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3-D microstructure reconstruction of polymer nano-composite using FIB–SEM and statistical correlation function

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3-D reconstruction of Halloysite nanotube (HNT) polypropylene composite has been performed using two different methods. In the first method, several slices of the composite material were obtained using focused ion beam (FIB), and scanning electron microscopy (SEM). A representative volume element (RVE) of the real material's micro/nanostructures was then constructed by stacking these morphological images using VCAT® software. In the second method, SEM images of the nano-composite were used to extract statistical two-point correlation function (TPCF), for reconstruction of an RVE of the nano-composite.

The resulting RVEs obtained from both methods were meshed for finite element (FE) simulation of deformation under tension and shear loadings. The FE results were then used to compute the stiffness tensor of the nano-composite.

In the statistical approach, the TPCF was obtained from a none-Eigen microstructure which can partially reflect statistical information of the microstructure. The mechanical constants obtained from statistical RVEs using FEM approach shows a 5.7% error compared with those obtained from real RVE, which could be attributed to the approximation using TPCF [1].

It is concluded that the statistical method using TPCF alone can produce an approximate microstructure that should be modified using other statistical descriptor such as two-point cluster function and lineal path function to have better reconstruction of heterogeneous nano-composites [2].

1. Introduction

In recent years, polymer nano-composites (PNCs) have increasingly gained more attention due to their improved mechanical, barrier, thermal, optical, electrical and biodegradable properties [3–5] in comparison with the conventional micro-composites or pristine polymer. With a modest addition of nanoparticles (usually less than 5 wt.% [4]), PNCs offer a wide range of improvements in moduli [6–8], strength, heat resistance [9], biodegradability [3,10], as well as decrease in gas permeability [5,8,11,12] and flammability [5,8,10,13,14].

Although PNCs offer enormous opportunities to design novel material systems, development of an effective numerical modeling approach to predict their properties based on their complex multiphase and multiscale structure is still at an early stage. Different experimental and simulation approaches are used to measure/calculate the thermomechanical properties in nanoscale. Molecular Dynamics (MD) is becoming a powerful computational tool for the simulation of matter at the molecular scale [15–18]. To estimate macro level or bulk properties of nano-composites, multiscale homogenization approaches are utilized based on continuum mechanics principles. The homogenization techniques can be categorized into the following six classes: statistical methods such as weak and strong-contrast [19,20], inclusion-based methods such as self-consistent or Mori–Tanaka [21], numerical methods such as finite element analysis and asymptotic methods [22], variational/energy based methods such as Hashin–Shtrikman bounds [23], and empirical/semi-empirical methods such as Halpin–Tsai and classical upper and lower bounds (Voigt–Reuss) [24].

Finite element method for continuum mechanics has also been successfully applied to the integrated representative volume elements (RVEs) with a nanometric secondary phase [25–27]. Regardless of the method to reproduce microstructures of the nano-composite, either with well aligned RVE [26,27], or randomly distributed RVE with Monte Carlo scheme [25], the final RVE

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cannot entirely represent the actual complex and highly heterogeneous nano-composite structures. Dong et al. [28] developed a framework to incorporate the microstructural images such as SEM micrographs into 2-D finite element modeling, the so called object-oriented finite element (OOF) technique. In their work, they combined data from the real microstructures such as particle size, shape, spatial position, and orientation distribution with fundamental material parameters including elastic modulus, Poisson's ratio, and coefficient of thermal expansion (CTE) of the constitutive phases to understand the overall material behavior. The OOF however, is limited to elasticity and thermal conductivity calculations in two-dimensional microstructures [29–32].

Several experimental and theoretical techniques such as X-ray computed tomography (CT), and focused ion beam/scanning electron microscopy (FIB/SEM) are being exploited to obtain three-dimensional microstructure as the input RVE for FEM software [33–35]. We have also used this method in the current work to obtain microstructure information of nano-composite. However, due to the high cost of sample preparation processes, simulation methods are often more desirable for the reconstruction of heterogeneous microstructures. Statistical reconstruction of heterogeneous materials using statistical correlation functions can be used as an alternative tool to reconstruct heterogeneous materials.

Two-point correlation function (TPCF) is the simplest statistical correlation functions that can convey some information about dispersion and distribution of inclusions in heterogeneous materials. Recently, Deng et al. [36] presented a statistical work based on 2-D realization of the microstructure obtained from SEM images of carbon black particle fillers dispersed in synthetic natural rubber. Their statistical approach is based on TPCF and two point cluster function using annealing technique.

In this study, unlike previous studies, the 3-D reconstruction of the microstructure of polypropylene nano-composites with 10 wt.% (7.2 vf.%) HNT fillers was achieved using (a) a three dimensional (3-D) morphology-based RVE, and (b) an RVE of nano-composite constructed using statistical TPCFs. To our knowledge, this is the first time a statistical reconstruction method based on two-dimensional microstructure information of nano-composite has been used to approximate the three-dimensional microstructure. Secondly, finite element analysis was used to deform the RVEs under tension and shear deformations to measure the effective stiffness tensor of the HNT polymer composite. Finally, the numerically predicted results obtained from both RVEs were compared against the measured experimental data, in order to assess the feasibility of the statistical approach in predicting the various properties of anisotropic nano-composites.

1.1. Materials and synthesis

The homopolymer polypropylene (PP) Pro-fax 6301 (LyondellBasell) and modifier (2% polypropylene-graft maleic anhydride, PP-g-MA) were first dried under vacuum overnight at 80 °C. The molten PP pellets and the modifier were mixed using a co-rotating twin-screw extruder (DSM Xplore), at 190 °C for 3 min and extruded and chopped into pellets. The pellets were compounded with different weight fractions (5 wt.%, 10 wt.% and 20 wt.%) of HNT (NaturalNano Inc.), at 190 °C for 3 min with a rotation speed of 100 rpm. HNT polypropylene nanocomposite was processed without modifier as well. The HNT weight fraction used in this paper was 10 wt.% HNT/PP.

1.2. Mechanical properties

The evaluation of mechanical properties of nano-composite and the host polymer were carried out using a UTS mechanical testing system and properties were measured based on ASTM standard dogbone specimens. To check the reproducibility of the experimental data and to ensure their consistency, 5 specimens were tested for each formulation. The tensile modulus of the 10 wt.% HNT/PP and host polymer have been measured at 1.8 ± 0.03 GPa and 1.3 ± 0.04 GPa respectively. The effect of HNT loading on the tensile modulus of nano-composite with and without modifier is depicted in Fig. 1. This plot shows that by adding polypropylene-graft maleic anhydride as modifier, tensile modulus will be enhanced by 17%. Modifier enhances the bonding between HNT and PP.

1.3. Serial sectioning of the nano-composite using FIB–SEM

Simultaneous sectioning and imaging of the nano-composite (10 wt.% HNT + PP) was performed using a dual column focused ion beam (FIB)-SEM (Carl Zeiss Auriga CrossBeam). Serial sectioning involved the removal of a known volume of the material by the ion beam followed by an incremental analysis with the electron beam. Because sputtered material may redeposit onto the surface under analysis, significant in situ sample preparation was required. To begin, a trapezoid was milled into the composite such that the shorter face was in a position to be imaged by the electron beam. The wider end of the trapezoid allowed for an unobstructed view of the analysis face. Two wings were on either side of the short face, such that after milling a shape similar to Fig. 2a was observed. The wings were used as channels for sputtered material to redeposit away from the surface of interest. A large beam (30 kV, 20 nA) was used to excavate the bulk of the material and a smaller beam (30 kV, 4 nA) was used to square the edges. The trenches were milled to a depth of 20 μm. Water vapor was leaked into the chamber above the sample to assist the etching. A polished face was created by milling with a fine current beam (30 kV, 1 nA) to a depth of 20 μm. A volume was then established in the software (SmartSEM, Carl Zeiss) with a width and height larger than the viewing area. A milling current of 1 nA was used again. A schematic of the serial sectioning is shown in Fig. 2b and the real images recorded during the FIB procedure are presented in Fig. 3.

The width of each slice was 50 nm, therefore 50 nm of the nano-composite would be milled away with the ion beam followed by an image capture with the electron beam. The image contrast was turned slightly higher than what would normally be used to acquire a good image to accentuate the HNT from the matrix and aid in the reconstruction. Around sixty to one hundred slices were taken per sample, a process that took 2–3 h. A series of 2D images representing slices or cross sections of the RVE is generated through FIB–SEM cutting. The advantage of using serial sectioning

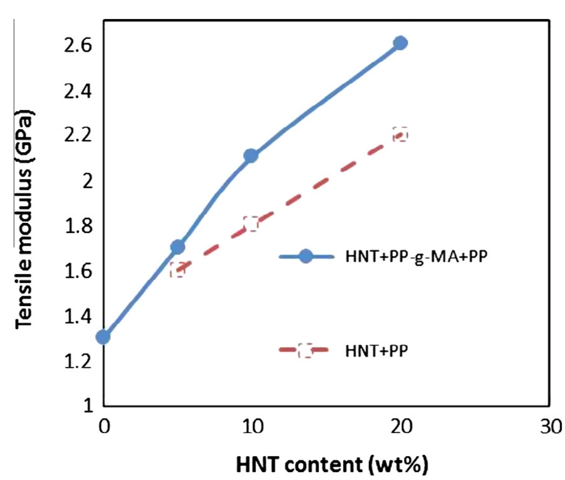

Fig. 1. Tensile modulus of HNT/PP and PP-g-MA-HNT/PP nano-composites.