicate due to lack of information required by various other models, the strengthening models may assist to qualitatively evaluate the interfacial strength between the intercalated silicate and epoxy in this study. When the interfacial strength between the filler and matrix is weak, the strengthening models estimate a decrease in strength of a polymeric material by introduction of rigid filler, while an increase in strength is expected if a strong adhesion takes place between components [13, 21, 23]. Considering this and the experimental results in the present study, which show a limited increase in yield strength (Figure 6), the possibility of presence of a relatively modest adhesion between the intercalated layered silicate and epoxy resin rather than weak adhesion in these intercalated systems is suggested. In addition, the following equation may help to qualitatively evaluate the interaction between filler and matrix [23].

$$\sigma_{yc} = \sigma_{ym} \frac{1 - \varphi_f}{1 - k\varphi_f} \qquad (7)$$

where σ_{yc} and σ_{ym} are the yield strengths of composite and unfilled epoxy matrix, respectively and φ_f is the volume fraction of filler. k is a parameter which is an indicator of the interaction between filler and polymeric matrix. In the case of using either soft particles or voids, the yield strength of the compound decreases by increasing the filler content and the results can be modeled assuming $0 \le k < 1$. While using rigid particles with perfect adhesion, the yield strength of the filled polymer increases when the filler content is increased and are modeled using $k > 1$. Higher values of k are due to a significant amount of load transfer to the fillers. Interestingly, some have claimed that k may be negative if a rigid interphase formed around nanofillers [21].

Equation 7 predicts a linear relationship between the yield strength and volume fraction of filler, while the

experimental results showed a non-linear trend. At low concentrations of filler (up to 5 wt%), the plot in Figure 6 suggests an approximate value of 2.7 for k could be used to fit the compressive yield strength data. Such a value of k indicates a modest load bearing capability of the fillers. Therefore, the observation of a modest increase in yield strength suggests the presence of a modest amount of interaction between filler and the epoxy resin.

4. CONCLUDING REMARKS

Both TEM and XRD reveal that the layered silicates are intercalated and that the spacing between platelets is 2-3.5 nm. Addition of intercalated layered silicates into the epoxy resin does not result in a significant change in compressive yield strength. The yield strength of epoxy increases only 4% by introduction of 3 wt% layered silicate. Young's modulus increases 30% with incorporation of intercalated layered silicates. The modest increase in stiffening was presumably due to low aspect ratio. The presence of a layer of surfactant on the filler may prevent the binding of the polymer to the filler, lessening the reinforcement. Effective stiffness particle models were used to rationalize the modest increase in stiffness for this layered silicate-filled polymer with an intercalated morphology. The importance of this study is that the strengthening model used proposed the possibility of presence of a relatively modest adhesion between the intercalated layered silicate and epoxy resin rather than weak adhesion in these intercalated systems.

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Modeling of Stiffening and Strengthening in Nano-Layered Silicate/Epoxy

RESEARCH NOTE

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P A P E R   I N F O

چکیده

هدف این مقاله بررسی خاصیت چسبندگی بین نانوفیلرهای لایه‌ای و زمینه پلی‌مری با استفاده از ترکیبی از آزمون تجربی و مدل‌های میکرومکانیک و بررسی تغییرات مدول و استحکام تسلیم نانوکامپوزیت سیلیکات لایه‌ای/ اپوکسی است. نتایج نشان داد که افزودن سیلیکات لایه‌ای میان لایه‌شده (Intercalated) باعث افزایش مدول یانگ و استحکام تسلیم رزین اپوکسی گردید، هرچند که میزان افزایش مدول و استحکام تسلیم میانگین به ترتیب ۳۰٪ و ۴٪ است. به علاوه، نتایج تجربی با مدل‌های تخمین مدول و استحکام مقایسه شدند. قانون مخلوط‌ها حد بالایی افزایش مدول در این مواد را فراهم نمود در حالی که مدل Halpin-Tsi حد پایینی آن را در مقادیر پایین تعیین کرد. مدل استحکام‌دهی مورد استفاده امکان وجود چسبندگی متوسط بین سیلیکات لایه‌ای میان لایه شده و رزین اپوکسی را نسبت به چسبندگی ضعیف در این سیستم‌های میان لایه شده مرجح می‌داند.

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