Modeling Stiffness of Nanolayered Silicate-Modified Polyamide 6 via FEM Micromechanical Modeling and Analytical Composite Models

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ABSTRACT: In this work, numerical and analytical models are chosen to study reinforcement effect of nanolayered silicate modified polyamide 6 (PA 6) composites at ambient temperature. A numerical self-consistent unit cell model in conjunction with finite element method is applied to predict the stiffness of this polymer nanocomposite, which has been successfully applied for simulating mechanical behavior of metal matrix composites. In this work, a rectangular inclusion (layered silicate) is surrounded by PA 6 polymer matrix, which is again embedded in the PA 6/layered silicate nanocomposite. The stiffness of the composite is determined iteratively in a self-consistent manner. For comparison, two analytical composite models (Halpin–Tsai model and Tangdon–Weng model) are implemented to evaluate the stiffness of this nanocomposite via calculations performed within MATLAB. In the modeling volume fraction, aspect ratio, exfoliation and orientation of the nanolayered silicate are taken into account. It is demonstrated that the numerical approach using the self-consistent embedded cell model coincides well with experimental results of the stiffness of the composite. J Appl Polym Sci 000: 000–000, 2012

Key words: micromechanical modeling; self-consistent embedded cell model; PA 6/layered silicate nanocomposite; analytical composite models

INTRODUCTION

Polyamide 6 (PA 6)/nanolayered silicate composites have attracted great scientific and industrial interest in commercial research and academic laboratories because they offer remarkable strengthening at very low filler concentrations. With $\sim$ 4.7 mass %-layered silicates content a doubling of Young's modulus and of strength of the nylon 6 matrix can be achieved.[1] The nanolayered silicate concentration is so low that the optical properties of the nylon 6 matrix are unaffected. They also provide significant enhancement in many other properties, such as flame retardancy, gas barrier properties, or thermal stability.[2] The reinforcing effect of nanolayered silicate is attributed to the presence of a large number of reinforcements due to the nanoscale arrangement, the exceptionally high surface area-to-volume ratio of the nanolayered silicate and the inhibition of polymer molecular motions near the nanolayered silicate surface.[3] Therefore, the reinforcement is strongly dependent on different levels of dispersion of the nanolayered silicate. Normally, the dispersion of the nanolayered silicate is divided into the following cases, e.g., silicate stacks, intercalated silicate, and fully exfoliated silicate (Fig. 1). Fully exfoliated silicate shows the most effective reinforcing effect due to the largest number of silicates and the highest surface area-to-volume ratio.

Not only the dispersion level of the nanolayered silicate affects the reinforcement but also many other factors such as volume fraction, aspect ratio, and the orientation of the nanolayered silicate do play an important role in the effectiveness of the reinforcement. For a better understanding of the mechanical behavior of the nanolayered silicate composite, it is indispensable to apply analytical and numerical models for studying the reinforcement effect based on the morphology and mechanical properties of each constituent phase. In this way, costly and time-consuming experiments will be largely avoided.

In this work, a finite element-based self-consistent numerical unit cell model is applied to predict the stiffness of this polymer nanocomposite. For comparison, two analytical composite models [the Halpin–Tsai (HT) model and the Tangdon–Weng (TW) model] are implemented to evaluate the stiffness of this

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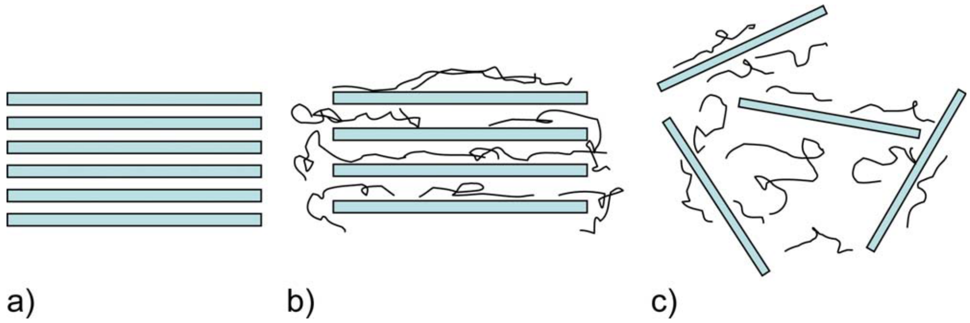

Figure 1 (a) Silicate in stack with few silicate surface to the polymer. (b) Intercalated silicate with increased platelet spacing. (c) Fully exfoliated silicate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanocomposite via calculations performed within MATLAB. In the modeling, the volume fraction, aspect ratio, exfoliation, and the orientation of the nanolayered silicate are taken into account. It is demonstrated that the numerical approach using the self-consistent embedded cell model coincides closely with the experimental results concerning the stiffness of the composite.

INVESTIGATED MATERIAL

The matrix material of the analyzed polymer composite is a PA 6 (Ultramid B40) provided by BASF, Ludwigshafen, Germany. The nanolayered silicate (Cloisite 93A) with thickness $d = 1$ nm was formed by ion exchange of sodium montmorillonite with a tertiary and quaternary ammonium salt. The morphology of the composite and the mechanical properties of each constituent phase are summarized in Figure 2 and Table I.

NUMERICAL SELF-CONSISTENT EMBEDDED UNIT CELL MODEL

A numerical self-consistent embedded unit cell model (SCEUC) in conjunction with finite element method

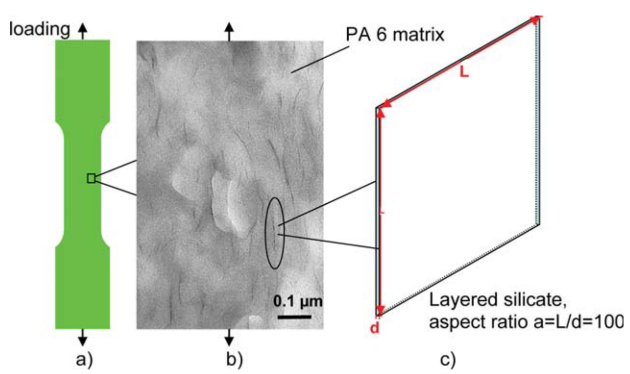

Figure 2 TEM image of exploited nanolayered silicate modified PA 6 (PA 6 + 4.96 mass % layered silicate). The silicates are oriented in the loading direction. (a) Tensile bar sample. (b) Microstructure of the composite. (c) Definition of the aspect ratio *a* of the layered silicate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was chosen to predict the elastic property of this polymer composite, which has been successfully applied for evaluating the mechanical behavior of metal matrix composites[6,7] and semicrystalline PA 6 as well as PA 6/elastomer composite[8] in the past. Based on the morphology of the composite, the nanolayered silicate is assumed to possess an approximately rectangular shape. Therefore, in the embedded unit cell model, a rectangular silicate is surrounded by PA 6 matrix, which is again embedded in an equivalent homogenous PA 6/nanolayered silicate composite with mechanical properties to be determined iteratively in a self-consistent manner. To avoid interactions of the outer boundary of the unit cell with the inner embedded cell and thus on the composite behavior, the edge length of the outer square D is here taken to be five times that of the rectangle d. In this model, the orientation of layered silicate in the composite can be realized by rotation of the embedded unit cell with respect to the applied loading direction (Fig. 3).

The two-dimensional model for the finite element analysis was generated and meshed using the commercial software MSC PATRAN. The chosen elements for the calculation were plane strain eight-noded biquadratic elements with full integration points (Fig. 4). The calculations were performed with ABAQUS at the Gauss integration points by integrating the polynomial terms in the element's stiffness matrix exactly.

The details of the modeling procedure were explained in the previous work of the authors.[8] The experimentally determined Young's modulus, Poisson's ratio, and volume fraction of the matrix and inclusions are at first assigned to the inner embedded

TABLE I
Input Parameters for Simulation Models

Phase	Young's modulus (GPa)	Poisson's ratio	Density (g/cm^3)	Source
Layered silicate	178.00	0.20	2.60	4,5
PA 6 matrix	2.81	0.35	1.30	Tensile test IKT and IMWF

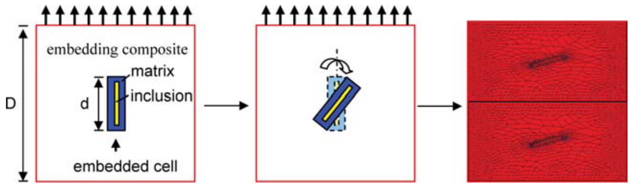

Figure 3 Sketch of the two-dimensional self-consistent embedded unit cell model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cell while the initially assumed material data of the composite is assigned to the embedding composite. The embedded cell model will then be stretched under axial displacement loading. The mechanical stress–strain behavior of the embedded cell and the surrounding embedding composite are then compared with each other. If they are not identical, then the improved overall stress–strain curve of the composite consisting of the embedding cell and the surrounding material from the previous iteration will be repeatedly assigned to the embedding composite for the next iteration step until the stress–strain curves of the embedded cell and the surrounding embedding composite are found to be identical within a pregiven limit. Thus, the obtained overall stress–strain curve is assumed to predict the mechanical behavior of the composite.

ANALYTICAL MICROMECHANICAL MODEL

Various analytical composite models based on mechanical and physical principles are developed or applied by many research groups for such nanocomposites.[5,9–15] These micromechanically oriented models are based on the properties of the pure constituent components and the morphology of the composites. Two most widely used approaches for the prediction of Young's modulus of composites are the HT model and the Mori-Tanaka (MT) model.[5,9–15]

The HT model attempts to estimate the composite modulus E_c based on the moduli of the matrix E_m and the reinforcement E_s, aspect ratio a, as well as the shape factor η and volume fraction f_s of the inclusion phase:

$$\frac{E_c}{E_m} = \frac{1 + 2af_s\eta}{1 - f_s\eta}$$

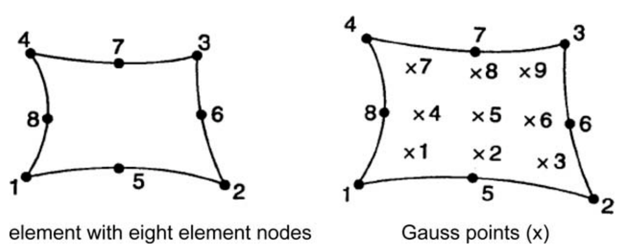

Figure 4 Element type for the mesh used in the self-consistent embedded unit cell.

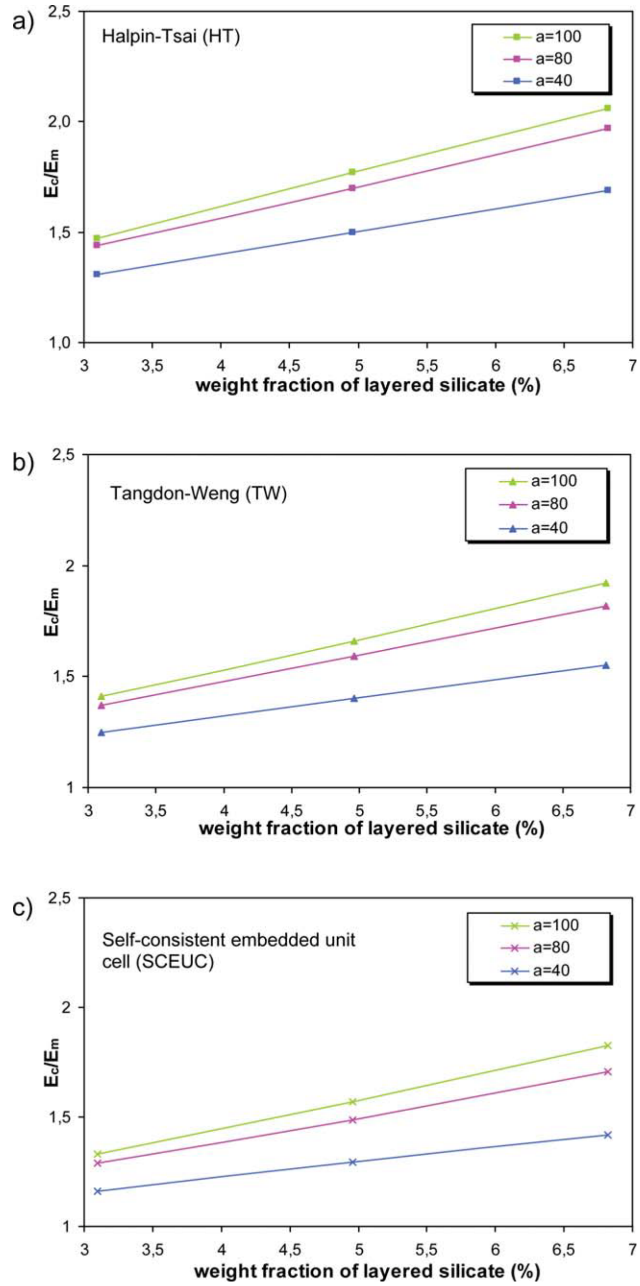

Figure 5 Parameter study (E_c and E_m are Young's moduli of composite and matrix depending on aspect ratio and weight fraction of the layered silicate using the HT (a), TW (b), and SCEUC models (c) for the exfoliated system with orientation of the layered silicate in loading direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where η is given by:

$$\eta = \frac{(E_s/E_m) - 1}{(E_s/E_m) + 2a}$$

The MT theory was derived from Eshelby's inclusion model. Tandon and Weng[15] used Mori-Tanaka's theory and Eshelby's solution to get fully analytical solutions for the elastic moduli:

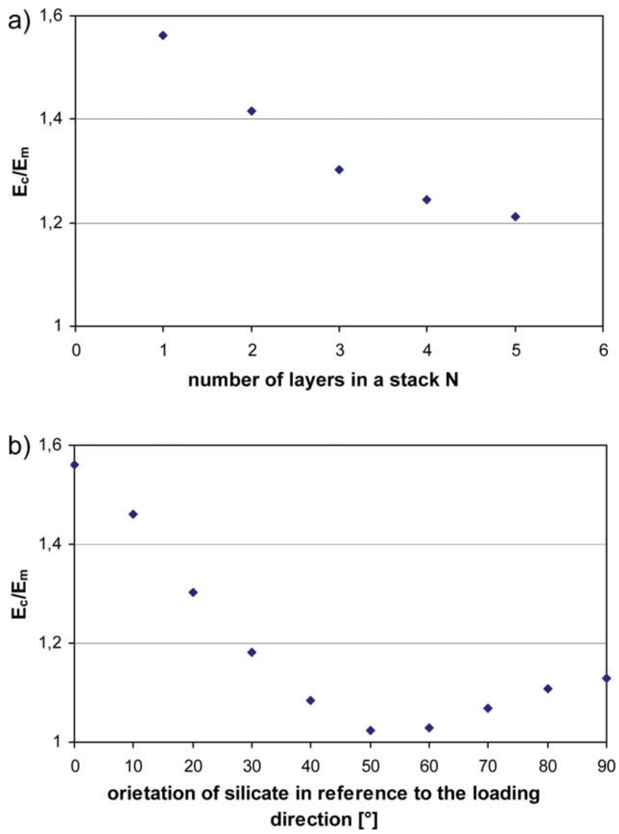

Figure 6 (a) Stiffness enhancement of composites with exfoliated silicate [$N = 1$] and silicate in stack [$N > 1$] in loading direction and (b) influence of the orientation of silicate platelets in reference to the loading direction on the stiffness enhancement in the exfoliated composite system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\frac{E_c}{E_m} = \frac{1}{1 + f_s(A_1 + 2\nu_m A_2)/A}$$

where v_m represents Poisson's ratio of the matrix and A, A_1, and A_2 are functions of Eshelby's tensor for inclusions.

RESULTS AND DISCUSSION

A parameter study was performed using the analytical approaches (HT and TW models), and the numerical SCEUC to investigate the role of the aspect ratio of nanolayered silicate on the stiffness property of the composite. The results of variation of the stiffness enhancement with changing aspect ratio, for exfoliated platelets, with varying filler fraction, are shown in Figure 5(a–c).

The overall elastic modulus of the nanocomposite is shown as a function of filler fraction with different aspect ratios. The Young's modulus of the composite is proportional to the filler fraction. As the aspect ratio of the silicate increases, the Young's modulus increases as well.

Based on the analytical solutions from TW model, a program within MATLAB was developed for the evaluation of the elastic moduli of the nanocomposites by a set of parameter studies. Detailed results of the parameter study are given elsewhere.[16]

As shown in Figure 6(a), the largest enhancement occurs in the case of full exfoliation of silicate platelets (number of silicate platelets in a single silicate stack $N = 1$). An increasing platelet number in a silicate stack results in a decreasing enhancement effect of the Young's modulus. The elastic behavior of this composite was also found to depend strongly on the silicate orientation with respect to the applied loading direction [Fig. 6(b)]. Nanocomposites with silicate platelets orientated in the loading direction show the best enhancement in the elastic behavior of the composites.

Therefore, the best reinforcement effects can be achieved through:

- possible high degree of exfoliation of the layered silicate;
- possible perfect orientation of the layered silicate in loading direction;
- possible high aspect ratio of the layered silicate.

Taking into account the above specified information, three nanocomposite systems with 3.1, 5, and 6.8 wt % silicate were manufactured und characterized.[16] Parameters from the experimental determination, e.g., $N = 1$ and $a = 100$, are taken into account in the analytical and numerical modeling. The comparisons are shown in Figure 7. From these graphs, a good agreement between experimental data and theoretical results is observed. All the models possess the same tendency of the elastic behavior for the nanocomposite with increasing filler fraction. The numerical embedded unit cell model provides

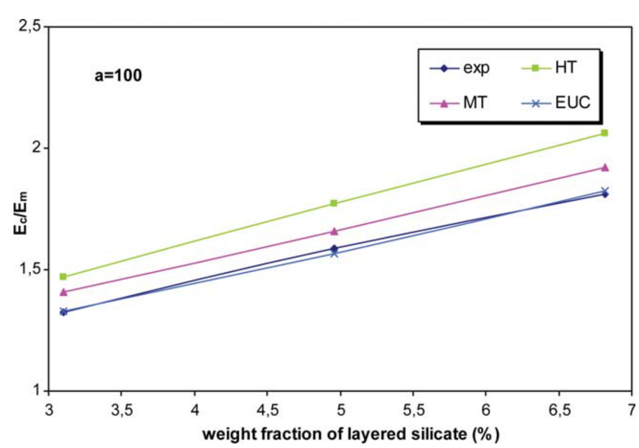

Figure 7 Comparison of analytical and numerical models with respect to experimental data of elastic properties of the composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the best agreement while the analytical results somehow overestimate the experiment data.

CONCLUSIONS

In this contribution, influence of the structural characteristics on the overall elastic behavior of nanolayered silicate modified PA 6 was investigated by means of analytical and numerical methods. It was found that the volume fraction, aspect ratio, exfoliation degree, and orientation of the nanolayered silicate played a very important role on the overall elastic behavior of the composite. The greatest enhancement of Young's modulus of the nanocomposite can be achieved through a large filler content, high aspect ratio, and high exfoliation degree of the layered silicate as well as perfect orientation of the layered silicate in loading direction. Different nanocomposite systems were manufactured and experimentally characterized, and their mechanical performances were predicted using analytical and numerical approaches. The comparisons indicate good agreement between experimental data and theoretical results. The numerical embedded unit cell model shows the best agreement with experimentally measured elastic properties of the composites. It can be used to successfully simulate the overall elastic behavior of the polymer nanocomposite.

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