

A TWO-LEVEL HOMOGENIZATION METHOD FOR POLYMER
NANOCOMPOSITES WITH COATED INCLUSIONS

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NANOCOMPOSITES WITH COATED INCLUSIONS**

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ABSTRACT

A TWO-LEVEL HOMOGENIZATION METHOD FOR POLYMER NANOCOMPOSITES WITH COATED INCLUSIONS

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Polymer nanocomposites are materials which have polymer matrices and nano-scale reinforcement elements. Other than the matrix and the reinforcement element, another phase in nanocomposite systems has been observed and some of the property enhancement or deficiency has been attributed to this phase. The third phase in the composite system is known as the interphase. The local properties of polymer nanocomposites are not easy to distinguish since the length scale is very small and characterization at the nano-scale is not a simple procedure. Macroscopic behavior of nanocomposites can be deduced by homogenization of a representative volume element in many different ways. The aim of the thesis is to propose a new homogenization approach to model the polymer nanocomposites with coated inclusions. Understanding the structure of nanocomposites, formation of the interphase and different characterization techniques for the interphase are important for this aim. Interphase properties affect the overall macroscopic mechanical behavior. So it is important to model the interphase and obtain the effective composite properties accordingly. Different homogenization techniques and applications related to this problem are studied and a new approach is proposed. This method aims to model load transfer between

the matrix and the reinforcement element through the interphase in a correct way. Furthermore, a computational gain is aimed with the proposed model in comparison to a full three-phase finite element simulation. Another goal is to extend the proposed method to viscoelasticity. For this purpose two-dimensional and three-dimensional finite element codes are developed for a viscoelastic homogenization framework. The formulations regarding the viscoelastic homogenization are derived and presented.

Keywords: homogenization, coated inclusion, interphase, polymer nanocomposites



ÖZ

KAPLAMALI TAKVİYEYE SAHİP POLİMER NANOKOMPOZİTLER İÇİN İKİ SEVİYELİ BİR HOMOJENLEŞTİRME YÖNTEMİ

Güzel, Dilek

Yüksek Lisans, Havacılık ve Uzay Mühendisliği Bölümü

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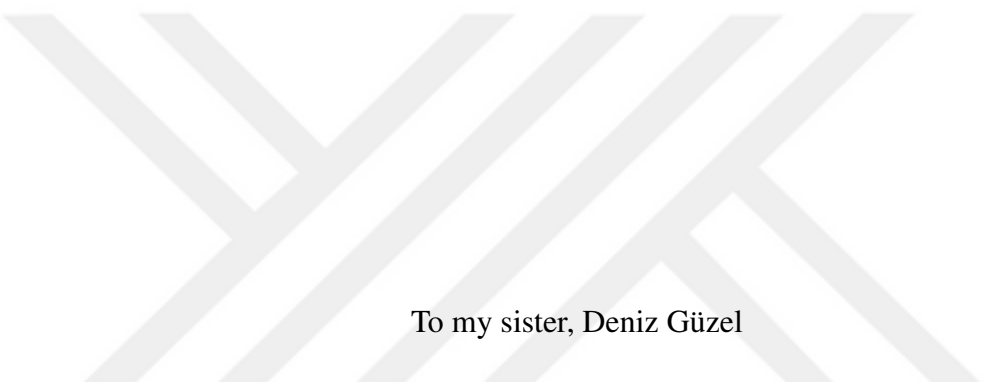
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Polimer nanokompozitler, polimer matris ve nano ölçekli takviye elemanlarından oluşan bir malzeme türüdür. Nanokompozitlerde matris ve takviye elemanı fazlarının haricinde bir diğer faz gözlemlenmiş ve bazı malzeme özelliklerinin güçlenmesi veya zayıflaması bu faza atfedilmiştir. Kompozit sistemdeki üçüncü faz, arafaz olarak bilinir. Uzunluk ölçeği çok küçük olduğundan ve nano ölçekte karakterizasyon basit bir prosedür olmadığından dolayı polimer nanokompozitlerin lokal özelliklerinin ayırt edilmesi kolay değildir. Nanokompozitlerin makroskopik davranışı, temsili hacim elemanının birçok farklı şekilde homojenleştirilmesiyle elde edilebilir. Tezin amacı, kaplamalı takviye elemanına sahip polimer nanokompozitleri modellemek için yeni bir homojenleştirme yaklaşımı önermektir. Nanokompozitlerin genel yapısını, arafaz oluşumunu ve karakterizasyon tekniklerini anlamak bu amaç için önemlidir. Arafaz özellikleri genel makroskopik mekanik davranışı etkiler. Bu nedenle, arafazı uygun şekilde modellemek ve buna bağlı olarak etkin kompozit özellikleri elde etmek önemlidir. Bu problem ile ilgili olarak farklı homojenleştirme teknikleri ve uygulamaları çalışılmış ve yeni bir yaklaşım önerilmiştir. Bu yöntem, matris ile takviye elemanı

arasındaki yük transferini arafaz boyunca doğru bir şekilde modellemeyi amaçlamaktadır. Ayrıca, önerilen yaklaşım ile üç fazlı sonlu eleman yöntemine kıyasla hesaplama süresi açısından kazanım amaçlanmıştır. Diğer bir amaç, önerilen yöntemin viskoelastik kompozitler için uygulanabilirliğini araştırmaktır. Bu amaçla, viskoelastik homojenleştirme yöntemi için iki boyutlu ve üç boyutlu sonlu eleman kodları geliştirilmiştir. Viskoelastik homojenleştirme yöntemine ilişkin formülasyonlar türetilmiş ve sunulmuştur.

Anahtar Kelimeler: homojenleştirme, kaplamalı takviye elemanı, arafaz, polimer nanokompozitler





To my sister, Deniz Güzel

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CHAPTER 1

INTRODUCTION

Polymer nanocomposites are materials which have polymer matrices and nano-scale reinforcement elements. Different from classical, conventional composites, nanocomposites exhibit some phenomena that can be explained by the nano-scale nature of the material [7]. Therefore, new theoretical principles and different experimental techniques are needed in order to understand the behavior of this new class of composites. In the 1980s, Toyota Central Research and Development Laboratories published and filed patents for polymer-clay nanocomposites, which were accepted as the pioneer works in polymer matrix nanocomposite research. There are many challenging problems in the area, such as preparation, synthesis, processing, and characterization of nanocomposites.

Commercial potential of polymer nanocomposites are really wide but the developments by means of nanocomposites are not as high as expected from theoretical calculations. Properties of nanocomposite systems depend strongly on the manufacturing techniques and intrinsic properties of the constituents; therefore, a common rule of thumb cannot be achieved easily. However, recent developments in the synthesizing of composite systems and experimental techniques in characterization prove the enhancement of material properties in polymer nanocomposites. Today, many experimental and numerical works on polymer nanocomposites are present in literature. The effect of matrix and reinforcement element's properties, size, shape, distribution as well as different production techniques and conditions have been studied and reported.

Other than the matrix and the reinforcement element, another phase in nanocomposite systems has been observed and some of the property enhancement or deficiency has

been attributed to this phase. The third phase in the composite system is known as the interphase. Since exploration of this phase, characterization and understanding of the interphase became very important in nanocomposite research. Since interphase properties, thickness and other related aspects are effective in order to understand macroscopic behavior of nanocomposites, different experimental and modelling techniques are studied.

1.1 Motivation of Thesis

The local properties of polymer nanocomposites are not easy to distinguish since the length scale is very small and characterization at the nano-scale is not a simple procedure. It is not easy to test or model local properties of the full scale nanocomposite systems. Macroscopic behavior of nanocomposites can be deduced by homogenization of a representative volume element in many different ways. Homogenization of two-phase composites is a common approach to understand material behavior. Instead of the local stress and strain results, an effective behavior can be obtained through homogenization.

Different techniques to homogenize two-phase composites are suggested. There is third phase of the homogenization problem for polymer nanocomposites, that is the interphase. The interphase properties are not easy to differentiate and as known, the interphase is an integral part of effective composite behavior. In order to understand the material behavior, how interphase stiffness and thickness affect the overall effective properties are significant. The interphase shows different properties than the bulk matrix and the reinforcement element. Therefore, it is possible to have interphases stiffer than the matrix or softer than the matrix. For these cases, how homogenization techniques estimate the overall properties is an important question.

1.2 Aim of Thesis

The aim of the thesis is to combine two very well-known homogenization techniques to model the polymer nanocomposites with coated inclusions. Interphase properties

affect the overall macroscopic mechanical behavior. So it is important to model the interphase and obtain the effective composite properties accordingly. Homogenization theory is very useful and powerful, however, many of the homogenization-based techniques have deficiencies. One of the aims of the thesis is to demonstrate the deficiency originated from the interphase modelling and overcome this problem by the proposed two-level homogenization method. For this purpose, different homogenization techniques and applications related to this problem are studied and a new method is proposed. This method aims to model load transfer between the matrix and the reinforcement element through the interphase in a correct way. Furthermore, a computational gain is aimed with the the proposed model in comparison to a full three-phase finite element simulation. Another goal is to extend the proposed method to viscoelasticity. For this purpose two-dimensional and three-dimensional finite element codes are developed for a viscoelastic homogenization framework. The formulations regarding the viscoelastic homogenization are derived and presented.

1.3 Outline and Scope of Thesis

In Chapter 2, a general overview of polymer matrix nanocomposites is given. Formation of the interphase and the interface and the effect of these phases on mechanical properties are explained. In order to characterize the interphase, different experimental methods are discussed and obtained results from literature are given. The last section of Chapter 2 deals with different interphase modelling approaches. Different mathematical representations are exemplified. A literature review on different interphase modelling approaches for various modelling techniques are provided.

In Chapter 3, the homogenization theory is presented. Classical homogenization techniques for two-phase composites are derived and demonstrated for an example problem. A detailed literature review on coated inclusion problem is given. Historical steps and recent applications of the theory in different areas are presented. Two-step and two-level homogenization concepts are explained. The viscoelastic homogenization in scope of coated inclusion theory is also presented.

In Chapter 4, in order to utilize in the proposed two-level homogenization technique,

the Double-Inclusion model suggested by Hori and Nemat-Nasser [8] and strain controlled tests by finite element analysis are presented. The proposed method and the necessity of a two-level homogenization technique in soft interphase case is demonstrated. Different comparisons for two-dimensional (circular) and three-dimensional (spherical) geometries are illustrated. The last section of the chapter is dedicated to an ellipsoidal inclusion example to model a short fiber reinforced composite.

In Chapter 5, the proposed methodology is extended to viscoelasticity. This is achieved by means of the Dynamic Correspondence Principle. Thus, in the first section, this principle is overviewed. Then, the Double-Inclusion model for viscoelasticity is discussed. For finite element analysis, a different approach for viscoelastic homogenization is proposed by Brinson and Knauss [9]. The details and formulation of this method are derived. Different comparisons two-dimensional (circular) and three-dimensional (spherical) geometries are presented. To show the importance of the interphase modelling, experimental results of a composite system consisting of PET/-Glass Beads [5] are modelled and obtained results are discussed.

In Chapter 6, a summary of thesis and concluding remarks as well as future work suggestions are presented.

CHAPTER 2

THE EFFECTS OF INTERPHASE CHARACTERISTICS ON MECHANICAL BEHAVIOR OF POLYMER NANOCOMPOSITES

Generally, polymer matrix nanocomposites have lower volume fraction of inclusion nanoparticle compared to classic, conventional fiber-reinforced composites. Since the surface area to volume ratio of the inclusions is really high, even a composite system with low volume fraction of reinforcement can change the final properties of the system significantly. It is well accepted that due to higher surface area of inclusions, nano-inclusions make significant improvements to overall mechanical properties such as elastic modulus, yield strength, toughness as well as electrical and optical properties.

In recent years, effects of mechanical and physical properties of nanoscale inclusions on particle reinforced composites are studied by many researchers. Elasticity of the constitutive phases, size, volume fraction and dispersion of nanoparticles have effects on macroscopic properties of nanocomposites. In order to obtain the desired improvements, nano-inclusions should be dispersed properly, aggregation and agglomeration of particles should be avoided. Apart from the factors listed, the interface and interphase regions that occur between the matrix and the inclusion also play a significant role on the macroscopic behavior of composites. In order to design a composite system with improved and desired characteristics, the interface and the interphase region should also have desired properties.

2.1 Formation of Interphase

Polymer nanocomposites consist of at least two phases, the polymer matrix and the nano-inclusion as the reinforcement phase. Optimization of the properties of constitutive phases as well as the composed interphase are key factors to have improved characteristics. Unlike micro-scale reinforcement elements, nanoscale reinforcement elements have larger surface to volume ratio. Depending on the dispersion state and surface area of the interfacial region, the interphase can be also an effective component on determination of the final properties.

Chemical composition, chemical polarity and morphology of the phases of nanocomposites cause the formation of interphase regions more complex than conventional composites. The mismatch in chemical, physical and mechanical properties between the polymer matrix and the reinforcement element is considered to be the driving force for the formation of interphase region. Depending on the differences in interactions between phases, interphase formation mechanisms may occur in different ways. However, the formation mechanisms of the interphase are out of the scope of this thesis, for further reading, reader may refer to the reference book [10].

As seen in Fig. 2.1, the two-dimensional surface composed due to interactions between matrix and inclusion is called the interface. However, the three-dimensional region, which has a specific thickness, developed between the matrix and inclusion phases is called the interphase region. The interactions that occur between the inclusion and the matrix may affect the properties of interphase region. These interactions determine the dispersion state of inclusions inside the matrix and as a result the interfacial surface area. Interface has a very thin thickness so it is assumed to be a surface, i.e., a two-dimensional domain. On the other hand, the interphase region has an apparent thickness which corresponds to a significant volume around the inclusion. So the interphase region is treated as a three-dimensional object. Since the thickness of the interphase region is assumed to be significant, the volume fraction corresponding to this phase is also assumed to be significant. When the volume fraction of the inclusion increases, it is also expected to have a higher volume fraction of the interphase.

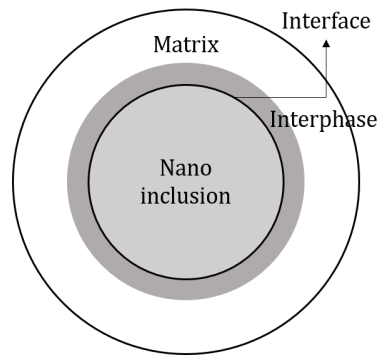


Figure 2.1: Illustration of a polymer nanocomposite system and two-dimensional interface and three-dimensional interphase region

It is accepted that the interphase region has different physical, chemical and mechanical properties compared to the bulk polymer matrix. Structural or chemical changes in the interphase region may affect the entire composite structure. Due to the interphase region, the average cross-linking density or crystal morphology of the composite may be altered. Furthermore, the molecular mobility of polymer chains may be affected. The change in the molecular mobility results in the change of mechanical and dielectric properties of the overall composite.

An important aspect of the nanocomposites is the dispersion state of inclusions. In the production of nanocomposites, when the inclusions are added to the polymer matrix, undesired aggregation (assemblage of particles which are loosely coherent [11]) and agglomeration (assemblage of particles rigidly joined together [11]) of particles can occur. These are not preferred and should be avoided when possible. In Fig. 2.2, well dispersed, aggregated and agglomerated particles are shown. The dispersion states corresponding to SEM images are illustrated in Fig. 2.2. The formation of clusters may be resulted due to van der Waals forces or chemical bonds between nanoparticles. Volume fraction of nanoparticles is sometimes attributed to aggregation/agglomeration state in some studies. Different researchers report that the change of volume fraction of inclusion may alter the size of the cluster (aggregation) for different composite systems [12, 13]. In a well-dispersed state, the interface can play a key role in composite behavior [12, 14, 15]. When the surface interactions between nanoparticles are weak while the surface interactions between the matrix and particles

are strong, desired, well-dispersed state is obtained. Many researchers have reported that the distribution of inclusions which have different geometries and structures in the polymer matrix can improve optical [16], thermal [17], electrical [18] and mechanical properties [19] of the composite.

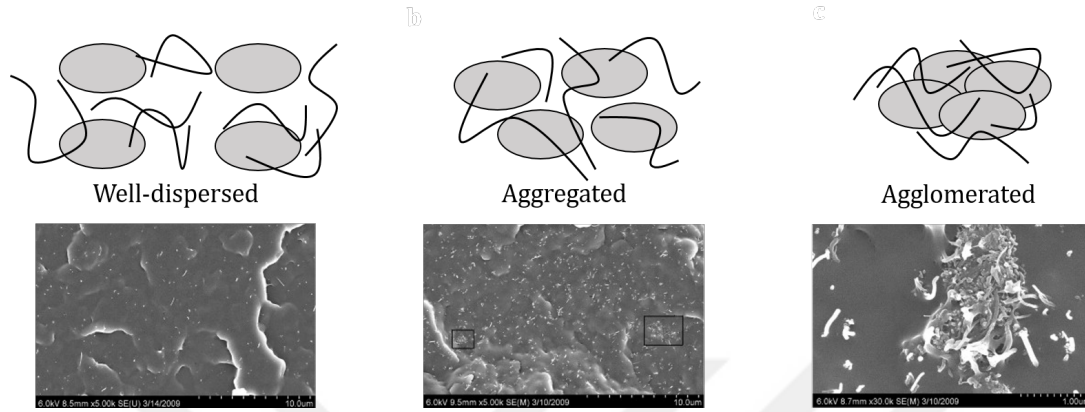


Figure 2.2: Above line: Illustration of different dispersion morphologies of a nanocomposite system. Below line: SEM images of PP/Carbon Nanotube systems with different volume fractions to show corresponding morphologies (a $\phi = 0.6\text{vol}\%$, b and c $\phi = 4.4\text{vol}\%$) [1]. Please notice that, in order to show the agglomeration, image c has a higher resolution than a and b.

It is extremely difficult to make definitive statements on the intrinsic properties of the interphase region. There is a lack of agreement on properties of the interphase region due to variety of composite systems and the manufacturing methods. The formation and the properties of interface and interphase regions depend on the type and dimensions of the polymer composite system. The structure of the interface can be affected by the surface thermodynamics especially surface energies and the resulting favourable or non-favourable interactions. It has been shown by many researchers that the structure and the properties of polymers result in different characteristics in composite systems. Whether the polymer matrix is a thermoset or thermoplastic, and whether it is amorphous or crystalline/semi-crystalline can affect the overall characteristics of a specific composite system.

The interphase region ensures the load transfer mechanically. This result has been shown for different reinforcement elements and matrix systems by experiments as

well as molecular dynamics simulations [20–23]. The interphase region contributes to reduction in the growth rate of fatigue cracks. Addition of inclusions to the polymer matrix may improve the fracture toughness and the fatigue resistance of polymer systems [24, 25]. Intrinsic interphase properties and the interfacial bond strength between the matrix and inclusions affect the fatigue strength of composites.

The existence of the interphase region may also improve the damping behavior of the composite. It has been reported that weak adhesion forces improve the damping properties of the overall composite significantly [26]. When there is a stiff interphase region between the matrix and inclusion, interface sliding may be prevented and as a result the storage modulus of the composite increases, while the loss modulus decreases. Remembering the definition of the damping ratio, a strong interphase results in a lower damping ratio. Therefore, to have enhanced damping characteristics, a softer interphase region is preferred. However, this weak adhesion region may cause insufficient load transfer. The interphase region has an important role for the improvement of mechanical properties of nanocomposites. The necessity to have a clear understanding and accurate modelling of the interphase structure is clear.

2.2 Experimental Methods for Interphase Characterization

Improvement of mechanical properties of polymer nanocomposites can be achieved with different mechanisms. For instance, dispersion state of particles is an important aspect. Arrangement of inclusions aligned with the direction of load also plays a significant role. And as outlined in the previous section, interphase formation is also a key factor for mechanical reinforcement of nanocomposites. Therefore, characterization of the interphase region is very important. After characterization of the interphase, the obtained properties and dimensions can be used to model effective properties of composite systems.

The experimental methods used for determining the properties of the interphase region can be divided into two categories, direct and indirect measurements [10]. As name indicates, in direct measurements, a local probe is used to obtain the properties directly. However, in indirect measurements, a local measurement is not conducted,

rather a macroscopic measurement is performed. To this end, responses of individual constituents other than the interphase to a systematic change are determined first. Then the overall response of the composite to the same systematic change is obtained. Knowing individual responses and the overall behavior, interphase properties can be deduced from the observed changes.

2.2.1 Direct Measurements

Nanoscale pull-out tests have been performed and widely used by different researchers to determine the micromechanical properties like the interfacial shear strength [27–29]. The single-fibre pull out test is a very common test for CNT and fiber reinforced composites. In this test technique, a single fiber inside the matrix is pulled out and the shear strength is measured. This measured shear strength value is used to evaluate the interactions between phases [30]. Furthermore, obtained fracture surfaces may indicate whether the interactions between the phases are sufficient to have proper load transfer. As seen in Fig. 2.3, for the composite system PEEK/CNT, first a tension test is performed [2]. After fracture occurs, as seen in the middle figure there is a single fiber isolated from the other reinforcement elements. This case corresponds to a single fiber pull-out test. The TEM image shows that the surface of CNT is smooth and it seems there is no bond between CNT and matrix. As a result of the fracture image it is reported that the interactions between phases are weak and there is insufficient load transfer.

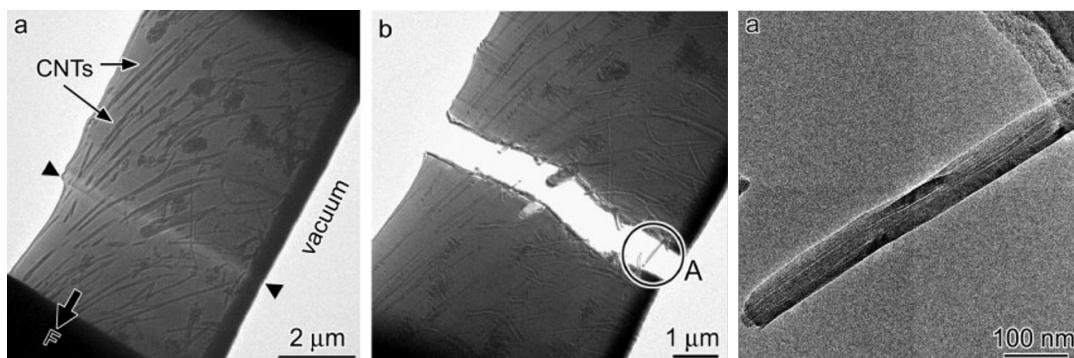


Figure 2.3: PEEK/MWCNT composite system, tension test, as a result obtained single fiber pull-out test condition and corresponding TEM image [2]

Single fiber pull-out tests can be performed when the reinforcement phase is a fiber. When the reinforcement element is a spherical particle, this test cannot be performed. Other than the pull-out test, the push-out and the microbond testing techniques are used to determine the properties of the surface debonding characteristics of composites. In microbond and pull-out testing methods, the shear strength is measured usually by observing the force required to pull a single fiber outside the matrix axially. However, in order to make such pull-out measurements the length of the embedded fiber is an important parameter. The fiber length should not be too small to break before the fiber is released. The microbond testing technique is discovered in order to overcome this problem [31]. In the microbond testing, instead of a single fiber, a fiber inside of a droplet of the matrix phase is pulled. This technique allows the existence of realistic interphases after curing operations. This is a very common technique and used by different researchers, [32–35].

Direct measurement methods use a local probe in the region of deformation. In the pull-out testing techniques, different scanning probe microscopy methods are utilized. For the estimation of the interfacial fracture energy of CNT reinforced polymer nanocomposites, for example Polyethylene Butene/MWCNT (Multi-walled carbon nanotube) composite system, atomic force microscopy and pull-out testing are utilized. Using the length of the fiber and the maximum pull-out force this energy estimated. Barber et al. [36] reported a relatively strong interface as a result of these measurements. For a PEEK/MWCNT composite system, an atomic force microscopy cantilever is utilized to measure the elastic deformation and the local value of interfacial shear strength [2].

Raman spectroscopy is a nondestructive testing method which is based on Raman scattering. When photons from a laser source interact with molecules of a material, photon's energy is shifted up or down. This up-down shift is a measure of vibrational modes of the material. The Raman spectroscopy is another popular technique to observe the interactions and measure the interfacial shear strength between matrix and reinforcement element. The Raman spectroscopy is usually performed to detect the vibrational modes of molecules, which can be used to examine whether the load transfer takes place. This technique gives insight for interactions and the interfacial shear strength by measuring the strain transferred to the reinforcement phase, such as CNT.

If the stress applied to the composite material is transferred to the CNT, the Raman peaks could shift a few cm^{-1} . Roy et al. [37] proposed a new technique to measure the interfacial shear strength with Raman spectroscopy. This testing technique is performed by different researchers [38, 39] to map the stress and strain distributions.

Atomic force microscopy (AFM) is another common technique to measure local properties of materials. The AFM is a type of scanning probe microscopy, which has a very high resolution that can be used for nanoscale observations. In the AFM there is a sharp probe which is placed at the tip of a cantilever to scan the substrate's surface. Topographical images, force-distance curves can be obtained by interactions between the probe and the substrate's surface. When the tip is close to the surface, interactions between the tip and the substrate cause bending of the cantilever. Up-down and left to right motions are monitored by a laser beam. Usually, techniques that are based on the local measurements have a deficiency due to the difficulty of separating the effect of the probe surface.

For example, the AFM can be used to evaluate the difference in molecular mobility of different regions of nanocomposites [40]. In this work, Tadiello et al. [40] observed that there is a region with reduced mobility that corresponds to the interphase region for Rubber/SiO₂ composite system. Transmission Electron Microscopy (TEM) is used and AFM morphological analysis is performed to evaluate the thickness of the interphase layer. For the same composite system, Tian et al. [41] used AFM measurements and observed that there are double layers around the inclusion corresponding to the interphase. For rubber nanocomposites **rubber bound** is another common term for the interphase. These aforementioned double layers are loosely bounded rubber (LBR) and tightly bounded rubber (TBR). The thicknesses of LBR and TBR were also reported. Brune et. al [42] used the AFM technique to observe the existence of the interphase and measure the elastic modulus of this region. They observed that the interphase properties change gradually. They also compared the experimental results with finite element analysis results. For a Rubber/CNT composite system the interphase region is characterized with TEM images and AFM measurements in [43]. The Young's modulus maps obtained from AFM measurements show that there is a gradual change in the elastic modulus. From these observations, the thickness of the interphase region is obtained. A different composite system that consists of reinforce-

ment elements, Thermoplastic Polyurethane (TPU), nano-fibrils, and binding matrix phase Polytetrafluoroethylene (PTFE) is characterized with different techniques [44]. Huang et al. [44] also reported an interphase region with gradually changing elastic modulus. Thickness and elastic properties of this region are obtained with AFM measurements.

The nano indentation method is a widely used method for measuring the hardness of nano-scale materials. Like macroscopic indentation techniques, a force is applied to a nano indenter with known geometric and material properties, and the hardness is calculated from the resulting displacement and the indentation load. Depth-dependent properties of materials are determined by continuous hardness measurements. In these methods, a reduced elastic modulus is obtained experimentally using the geometry, area of the indenter and slope of unloading curve. Then, using the experimentally obtained reduced modulus, the elastic modulus of composite can be deduced as follows.

$$E_r = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_C^2}{E_C} \quad (2.1)$$

In (2.1), E_i and ν_i correspond to the Young's modulus and the Poisson ratio of the indenter, while E_C and ν_C are the overall Young's modulus and the Poisson ratio of the composite.

The use of nano indentation for mechanical characterization has been extended to multiphase systems. Some researchers used AFM measurements for nano-scale indentation tests. The AFM measurements can produce results for vertical and torsional forces as a function of indentation depth. Then using the contact mechanics equations the Young's modulus of the interphase can be calculated [45]. For different nanocomposite systems, the hardness properties of the interphase were obtained by the nano indentation method. Obtained hardness values were then used to evaluate the elastic modulus of the interphase region. The gradual change of the elastic properties of the interphase region was also reported in these studies [46–48].

There are traditional thermal analysis techniques for polymers such as differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and differential

thermal analysis (DTA). The DSC provides information of heat flow changes, while the TGA gives mass change information and the DTA is used for temperature difference. Other than these thermal techniques, there is also a thermomechanical testing technique called Dynamic Mechanical Analysis (DMA). The DMA is a common technique to understand the viscoelastic behavior of materials by analysing them under controlled frequency, load and temperature. The DMA provides information about both the elastic and viscous nature of the material, critical temperatures like the glass transition temperature, and the complex moduli (storage and loss modulus) [49]. The DMA is a technique to characterize the viscoelastic behavior of materials by observing chain motions, molecular relaxations and their interactions. A dynamic mechanical imaging technique consisting of nanoscale dynamic mechanical analysis (nanoDMA) and AFM measurements was used to map dynamic mechanical properties of carbon fiber reinforced thermoset composites [50]. In another study in which direct measurement of the interphase of organic and inorganic nanocomposites was made by DMA, the presence of a soft interphase around the reinforcing elements was observed [51]. Cech et al. [52] used AFM, atomic acoustic force microscopy and nanoDMA measurements for exploring the interphase region of coated glass fibers (GF) in a Polyester/GF composite system.

For the characterization of structural and relaxation dynamics of the interphase, thermal analysis and nondestructive wide angle X-ray diffraction (WAXD) techniques can be performed. A PP/MWCNT composite system was investigated using these techniques [53]. The effective storage modulus of the composite for different volume fractions was measured at different temperatures and different frequencies. As a result of these measurements, it was observed that the rheological behavior of polymer samples with different volume fractions of inclusions did not change with temperature as expected, and this inverse temperature relationship was attributed to the presence of the interphase.

2.2.2 Indirect Measurements

In recent years, various studies have been conducted to examine the interphase properties indirectly. The main idea behind indirect measurements is to observe the overall

behavior of the composite system for a set of tests that can allow to distinguish properties. To single out the phase with unknown properties, the same set of tests are also performed to the known constitutive phases. This is an inverse problem approach in a way such that by modelling the experimental results, the properties of the interphase can be obtained. This inverse problem can be solved experimentally or by simulation methods, such as finite element method or molecular dynamics.

For example, the DMA is a common technique to understand the viscoelastic properties of a composite and it can be used to assess the viscoelastic behavior of the interphase indirectly by measuring the shifts and the change in the relaxation time distribution. Test conditions can be varied for temperature or frequency individually, simultaneously. Since the temperature and frequency (or time) data are not independent from each other, master curves corresponding to different frequencies can be obtained after DMA tests for different temperatures. When the properties of the overall composite, the bulk matrix and the reinforcement element are known from the master curves obtained, the dynamic modulus of the interphase can be calculated. For example in [54] the loss modulus of the Polycarbonate/CNT composite system is separated according to the contributions of the polymer matrix, the reinforcement element and the interphase.

For the solution of the inverse problem, sometimes some parameters can be obtained experimentally, such as the thickness of the interphase layer. Thus, by combining the experimentally obtained data and simulation techniques, more detailed information about the interphase and overall composite behavior may be comprehended. For example, Brinson et al. [55] used different interphase definitions in the modeling of the composite system with the finite element method after obtaining a deeper understanding of the interphase via AFM measurements. The interphase was modeled as a homogeneous phase or in a gradually varying manner and the appropriate parameters were determined [55].

Other than the mechanical properties, the dielectric relaxation of an interphase region can be deducted by indirect measurement methods as well. It was found that there is an unanticipated change in the dielectric constant of the overall composite. This can be attributed to the existence of the interphase. A consistent and efficient approach

for determining the dielectric properties of the interphase in polymer nanocomposites by solving the inverse problem with the adaptive optimization method is proposed in [56]. Note that the mechanical properties of the interphase can also be obtained with this method.

2.3 Interphase Modeling Approaches

The interphase region can have a significant volume ratio depending on the thickness of the region in polymer matrix nanocomposites. Although, nowadays interphase properties such as thickness, elastic modulus and density can be measured with experimental methods described above, the characterization in nano-dimension is still a difficult process with many problems and uncertainties.

It is possible to obtain the effective (macroscopic) behavior of the composite with classical mechanical tests. Homogenization methods for multiphase heterogeneous media is a very broad topic and it is still an active research area. To this end, the homogenization problem has been addressed by many different methods such as finite element analysis, empirical, semi-empirical models, micromechanical and statistical methods. An extensive summary of the homogenization theory including, methods and applications from the literature, is given in Chapter 3 of the thesis.

Recently, it has been observed that the interphase region is generally inhomogeneous throughout the thickness. This observation is realized by means of the frequent use of the AFM for the characterization of interphase. The models in which the interphase properties take different values depending on the position referred to as the **graded interphase** in the literature. Different mathematical models are used to model the position-dependent elastic moduli (Young's modulus, bulk modulus, shear modulus) distribution.

When modeling the graded-interphase in spherical nanoparticle composites, it can be assumed that the elastic modulus changes only in radial direction. Mean modulus of the interphase can be expressed as in (2.2) by integrating the position-dependent

elastic modulus.

$$\bar{E}_i = \frac{1}{r_i - r_f} \int_{r_f}^{r_i} E_i(r) dr \quad (2.2)$$

In (2.2), indices f corresponds to the reinforcement element and i to the interphase. E_i corresponds to the elastic modulus of the interphase, r is the radial direction from the center of the spherical inclusion and r_f and r_i are the radii of the inclusion and the interphase, respectively. Depending on how the elastic modulus of the interphase is modeled mathematically, the definition of the mean modulus may vary. The specific functional form of $E_i(r)$ has been assumed as constant, linear, power law, exponential by different researchers. Different mathematical models for the interphase region are illustrated in Fig. 2.4. Another method used by researchers is to assume a constant value throughout the thickness, apart from the variable elastic modulus approach depending on the position.

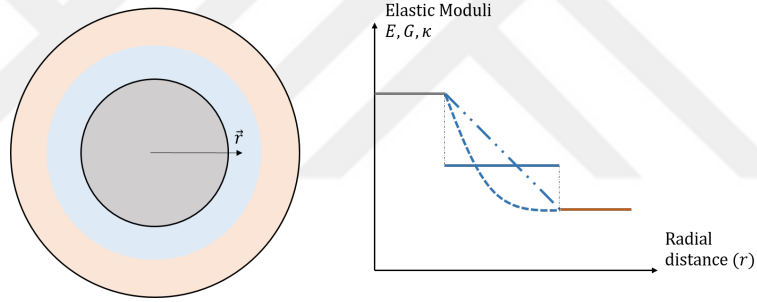


Figure 2.4: Different mathematical representations of elastic moduli for multiphase composite systems

A brief summary of modeling methods used by different researchers are given in Table 2.1. In Table 2.1, the modelling approach, the interphase model and a brief summary of the results are reported.

For the current study, the main aim is to calculate effective mechanical properties in the presence of interphase phase. The bonding between the matrix and the inclusion is assumed to be perfect. However, this is not very realistic and in order to model the nanocomposites realistically, the interfacial effects should be taken into account [57, 58]. As seen in Fig. 2.1, there is also *interface*, which has a very thickness,

almost zero-thickness, it is assumed to be a surface. In the thesis, proposed framework is limited to the perfect interface assumption. All examples are assumed to have perfect bonding, which corresponds to displacement and traction continuity across the interface. It is possible to model the interface according to displacement and traction jumps, general interface cases [59]. In [59], two analytical approaches were developed to account for general interface models. In [60], a new micromechanical model was proposed for composite materials with ellipsoidal inclusions. For the case of unidirectional composites, an analytical method was derived for homogenized and localized responses with imperfect interfaces [61].



Table 2.1: Interphase modelling approaches and obtained results in the literature

Researchers	Modelling Approach	Interphase Characteristic	Summary
Yao et al. [62]	Shear-lag model	Power law, linear	The effect of different graded interphase models on stress transfer for fiber composites
Bian et al. [63]	Analytical methods, FEA	Constant, power law	The effect and comparison of constant or varying interphase models on stress transfer for fiber composites
Xu et al. [64]	Micromechanics	Power law	A novel model for the graded evolutions of porosity and the elastic modulus of the interphase for non-spherical particles
Sabiston et al. [65]	Micromechanics	Linear, second order polynomial and exponential	A new structural model for the elastic behavior including the interphase is developed after examining different interphase models and comparing them with experimental data
Li [66]	Micromechanics	Radial-dependent function based on aspect ratio	Thermoelastic behavior model in the case of functionally graded interphase for multiphase composites
Ma et al. [67]	FEA	Power law	Modelling of very strong nanocomposites with interphase structure in plastic behavior and damage

Gülaşık et al. [68]	FEA	Continuous and smooth	A model based on the determination of the distribution of the properties of the interphase with the gradient elasticity theory
Taş and Gürses [69]	Micromechanics, FEA	Constant, linear and exponential	A two-level homogenisation approach model for functional interphase fiber composites
Sburlati et al. [70]	Analytical methods	Power law	Rethinking of Hashin limits with an interphase defined by the power law
Giannopoulos et al. [71]	FEA	Exponential	Multiscale hybrid FE method in the presence of interphase to determine the elastic properties of graphene-based nanocomposites
Boutaleb et al. [72]	Micromechanics	A higher order equation to account for separation of phases	Effect of an inhomogeneous interphase on initial yield surface
Ben et al. [73]	Analytical methods	Power law	Nonlinear cohesive model for surface separation in the coated inclusion problem
Cheng et al. [74]	Micromechanics, FEA	Linear, second order polynomial and exponential	A homogenization approach based on successive addition of interphase layers for the coated inclusion problem
Fankhänel et al. [75]	MD, FEA	MD based	After getting properties of interphase from MD simulations, an homogenization approach based adding the interphase layers in a full FEA model is discussed

Kim et al. [76]	Micromechanics, MD	MD based	A multiscale framework for Epoxy/Silica nanoparticles is discussed, on the first scale MD simulations are used for interphase characterization and this information is transferred to continuum model.
Odegard et al. [77]	Micromechanics, MD	MD based	Using an effective particle approach which is common for micromechanics, such as Mori-Tanaka method, different range of nanoparticle radii
Tserpes et al. [78]	FEA	A continuous and non-monotonous function is defined	Modelling of yield strength for PP/MWCNT with a two-scale FEM approach when clustering and interphase effects are included in the model



CHAPTER 3

HOMOGENIZATION THEORY

Homogenization theory is well-established and well-researched area for analyzing heterogeneous materials. The **effective** or **homogenized** properties of a heterogeneous medium can be calculated with different numerical or analytical techniques. In general, every material in nature exhibits heterogeneous behavior at some scale. Particle reinforced composites such as polymer matrix nanocomposites are a typical example for heterogeneous materials. Generally, there are at least two phases, the matrix and the inclusion in these materials. Usually the length scale corresponding to the inclusion is smaller than the length scale corresponding to macrostructure.

In a system, defects such as pores, cracks, grain boundaries, secondary phases or particles added for the reinforcement can be the reasons for heterogeneity. Accounting for all these effects to model the composite can be an involved and difficult procedure. Therefore, instead of a very detailed and complex model based on the microstructure, a macroscopic behavior of material can be sought in some cases. Homogenization theory is used to understand the overall macroscopic behavior of heterogeneous media as illustrated in Fig. 3.1.

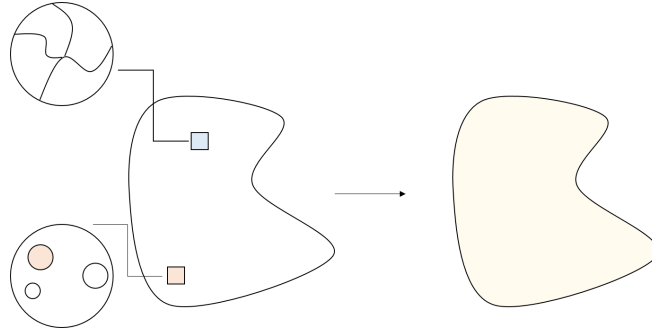


Figure 3.1: An illustration of homogenization problem, a real material can have defects or other heterogeneities but by means of homogenization theory homogeneous material can be replaced

Understanding of how a heterogeneous material behaves in a macroscopic scale is important. In order to estimate bulk properties of heterogeneous materials various homogenization techniques are utilized. Bulk properties of heterogeneous materials are not limited to mechanical properties, it can be thermal or electrical as well. These homogenization techniques can be categorized as follows, classical bounds such as the Voigt-Reuss bounds, variational/energy-based methods such as the Hashin-Shtrikman bounds, micromechanics based methods such as the Mori-Tanaka method, the self consistent scheme, empirical, semi-empirical methods such as the Halpin-Tsai model and statistical methods. The latter most approach is out of scope of this thesis, therefore it is not further discussed. However, for the further reading of this subject, the reader may refer to reference books [79] and [80].

3.1 Homogenization Techniques

The Voigt and Reuss bounds are very well-known and one of the earliest works regarding the homogenization of heterogeneous media. The Voigt bound assumes a constant strain field [81], while the Reuss bound assumes a constant stress field in an heterogeneous material [82]. As a result of these assumptions, these two approaches create an upper bound and a lower bound for the material. The Voigt bound gives the maximum possible moduli of the material while the Reuss bound corresponds to the minimum possible moduli. These methods generally provide very broad limits

for a heterogeneous medium. In order to calculate the effective moduli, both methods use elastic moduli of constituents (E_m , the elastic modulus of matrix and E_i , the elastic modulus of inclusion) and corresponding volume fractions (ϕ_m , the volume fraction of matrix and ϕ_i , the volume fraction of inclusion), as shown in (3.1). Any information regarding topology is not present in these methods.

$$\begin{aligned} E_{\text{Voigt}} &= \phi_m E_m + \phi_i E_i \\ \frac{1}{E_{\text{Reuss}}} &= \frac{\phi_m}{E_m} + \frac{\phi_i}{E_i} \end{aligned} \quad (3.1)$$

These two bounds create an envelope energetically such that any heterogeneous system should be placed between these limits. Using these known bounds, the Voigt-Reuss-Hill average can be calculated as well. This is a simple average that uses the Voigt and the Reuss bounds, i.e.,

$$E_{\text{Hill average}} = \frac{E_{\text{Voigt}} + E_{\text{Reuss}}}{2} \quad (3.2)$$

A two phase composite is modeled for illustration purposes using different homogenization techniques. The overall macroscopic or effective properties are calculated for inclusion volume fractions ranging from 0 to 1. Material properties for the illustrative two-phase composite are given in Table 3.1. Using given example problem, the Voigt bound, the Reuss bound and the Hill average results are illustrated in Fig. 3.2. These bounds are known as the "Rule of mixtures" and this derivation can be extended to different properties of heterogeneous materials such as mass density or ultimate tensile strength.

Table 3.1: Material properties of two-phase composite system for homogenization examples

Phase	Young's modulus (E) [GPa]	Poisson ratio (ν) [-]
Matrix	3	0.30
Inclusion	70	0.27

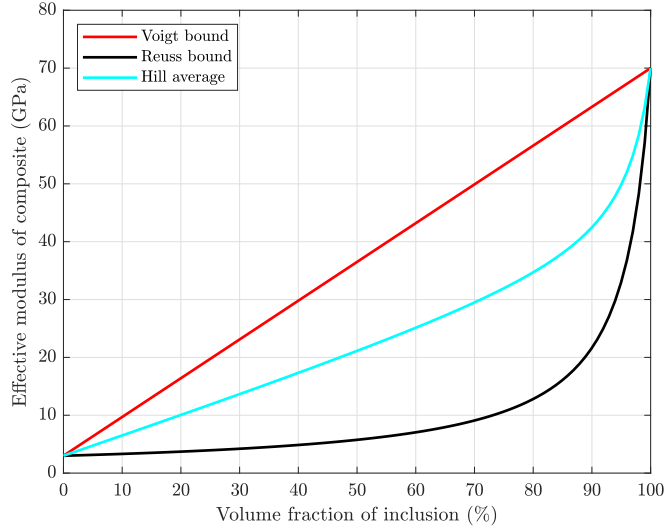


Figure 3.2: Comparison of Voigt and Reuss bounds and the Hill average for spherical inclusions

The Hashin-Shtrikman (H-S) approach provides another well-known upper/lower bound pair for heterogeneous media [83]. The constituent's elastic moduli and the corresponding volume fractions are the only inputs of the approach. However, the corresponding bounds are narrower than the Voigt and the Reuss bounds. The Hashin-Shtrikman approach calculates the bounds on the bulk and the shear moduli by a variational approach. Derivation of the elastic moduli is based on the minimization of strain energy. These bounds can be used for thermal conductivity, electric conductivity, dielectric permittivity as well. The H-S variational principle is not created for two-phase heterogeneous media only, for multi-phase systems related equations can be found in [83]. Here as an example, a two-phase system is used and homogenized

properties for the shear and the bulk moduli are given in (3.3).

$$\begin{aligned}
K_{HS+} &= K_i + \frac{\nu_m}{\frac{1}{K_m - K_i} + \frac{3\nu_i}{3K_i + 4G_i}} \\
K_{HS-} &= K_m + \frac{\nu_i}{\frac{1}{K_i - K_m} + \frac{3\nu_m}{3K_m + 4G_m}} \\
G_{HS+} &= G_i + \frac{\nu_m}{\frac{1}{G_m - G_i} + \frac{6(K_i + 2G_i)\nu_i}{5G_i(3K_i + 4G_i)}} \\
G_{HS-} &= G_m + \frac{\nu_i}{\frac{1}{G_i - G_m} + \frac{6(K_m + 2G_m)\nu_m}{5G_m(3K_m + 4G_m)}}
\end{aligned} \tag{3.3}$$

Fig. 3.3 shows how H-S bounds create a narrower bound.

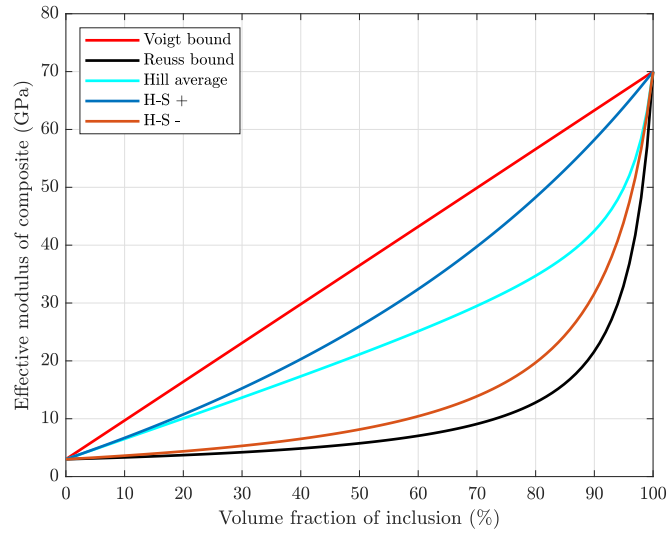


Figure 3.3: Comparison of the Hashin-Shtrikman upper (H-S +), the Hashin-Shtrikman lower (H-S -), the Voigt, the Reuss bounds and the Hill average for spherical inclusions

Another category of homogenization approaches is the inclusion based, micromechanics methods. Micromechanics-based homogenization techniques are originated from very well-known Eshelby's inclusion problem [84]. In the Eshelby's inclusion problem, there is a heterogeneity which can be inclusions as well as cracks or voids. While this inclusion is removed from the surrounding matrix, the assumption states that there is a uniform strain, **eigenstrain** and the inclusion experiences no stress. But since there is a matrix around the inclusion, the inclusion cannot be in a zero stress

state, instead both of the constituents are expected to deform and experience stress fields. The Eshelby's inclusion solution is based on this problem. By using the superposition principle of linear elasticity and Green's functions, constituents' stress and strain fields are calculated. Eshelby tensors are given in Chapter 4 for spherical and ellipsoidal (with an arbitrary aspect ratio) inclusions.

Using the solution of Eshelby's inclusion problem, different micromechanics-based methods are suggested, namely the dilute assumption, the Mori-Tanaka method [85], the Double-Inclusion method [8], self-consistent scheme [86, 87]. Usually, the Eshelby's inclusion problem deals with a single inclusion in two-phase composites. The volume fraction of inclusion is expected to be low. These conditions correspond to the dilute solution in which inclusions are embedded in an infinite medium which has matrix properties. Interactions among inclusions are expected to be non-existing and since the volume fraction of inclusions are low, this is an acceptable assumption. The strain concentration tensor ($\mathbb{A}_{\text{dilute}}$) and the corresponding elasticity tensor ($\mathbb{C}_{\text{dilute}}$) for the dilute solution are given in (3.4). $\mathbb{C}_m$, $\mathbb{C}_I$, $\mathbb{S}$, $\mathbb{I}$ are the elasticity tensor of matrix, elasticity tensor of inclusion, the Eshelby tensor and the identity tensor, respectively. This technique is not valid above the dilute limit. As it can be observed from Fig. 3.4, the effective modulus is underestimated.

$$\begin{aligned}\mathbb{A}_{\text{dilute}} &= \left[\mathbb{I} + \mathbb{S} : \mathbb{C}_m^{-1} : (\mathbb{C}_I - \mathbb{C}_m) \right]^{-1} \\ \mathbb{C}_{\text{dilute}} &= \mathbb{C}_m + \phi_i (\mathbb{C}_I - \mathbb{C}_m) : \mathbb{A}_{\text{dilute}}\end{aligned}\tag{3.4}$$

The dilute solution has a deficiency above the dilute limit, which is due to the lack of interactions between two fillers. In order to overcome this problem, a method taking the interactions into account is needed. The Mori-Tanaka method is a very popular method since it is an explicit, closed form expression which is given in (3.5) [85].

$$\begin{aligned}\mathbb{A}_{\text{M-T}} &= \left[\mathbb{I} + \mathbb{S} : \mathbb{C}_m^{-1} : (\mathbb{C}_I - \mathbb{C}_m) \right]^{-1} \\ \mathbb{C}_{\text{M-T}} &= (\phi_m \mathbb{C}_m + \phi_i \mathbb{C}_I : \mathbb{A}_{\text{M-T}}) : (\phi_m \mathbb{I} + \phi_i \mathbb{A}_{\text{M-T}})^{-1}\end{aligned}\tag{3.5}$$

This method relates the average stress and strain fields in the inclusion to corresponding fields in the matrix, so that the interactions among the inclusions are taken into

account. This technique is limited to aligned ellipsoidal inclusions only. In Fig. 3.4, the H-S lower bound and the Mori-Tanaka estimates look like they coincide, indeed the results are very close but not identical. The Mori-Tanaka method can be used for different ellipsoidal geometries and different material orientations. Another popular technique is the Double-Inclusion model [8], details of which are given in Chapter 4.

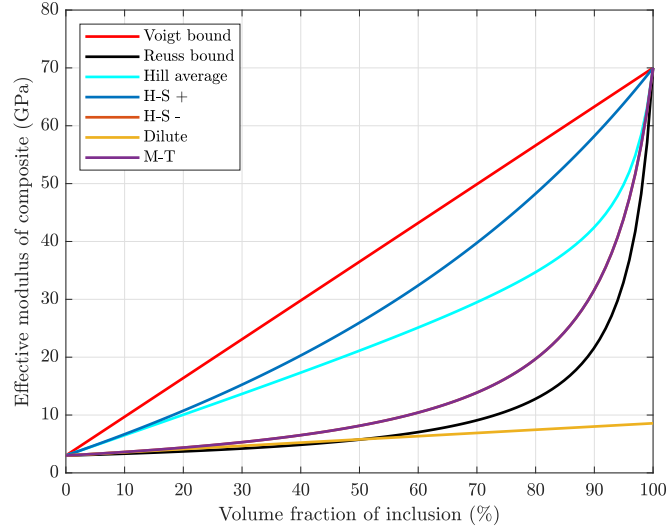


Figure 3.4: Comparison of various micromechanics-based homogenization techniques for spherical inclusions

The Halpin-Tsai model is accepted as a semi-empirical model, which is used to determine the effective modulus of the fiber reinforced composites generally. This method accounts for the geometry, packing, aspect ratio of the inclusion and loading conditions as well. There is a geometry parameter (ζ) in the relations to describe the listed variables. Transverse and longitudinal moduli of the composite can be calculated in this approach. The equations regarding the composite moduli are given in (3.6).

$$E_{\text{Halpin-Tsai}} = E_m \left(\frac{1 + \zeta \eta \phi_i}{1 - \eta \phi_i} \right) \quad (3.6)$$

$$\eta = \frac{E_i/E_m - 1}{E_i/E_m + \zeta}$$

Here ζ parameter changes according to whether transverse or longitudinal modulus is searched. For the case of longitudinal modulus $\zeta = 2\frac{l}{d}$ is taken, and for the trans-

verse modulus, $\zeta = 2$ is taken. l and d correspond to the length and the diameter of the fiber. As expected for the transverse modulus $l = d$ results in $\zeta = 2$. For the case of spherical two-phase composite, $l = d$ is used, therefore obtained result gives equal transverse and longitudinal moduli. Comparison with different homogenization techniques can be summarized in Fig. 3.5a.

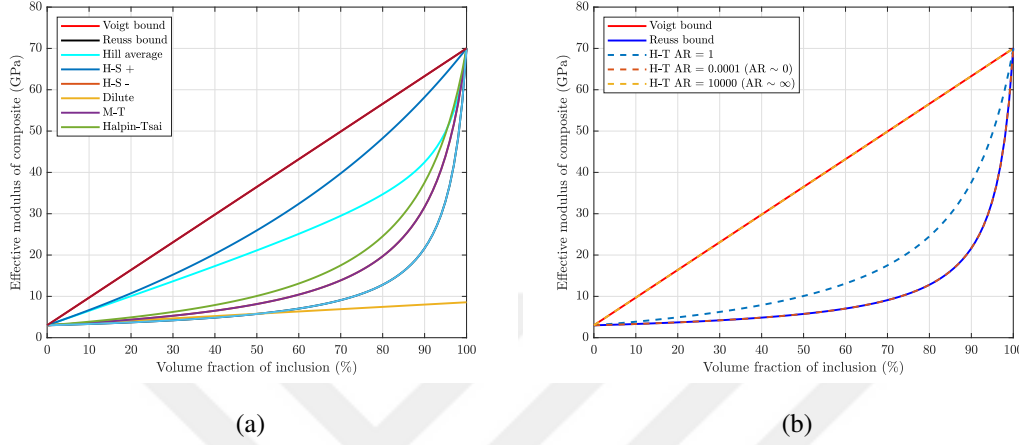


Figure 3.5: (a) Comparison of Halpin-Tsai model with other homogenization methods, (b) Effect of the aspect ration in Halpin-Tsai model

When Fig. 3.5b is examined, it can be seen that ζ parameter changes the effective modulus of composite significantly. There are specific limits for this model. When the aspect ratio becomes zero these results coincide with the Reuss bound and when the aspect ratio becomes infinity, the Voigt bound is obtained.

3.2 Coated Inclusion Problem

In order to calculate the effective mechanical properties of heterogeneous materials properly, mechanical properties and volume fractions of each constituent as well as the topology should be taken into account. To increase the overall performance of a polymer nanocomposite system, various efforts have been made. For a simple two-phase composite system, other than matrix and inclusions, the existence of a third phase at the interface of these two-phases has been accepted for many years [88].

The properties of this mentioned interphase region significantly affect the performance of the composite material. Since the establishment of weak or strong interface interactions between the polymer matrix and the inclusion affects the composite's behavior, it should be taken into account when modeling the composite. Some properties of the interphase can be obtained experimentally [41–44, 52, 89], or by molecular dynamics and similar simulation methods [75–77]. In order to model the macroscopic behavior of nanocomposite materials, it has become a necessity to investigate the general structure and properties of the interphase region.

There are different approaches in the literature for modeling the interphase and analyzing the effect of the interphase properties on the macroscopic behavior of the composite. The proposed method in the thesis is based on the approach of evaluating the interphase as a coated region or a layer around the inclusion. This approach, which is used to estimate effective elastic moduli of multi-phase composites, considers the interactions between the phases during the homogenization of the heterogeneous medium. These approaches are known in the literature as the "coated inclusion problem". This problem has been discussed in the literature number of times and many solution methods have been proposed over the years. Works dealing with the coated inclusion problem are quite extensive in the literature, following works [79, 90, 91] are suggested for further reading.

In order to determine the effective mechanical properties of the n-phase heterogeneous environment, a model called Composite Sphere Assemblage was proposed by Hashin in 1962 [92]. The Composite Sphere Assemblage is based on Eshelby's well-known analytical results [84] and it is a method used to determine the limits of bulk and shear moduli of spherical and cylindrical inclusion problems. In the thin interphase approach proposed by Walpole [93], the interphase is considered as a very thin layer between the matrix and the reinforcing element. During the determination of the elastic properties of this medium, the interphase is assumed to be absent and the stress distribution and the effective elastic moduli of the n-phase composite are calculated analytically by using Hill's interfacial operators [94]. Later, Benveniste et al. [87] introduced a micromechanical-based approach using the "average stress in the matrix" concept developed by Mori-Tanaka [85]. Since for high inclusion volume fractions the Mori-Tanaka model does not work properly, another micromechanical-

based approach known as the Generalized Self-Consistent Scheme (GSCS) is developed [86, 95]. In this method, the phase that creates heterogeneity is assumed to be embedded in an environment with effective composite properties. By means of an iterative algorithm, effective thermo-elastic properties of the composite can be calculated. In 1993, the Double-Inclusion model was presented by Hori and Nemat-Nasser [8]. The Double-Inclusion model is one of the most well known, accepted and implemented methods by the date. This model deals with the general case of coated ellipsoidal inclusions in an anisotropic medium in which the inter-inclusion interaction is also evaluated. However, the simplifying assumption of uniform strain field inside the coating is still accepted.

Following these pioneer works in the coated inclusion problem, significant amount of research has been conducted in this area. Within the framework of spherical elasticity the general case of anisotropic elasticity, micromechanics models, based on Green's functions technique and integral equations, are proposed. To solve the local stress and strain fields the Green's function technique and integral equations were utilized, then effective moduli were obtained by using GSCS [96,97]. In [98] effective moduli and stress and strain fields for the composite were obtained for fibre-reinforced composites by using GSCS. In order to calculate effective thermoelastic moduli of multi phase heterogeneity, effective medium field approximation approach was used [99]. Moreover, an explicit Eshelby-type estimator was developed to calculate equivalent moduli in [100]. Different solution techniques for the replacement procedures were discussed [101] and [3], various mean-field homogenization procedures were used for the replacement procedures. The Annular Coated Inclusion (ACI) model was developed for spherical inclusions [102] and later it was extended to cylindrical inclusions [103]. Furthermore, these approaches have been extended to the other important phenomena, such as viscoelasticity [104–107], graded interphase [64, 66, 108, 109], magneto-electro-elasticity [110, 111] and piezoelectric (PZT) particles [112, 113].

In 2006, Friebel et al. [3] proposed two new techniques, two-level and two-step homogenization, for the general solution to the coated inclusion problem. The two-level approach is based on the matrix seeing the inclusion and the interphase, surrounding coating region as a composite structure. Generally, two-level homogenization methods have a replacement procedure at the first level of homogenization. At the first

level, the coated inclusion is treated as a two-phase composite and is homogenized using different methods. At the end of the first level, the new effective inclusion is placed inside the matrix, then at the second level the matrix and the effective inclusion can be homogenized in order to model the overall effective composite behavior. The two level homogenization scheme has been implemented by different researchers as a common practice. Some researchers used modified Rule of Mixtures, [114], while some extended micromechanics-based frameworks, [107, 115], using different effective medium approximations, such as dilute model, [116], generalized self consistent scheme (GSCS), [101, 117], Mori-Tanaka model, [118], Double-Inclusion model, [109].

Another method proposed by Friebel et al. and accepted by many researchers is the two-step homogenization approach [119]. In this approach, the coating is considered to be another reinforcing element with different set of properties. This approach is based on the concept of pseudo-grain, which can be thought of as imaginary regions in a composite. There are two regions, the region consisting of the matrix and the inclusion and the region consisting of the matrix and the coating layer (interphase). The coating is treated as the inclusion in this approach. These two different imaginary regions are used to calculate the effective modulus after they are homogenized individually. Both aforementioned methods are schematically visualized in Fig. 3.6.

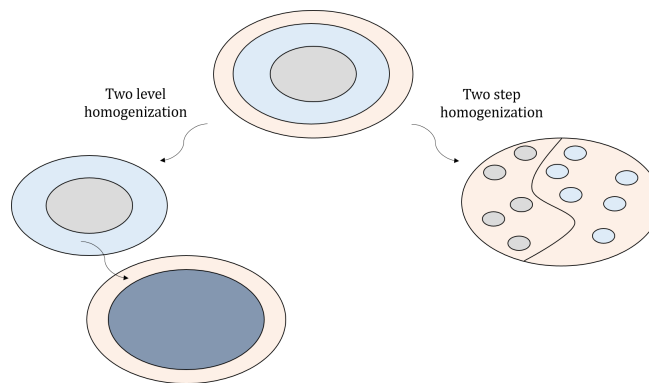


Figure 3.6: An illustration of two-level and two-step homogenization techniques proposed by Friebel et al. [3]

In many studies for different polymer composite systems, it is assumed that the polymer matrix phase and the interphase are viscoelastic, while the inclusion is assumed

to be elastic. For this systems a viscoelastic homogenization is needed. In order to obtain macroscopic viscoelastic properties, time domain or frequency domain homogenization is conducted. Utilizing Elastic-Viscoelastic Correspondence Principle, expressions obtained for elasticity can be derived for viscoelasticity in the frequency domain as well [120]. This well-known approach enables to obtain viscoelastic properties in the frequency domain instead of time domain by means of Laplace transform. By simply substituting the complex moduli instead of the real moduli in the elastic formulation, analytical, semi-analytical, approximate solutions for an elastic problem can be extended to viscoelasticity.

Many researchers use the Dynamic Correspondence Principle to obtain solutions for the viscoelastic homogenization problem. Wang and Weng [121] used the Mori-Tanaka approximation to understand the influence of inclusion shape. They showed that for sphere inclusions obtained bulk modulus is identical to Hashin's CSA results [92] and well-known Hashin-Shtrikman upper and lower bounds. Brinson and Knauss [9] also studied the solution of two-phase viscoelastic homogenization problem with Mori-Tanaka (M-T) approximation and Finite Element Analysis, and discussed different analytic bounds. Later Brinson and Lin [4] used the proposed FEA approach and micromechanics based M-T method to investigate the effect of volume fraction and packing array type of inclusions. Cruz et al. [5] compared the M-T and the self consistent method predictions with experimental data for PET/Glass Beads. These predictions were based on the assumption that only two phases, the matrix and the inclusion are present in the model. Their results showed a discrepancy between experimental results and micromechanics predictions and they discussed that this difference might be explained with reduced molecular mobility region near the inclusion. Diani et al. [122] showed a similar discrepancy between experimental and Christensen and Lo's self-consistent predictions for Rubber/Carbon Black composites with different volume fractions. They suggested the existence of the interphase region with reduced molecular mobility, which affects mainly the rubbery behavior, in the low frequency range. A four-phase self-consistent model showed a good agreement with experimental results. Later Diani and Gilormini [123] proposed a morphological representative pattern in a self consistent framework in order to account for different morphological dispersions. Honorio et al. [106] investigated the aging in viscoelastic

framework for n-phase spherical coated inclusion problem where the Generalized Self Consistent Scheme, the M-T mean field approach and FEA results were employed.

To model the interphase, Fisher and Brinson [124] extended the Mori-Tanaka and Benveniste's micromechanics-based methods for multi-phase viscoelastic composites and compared the results with FEA solutions. It was assumed that the inclusion behaves elastically, while the matrix and the interphase are viscoelastic. They studied the effect of interphase stiffness and expressed that while the interphase is stiffer than the matrix FEA results and micromechanical approaches are in good agreement. However, when the interphase is softer than the matrix, mentioned methods show discrepancy. Friebel et al. [3] suggested a two-step method in order to overcome this problem in the soft interphase composites. For the first step of the homogenization, interpolative Double-Inclusion approach is suggested, later pseudo-grains are homogenized using Voigt model. Their two-step homogenized property results show better agreement with Fisher and Brinson's FEA results compared to the multi-phase M-T and Benveniste solutions. Schöneich et al. [104] proposed a two-level scheme in which coated effective inclusions are obtained using the D-I and the Reconsidered Double-Inclusion (RDI) model. Then, at the second level the classical M-T scheme is employed and the proposed formulation is compared with experimental results. Baral et al. [125] created a purely inelastic framework in which the coating layer is taken into account. Transformation Field Analysis (TFA) and the M-T were combined in this framework so that the overestimation due to uniform stress-strain assumption in mean field homogenization schemes is prevented. Viscoelastic homogenization framework with classic mean field homogenization methods is also extended to different phenomena usually discussed in elastic framework such as PZT particles [126], graded interphase [109].

The method proposed in the thesis is also a multi-level homogenization approach. In the first level, the inclusion and the coating (interphase) are homogenized by finite element method, then the effective inclusion and the matrix can be homogenized with the Double-Inclusion model based on micromechanics, so that the macroscopic behavior of the elastic or viscoelastic composite can be obtained.



CHAPTER 4

TWO-LEVEL HOMOGEZATION METHOD FOR COATED INCLUSION PROBLEM IN ELASTICITY

4.1 Homogenization Methodology for Linear Elasticity

4.1.1 Double-Inclusion Model

In order to estimate the effective moduli of multi phase composites, there are different approaches dealing with interactions, some well-known models are the composite sphere assemblage [92], the n-phase model [98], the generalized self-consistent model [86], the Double-Inclusion (D-I) model [8]. A detailed summary of the literature is presented in Chapter 3. In this work, the Double-Inclusion model, proposed by Hori and Nemat-Nasser [8], is used for the proposed homogenization technique and for comparison purposes. Therefore, first the tools that are used in the proposed model will be explained. These methods are the D-I model and the finite element based homogenization technique.

The coated inclusion problem in two dimensions is schematically shown in Fig. 4.1. In the matrix, interphase and inclusion regions, the elasticity tensor is assumed constant. Even though it is possible to model a graded elasticity tensor through thickness in the D-I model as reported by researchers, here a simplifying assumption is preferred. As a further simplifications, an isotropic, elastic behavior is assumed for each phase. Therefore, only two material constants are given, the Young's modulus E and the Poisson ratio ν in Table 4.1. Two cases are studied, namely, the interphase being softer than the matrix and the interphase being stiffer than the matrix. The corresponding Young's modulus for the soft and the stiff interphases are $0.1 \times E_m = 0.25\text{GPa}$ and

$10 \times E_m = 25\text{GPa}$. For both cases, $\nu = 0.3$ is chosen. In the micromechanics-based model proposed by Hori and Nemat-Nasser [8], the inclusions and coating phases are assumed to be ellipsoidal. Also, the inclusion and the coating are assumed to be coaxial. In Fig. 4.1, a sphere is demonstrated as a specific case of an ellipse and the coaxiality can be observed.

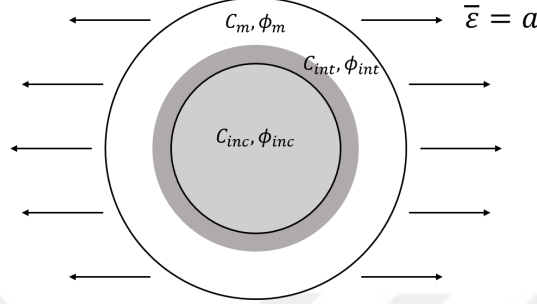


Figure 4.1: Coated inclusion problem in two dimensions, here subscript m corresponds to the matrix, while inc and int correspond to the inclusion and the interphase, respectively

Table 4.1: Material properties for the composite system

Material	Young's modulus E[GPa]	Poisson ratio (ν)
Matrix	2.5	0.34
Interphase	0.25 or 25.0	0.30
Inclusion	1000	0.30

The D-I model is not limited to isotropy, elasticity of phases, inclusion, its heterogeneity and infinitely extended homogeneous domain as stated originally in article *Double-inclusion model and overall moduli of multi-phase composites*, can be arbitrary. Average field quantities are obtained analytically like the self-consistent methods or the Mori-Tanaka method. The D-I model uses the outcomes of the Mori-Tanaka theorem to generalize the method for two-phase composites. The theorem was also extended to multi-phase composites and an analytical solution was reported. The coated inclusion problem can be solved by means of this extension. The elasticity

tensor of a multi-phase composite $\mathbb{C}$ is given in (4.1).

$$\begin{aligned}\mathbb{C} &= \mathbb{C}^{inf} : [\mathbb{I} + (\mathbb{S} - \mathbb{I}) : \Lambda] : [\mathbb{I} + \mathbb{S}\Lambda]^{-1} \\ \Lambda &= \sum_{i=1}^n \phi_i \Lambda_i\end{aligned}\tag{4.1}$$

where ϕ_i is the volume fraction of i^{th} phase, $\mathbb{C}^{inf}$ is the elasticity tensor of a infinitely extended homogeneous domain, $\mathbb{I}$ is the fourth order identity tensor, $\mathbb{S}$ is the Eshelby tensor for ellipsoidal inclusion [84]. The Eshelby tensor $\mathbb{S}$ for spherical geometry is given in (4.2). This set of equations is a simplification of the Eshelby tensor from an ellipsoidal inclusion to a spherical inclusion due to isotropy. Generally, aspect ratio of the ellipsoid is a parameter for the Eshelby tensor. Whenever aspect ratio is chosen as one, an ellipsoid is simplified to a sphere. Other parameter to calculate the Eshelby tensor is the Poisson ratio of the constituent.

$$\begin{aligned}S_{1111} &= S_{2222} = S_{3333} = \frac{7 - 5\nu}{15(1 - \nu)} \\ S_{1122} &= S_{2233} = S_{3311} = S_{1133} = S_{2211} = S_{3322} = \frac{5\nu - 1}{15(1 - \nu)} \\ S_{1212} &= S_{2323} = S_{3131} = \frac{4 - 5\nu}{15(1 - \nu)}\end{aligned}\tag{4.2}$$

The parameter Λ in (4.1) should be evaluated for every phase (n-phase). If the elasticity tensor is uniform in each phase, Λ can be expressed as in (4.3). The D-I model allows the phases to be non-uniform for graded evolution of any of the phases, reader may refer to [66].

$$\Lambda_i = [(\mathbb{C}^{inf} - \mathbb{C}_i)^{-1} : \mathbb{C}^{inf} - \mathbb{S}]^{-1}\tag{4.3}$$

Some remarks should be made at this point, the elasticity tensor of infinitely extended homogeneous domain, $\mathbb{C}^{inf}$ has an initial, arbitrary value, since this is an iterative procedure, at every step this tensor should be updated until the convergence is achieved. Choosing the homogeneous material's elasticity tensor creates the iterative procedure.

Instead of using the elasticity tensor for fictitious domain, other constituents' elastic-

ity tensors can be chosen. The D-I model is proven to be a generalization of some well-known micromechanics-based homogenization schemes [127], such as Ponte Castaneda-Willis, Mori-Tanaka, and Kuster-Toksoz models. In [127] it was shown they prove that for special cases of strain concentration tensors and choosing elasticity and Eshelby tensors of one of the phases instead of the fictitious domain may result in different techniques. The Ponte Castaneda-Willis model and the Kuster-Toksoz model are not reviewed in the thesis. However, the Mori-Tanaka method is examined and modelled for different comparison purposes.

In (4.1), if C_m is used instead of C^{inf} and if the matrix's Poisson ratio is used instead of the fictitious domain's Poisson's ratio for the calculation of the Eshelby tensor $\mathbb{S}$, then, the obtained equation is equal to the Mori-Tanaka's elasticity tensor. This is an important result for comparison of these techniques, because the Mori-Tanaka method is closed form, explicit and easy to implement. While, the D-I uses an iterative scheme because $\mathbb{C}$ and $\mathbb{S}$ tensors are calculated for the fictitious homogeneous media. Using an iterative process is time consuming and has a higher computational cost.

Another important aspect of the method is related with the interactions between different inclusions and between an inclusion and surrounding coating phase. The D-I model uses a strain concentration tensor approach, these interactions are taken into account. However, the fact that the inclusion is surrounded by the interphase appears to be not taken into account properly. In the D-I model, analytical estimates of a nested ellipsoidal geometry was reported by Hori and Nemat-Nasser [8]. This specific geometry definition provides stress and strain fields for inclusions to be affected by this nested structure. However, it was pointed out by Wang et al. [102], when the aspect ratios of the inclusion and the coating are the same the D-I model becomes equivalent to the Mori-Tanaka method. This is shown analytically for spherical and cylindrical inclusions as well [102], [103]. This result implies that the D-I model does not see the interphase as a coating region around the inclusion, but it sees as a different filler phase with interphase properties. This situation is demonstrated in Fig. 4.2. Therefore the stress transfer between phases due to nested structure cannot be modelled by means of the D-I model. In the D-I model, coating phase behaves as it was a separate phase in matrix. This deficiency is expected to be significant in softer

interphase case.

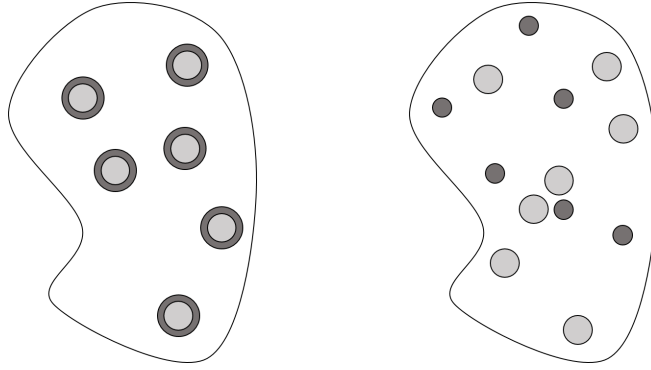


Figure 4.2: Comparison of multi-phase structures, left reality, right the way how the D-I and the Mori-Tanaka models see the reality

4.1.2 Homogenization with Finite Element Method

For a heterogeneous medium, when the balance of linear momentum, boundary conditions and the constitutive equation are considered, due to heterogeneity of the microstructure, stress and strain fields are expected to be oscillatory in nature. In such complex problems homogenization method provides a simple solution for the effective material behavior. A static problem can be posed as follows.

Conservation of linear momentum

$$\text{div}(\bar{\sigma}) + \bar{\rho}b = 0 \quad (4.4)$$

Boundary conditions of the problem

$$\bar{u} = u \text{ on } \partial R^u \quad (4.5)$$

$$\bar{t} = \bar{\sigma}n = t \text{ on } \partial R^t \quad (4.6)$$

Constitutive equation for homogeneous material

$$\bar{\sigma} = \bar{\mathbb{C}} : \bar{\epsilon} \quad (4.7)$$

Here all the quantities with a bar are the effective (homogenized) quantities of the heterogeneous material. The formulation shows that as long as homogenized prop-

erties of the problem are known, it simplifies to a static solid mechanics problem. However, finding the effective properties is not always straightforward and different homogenization techniques can be used as explained earlier. the main aim of homogenization is to obtain the homogenized modulus $\bar{\mathbb{C}}$. Finite element method can be used as a numerical homogenization technique obtain effective properties. There are different boundary conditions that can be employed in homogenization. The most classical boundary conditions are the uniform displacement, uniform traction and periodic displacement/anti-periodic traction boundary conditions. In this study strain controlled (driven) tests are conducted and uniform displacement boundary condition is applied to the representative volume element (RVE). After obtaining the homogenized stress and strain tensors, effective properties can be obtained. The representative volume element is an important concept for homogenization. Instead of modeling complete microstructure of a material, a finite-sized sample is chosen to analyse the model. This sample is called RVE and it shows the macroscopic behavior of the material. There are some size requirements for a finite-sized sample to be qualified as an RVE [128].

- The typical dimension of RVE (L) is larger than the typical dimension of heterogeneity (d): $L > d$
- First requirement creates the condition, in the limit $\frac{d}{L} \rightarrow 0$, sample is a homogeneous material
- The typical dimension of microstructure (D) is larger than typical dimension of heterogeneity (d): $D > L$
- Combining the size requirements: $D > L > d$ is also known as the *micro-meso-macro principle*, it is illustrated in Fig. 4.3 (In [129], this principle is referred as *micro-mini-macro principle*)

As given in (4.7), when the homogenized stress and strain results are known, effective elasticity tensor $\bar{\mathbb{C}}$ can be obtained. For an anisotropic material, stress-strain relation

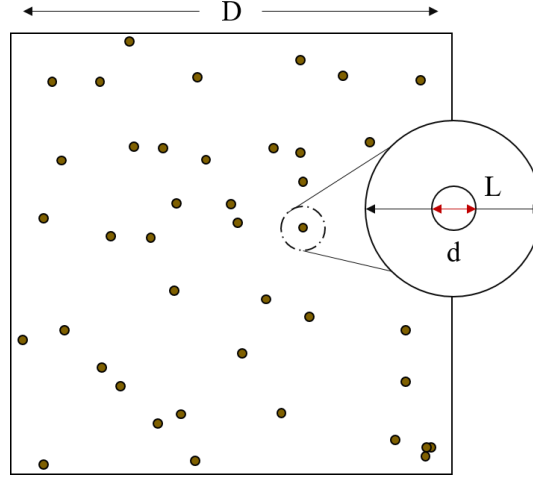


Figure 4.3: Size requirements of representative volume element, illustration of *micro-meso-macro principle*

in Voigt notation is given in (4.8)

$$\begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{12} \\ \sigma_{23} \\ \sigma_{13} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ sym & & & & & C_{66} \end{bmatrix} : \begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ 2\epsilon_{12} \\ 2\epsilon_{23} \\ 2\epsilon_{13} \end{bmatrix} \quad (4.8)$$

For the general case of anisotropic elasticity, the elasticity tensor $\mathbb{C}$ has 81 components (21 of which are independent). Thus, 21 equations are needed to obtain 21 constants. Macroscopic stress tensors are calculated by performing strain-controlled finite element analyse. In order to determine each column of the elasticity matrix given in (4.8), only one component of the strain tensor is specified to a non-zero value while all the other components are set to zero. By conducting finite element

analyses of the six load cases given in (4.9), the elasticity tensor can be computed.

$$\begin{bmatrix} a & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & a \end{bmatrix}, \begin{bmatrix} 0 & a & 0 \\ a & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & a \\ 0 & a & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & a \\ 0 & 0 & 0 \\ a & 0 & 0 \end{bmatrix} \quad (4.9)$$

In (4.9), a is a fixed loading parameter. The first three loadings in (4.9) are for uniaxial tests while the last three are simple shear tests. The first loading corresponding to a uniaxial deformation in x-direction gives C_{11} , C_{12} , C_{13} , C_{14} , C_{15} and C_{16} . Similarly, the second loading corresponding to a uniaxial deformation in y-direction gives C_{21} , C_{22} , C_{23} , C_{24} , C_{25} and C_{26} . The third uniaxial loading in a similar manner gives C_{31} , C_{32} , C_{33} , C_{34} , C_{35} and C_{36} . The fourth loading is a simple shear in x-y plane and this loading gives C_{41} , C_{42} , C_{43} , C_{44} , C_{45} and C_{46} . The fifth loading corresponds to a simple shear in y-z plane and this loading gives C_{51} , C_{52} , C_{53} , C_{54} , C_{55} and C_{56} . The final loading is a simple shear in y-z plane that yields C_{61} , C_{62} , C_{63} , C_{64} , C_{65} and C_{66} . The elasticity tensor to be obtained as a result of the six loadings expresses the general elasticity condition. Then the physical material parameters can be calculated. For isotropic material, the elasticity tensor is simplified and expressed as shown in (4.10).

$$\begin{aligned} \mathbb{C} &= \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{55} & 0 \\ sym & & & & & C_{66} \end{bmatrix} \\ &= \frac{E}{(1+\nu)(1-2\nu)} \begin{bmatrix} 1-\nu & \nu & \nu & 0 & 0 & 0 \\ & 1-\nu & \nu & 0 & 0 & 0 \\ & & \nu & 0 & 0 & 0 \\ & & & \frac{1-2\nu}{2} & 0 & 0 \\ & & & & \frac{1-2\nu}{2} & 0 \\ sym & & & & & \frac{1-2\nu}{2} \end{bmatrix} \end{aligned} \quad (4.10)$$

For isotropic materials, there are only two independent material parameters, therefore even though general six loading cases give every component of the elasticity tensor one by one, use of only one uniaxial loading is enough. In the thesis generally spherical (circular) RVEs with spherical (circular) inclusions are considered. Therefore, it is expected to obtain homogenized elasticity tensors representing isotropic behavior. However, throughout this study, isotropy is not given as a prerequisite, on the contrary, it is observed from the results.

In two-dimensional problems a circle is chosen as a RVE and in three-dimensional problems a sphere is chosen as a RVE. In the last part of this chapter in order to show the capability of the proposed method also an ellipsoid RVE is discussed. Abaqus/Standard is used for the finite element analyses [130]. The geometry, load conditions and boundary conditions are created in Abaqus. In Fig. 4.4a, a cutout image of the RVE is shown where red part is the matrix, while green is the interphase and blue is the inclusion. Corresponding two-dimensional view of the mesh is illustrated in Fig. 4.4b. As seen in Fig. 4.4b, a structured mesh is used. A linear, 8-noded brick element (C3D8) with full integration is chosen for three-dimensional analyses. A linear 4-noded, plane strain, quadrilateral element (C2D4) with full integration is chosen for two-dimensional analyses. Due to partitioned nature of geometry, it is possible to use a structured mesh.

Fig. 4.5a shows the deformed shape of the spherical volume element under uniaxial loading in x direction. The contours of the figure correspond to the magnitude of the displacement vector. Fig. 4.5b shows the deformed shape of the spherical volume element when subjected to a simple shear in x - y plane. This load corresponds to the fourth load case shown in (4.9). In Fig. 4.5b shows the magnitude of the displacement vector is depicted. The other two uniaxial load cases and two other simple shear load cases lead to similar deformed views.

After applying a load case to the RVE, the homogenized stress tensor should be computed. Since a uniform displacement boundary condition is applied to the entire surface of the RVE, the homogenized strain tensor is prescribed. For this purpose, during the finite element analysis of the RVE, the volume of each integration point is also stored. By a simple Python code, the homogenized stress and strain tensors are com-

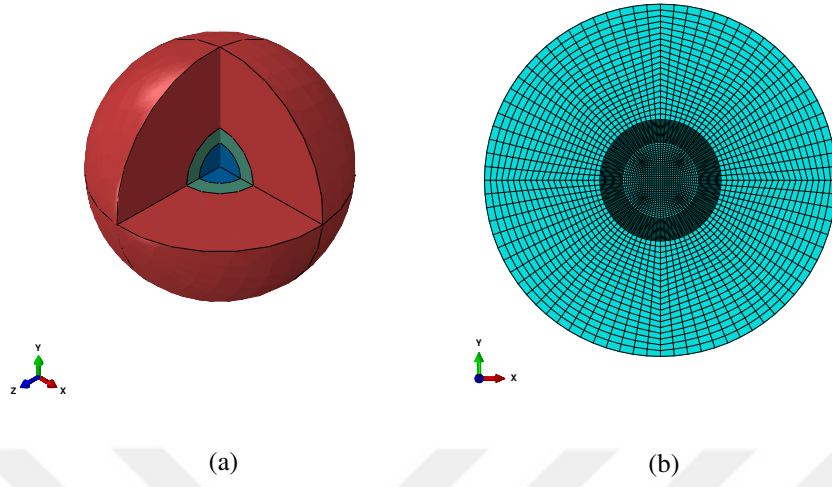


Figure 4.4: The spherical representative volume element and the corresponding finite element mesh for coated inclusion problem

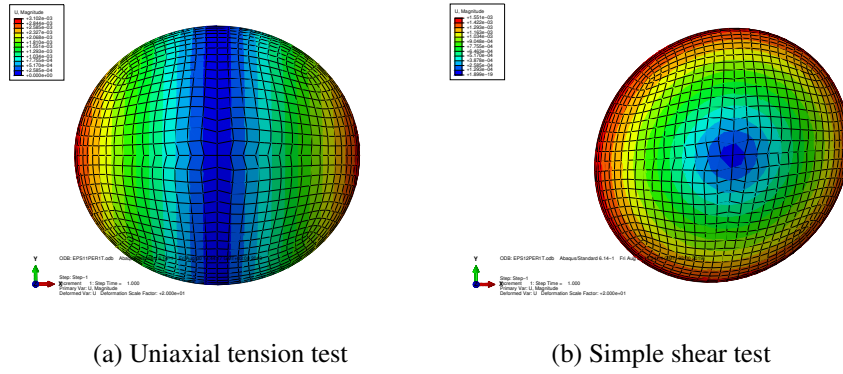


Figure 4.5: Deformed views of the RVEs for the uniaxial test in x-direction and the simple shear in x-y plane. The contours correspond to the magnitude of the displacement vector.

puted by using the stress and strain tensors at the integration points which is depicted in (4.11).

$$\begin{aligned}\bar{\sigma} &= \frac{\sum_{i=1}^{\text{NIP}} \sigma_i V_i}{\sum_{j=1}^{\text{NIP}} V_j} \\ \bar{\epsilon} &= \frac{\sum_{i=1}^{\text{NIP}} \epsilon_i V_i}{\sum_{j=1}^{\text{NIP}} V_j}\end{aligned}\tag{4.11}$$

In (4.11), σ_i and ϵ_i correspond to the stress and the strain tensors at the integration point i , V_i is the volume of that integration point and NIP is the total number of integration points of the FE model.

4.1.3 Proposed Two-Level Methodology

Previous sections explain the micromechanics-based D-I model and homogenization procedure by FEA. As explained earlier, the D-I method lacks the interactions between nested heterogeneities. This is expected to cause a problem especially in softer interphase cases. This is because of the "stress shielding" effect. In a composite system where the interphase between the matrix and the inclusion is softer than the matrix itself, load transfer is poorly achieved. The soft interphase region prevents appropriate load transfer to the inclusion. This mechanism cannot be modeled with the D-I model as reported by Wang et al. [102] where a new analytical formulation for annular coated inclusions was proposed. The formulation in [102] takes the interactions into account better.

The proposed methodology in this thesis uses a two-level homogenization technique. Two-level technique is a common practice for coated inclusion problems. Forming an **effective inclusion** is the main goal at the first level. Then any homogenization technique can be used in the second level to homogenize the obtained two-phase composite. In this study, a two-level technique based on micromechanics and FEA is proposed and the results are reported for elastic and viscoelastic material behavior. The proposed method can be utilized even if constituents are anisotropic or the macroscopic response is anisotropic due to the shape of inclusion.

The method is briefly illustrated in Fig. 4.6. There are three distinct phases, the matrix (orange), the interphase (blue) and the inclusion (gray). At the first level the interphase and the inclusion are homogenized by using finite element analysis technique and an effective inclusion (dark gray) is obtained. The effective inclusion's elasticity tensor and physical material constants are determined at the end of first level. Then a two-phase composite consisting of a matrix and an effective inclusion is obtained. In the second level the D-I iterative method is used to find the effective properties of two-phase composite. Finally a homogenized, effective material (yellow) is obtained.

An algorithm chart for the proposed model is presented in Algorithm 1.

Algorithm 1: Proposed methodology for elastic problem

Result: Effective material properties of three-phase polymer nanocomposite

- 1 Create the geometry with Abaqus for specific volume fraction of inclusion $\phi_{\text{inclusion}}$;
 - 2 Apply six load cases;
 - 3 Perform the following algorithm via Python script in Abaqus PDE;
 - 4 **while** $j \leq \text{load cases}$ **do**
 - 5 **while** $i \leq n$ (*total number of integration points*) **do**
 - 6 $\bar{\sigma} = \frac{\sum_{i=1}^n \sigma_i V_i}{\sum_{i=1}^n V_i}$ $\bar{\epsilon} = \frac{\sum_{i=1}^n \epsilon_i V_i}{\sum_{i=1}^n V_i}$
 - 7 **end**
 - 8 $\bar{\mathbb{C}}(, j) = \frac{\bar{\sigma}(, j)}{\bar{\epsilon}(j, j)}$
 - 9 **end**
 - 10 Place the moduli of the effective inclusion into Double-Inclusion method script in Matlab and calculate the homogenized elastic modulus of three-phase composite with an iterative solution;
 - 11 Compute the physical material parameters from the elasticity tensor according to whether the obtained result shows isotropy or not
-

In this section, homogenization results for two-dimensional and three-dimensional RVEs are reported. To this end, some parametric studies are conducted.

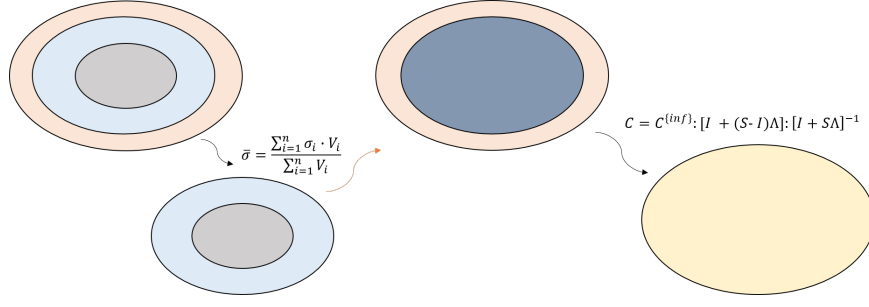


Figure 4.6: Illustration of proposed two-level homogenization methodology for the coated inclusion problem

4.2 Results

4.2.1 Two-Dimensional Results for Double-Inclusion Model

In two-dimensional analyses, some modifications are needed in the formulation of micromechanics-based D-I model. First of all, the volume fraction is defined differently in two- and three-dimensions as can be seen in (4.12). A_i and V_i correspond to the area and the volume of the i^{th} phase. Thus, for spherical and circular geometries both of these definitions are depend on radius (r_i) of the phases.

$$\begin{aligned} \phi_i^{2d} &= \frac{A_i}{\sum_{i=1}^n A_i} = \frac{r_i^2}{\sum_{i=1}^n r_i^2} \\ \phi_i^{3d} &= \frac{V_i}{\sum_{i=1}^n V_i} = \frac{r_i^3}{\sum_{i=1}^n r_i^3} \end{aligned} \quad (4.12)$$

The Eshelby tensor $\mathbb{S}$ is not updated for two-dimensional problems. However, in order to use the Eshelby tensor in two-dimensions, aspect ratio information is changed to $[1 \ 1 \ \infty]$. Normally for a spherical particle, aspect ratio is set as $[1 \ 1 \ 1]$. In two-dimensional problems for a circular inclusion, two of the radii are equal, the last one should be a very high value. It seems like it is a cylinder and a cut in $x - y$ plane is obtained.

In three-dimensional models, all the phases are assumed to be isotropic. In two dimensional problems, in addition to isotropy, plane strain and plane stress assumptions are assumed. To see how these assumptions affect the overall effective elastic mod-

ulus. For this purpose, models with different volume fractions are created in Abaqus and are solved for plane strain and plane stress conditions. Throughout this study, finite element homogenization results for three-phase models are accepted as reference solutions. Fig. 4.7 demonstrates that, the elastic moduli for plane strain and plane stress conditions are not same, while they seem very close for lower volume fractions. The plane strain effective moduli both for the soft and the stiff interphase are higher than the plane stress moduli. However, results do not diverge and they seem quite close. The plane strain condition is used in the remaining two-dimensional studies of the thesis.

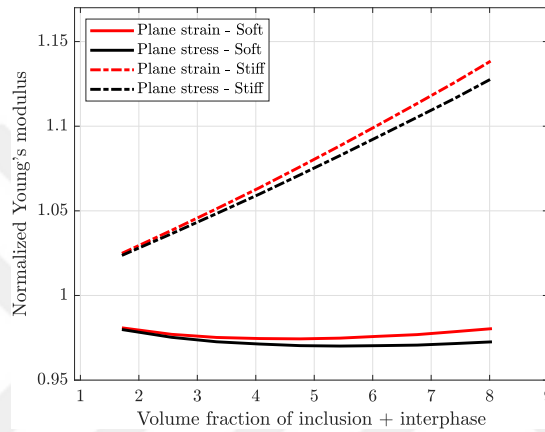


Figure 4.7: Effective Young's modulus comparison as a reference solution for plane strain and plane stress condition

As explained earlier, when the interphase is soft, due to the **stress shielding effect**, stress transfer from matrix to inclusion is limited. The purpose of this study is to take this interactions into account using a two-level homogenization scheme. First, two cases are compared, the first one is a three phase D-I solution and the second one is a three phase FEA solution, which will be accepted as the reference solution. Here the interphase thickness is an important parameter as well as interphase material properties. This thickness is equal to $t_0 = 0.6 \times r_{\phi=0.01}$, this is 0.6 times of the inclusion radius when the volume fraction is 0.01. The same thickness is used for different inclusion volume fractions in constant thickness cases. Later, studies with different interphase thicknesses are also performed. The reference thickness is chosen as t_0 and the following results are obtained. First, Fig. 4.8a is given in order to illustrate the stress shielding effect, in two-dimensions. If the interphase is stiffer

than the matrix, the Double-Inclusion and the FEA (reference solution) show very good agreement. However, when the interphase is softer than the matrix, the results differ significantly. In Fig. 4.8b, the results of the proposed method are added to the graph. The results of all three models are very close for the stiff interphase case. The results of the proposed method and FEA results are very close for the soft interphase case as well, while the D-I model significantly overestimates the elastic modulus.

Note that in the figures, the volume fraction of the interphase and the inclusion is used, instead of the volume fraction of the inclusion only. Normally, the volume fraction of the inclusion goes up to 5%, however, due to the interphase, the overall volume fraction is higher than this maximum value. As the volume fraction of effective inclusion increases, the differences between the FEA and the D-I as well as the FEA and the proposed model increase. Fig. 4.8 shows that for constant thickness t_0 case, the proposed method promises a remarkable improvement compared to the D-I model. Still, the proposed method still slightly overestimates the FEA solution for the soft interphase case.

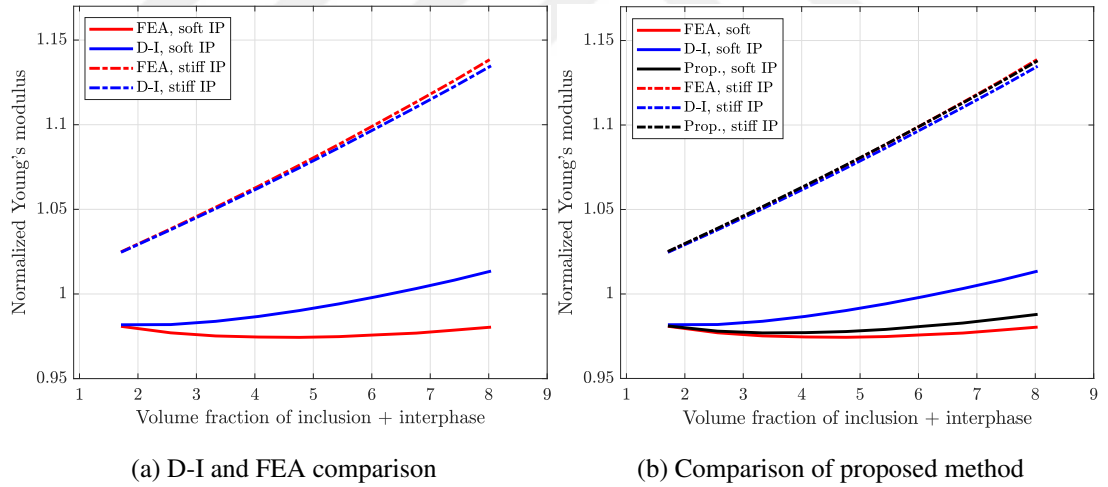


Figure 4.8: Two-dimensional reference results for thickness t_0 case

In order to verify the mesh, a mesh study is conducted. The results are tabulated in Table 4.2 and presented in Fig. 4.9, the mesh with total number of 4400 elements is chosen.

Table 4.2: Mesh study results for two-dimensional problems

Total element number	C_{11}	C_{12}
1100	7.4432	3.9151
2504	7.4407	3.9140
4400	7.4397	3.9136
6924	7.4392	3.9134
9900	7.4390	3.9134

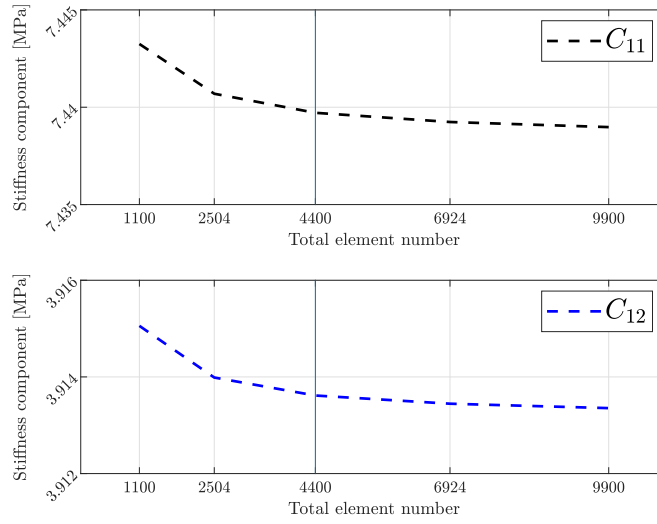


Figure 4.9: Mesh study for different stiffness components in two-dimensions

4.2.2 Variation of Interphase Thickness in Two-Dimensions

In the former section, the proposed method is compared to the reference FEA solution and the micromechanics-based D-I solution for one interphase thickness only. The results show that, by means of a two-level homogenization, a remarkable improvement is achieved. In order to observe how interphase thickness affects the performance of the proposed model, four different interphase thicknesses are chosen, $t_0/2$, $3t_0/4$, t_0 and $5t_0/4$. t_0 is accepted as the reference thickness, which corresponds to 0.6 of radius of inclusion having 0.01 volume fraction. This is chosen as a specified inter-

phase thickness for different volume fractions. Therefore, the interphase thickness is held constant in every subcase as volume fraction of interphase changes for different volume fractions of inclusion. Fig. 4.10 demonstrates, for different interphase thicknesses how the volume fraction of the interphase changes nonlinearly with altering the volume fraction of inclusion. In this study the inclusion volume fraction is chosen between %0.5 and %5 and the corresponding interphase volume fractions are illustrated in Fig. 4.10. While a specific inclusion volume fraction is selected, depending on the interphase thickness different volume fractions of interphases are obtained. As a result the total volume fraction of inclusion and interphase differs for different interphase thicknesses, whereas every subcase have the same range of inclusion volume fraction.

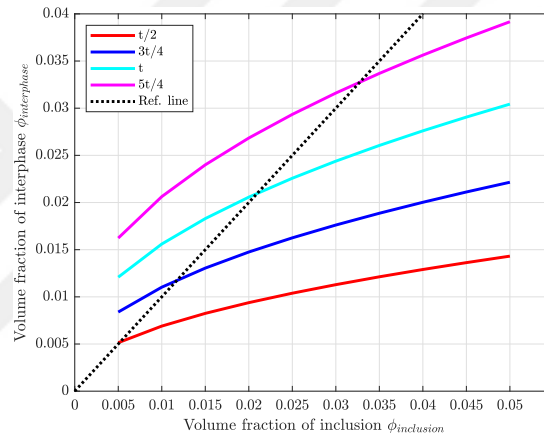


Figure 4.10: Variation of volume fraction with volume fraction of interphase and inclusion for different interphase thicknesses

Four different interphase thickness subcases are investigated and the results are presented in Fig. 4.11. When the stiff interphase cases are compared, for every thickness case, the D-I and the FEA results are in a good agreement, therefore, a two-level scheme is not needed. In stiff interphase subcases, the D-I model underestimates a little, and the proposed method gives better results. However, the need for the proposed method is apparent for soft interphase cases. As can be seen from Fig. 4.11 the performance of the proposed method does not seem to be affected by the thickness of the interphase in the range considered in the study. Fig. 4.11 states that the proposed method works for different interphase thicknesses and it provides an improvement,

compared to the D-I model.

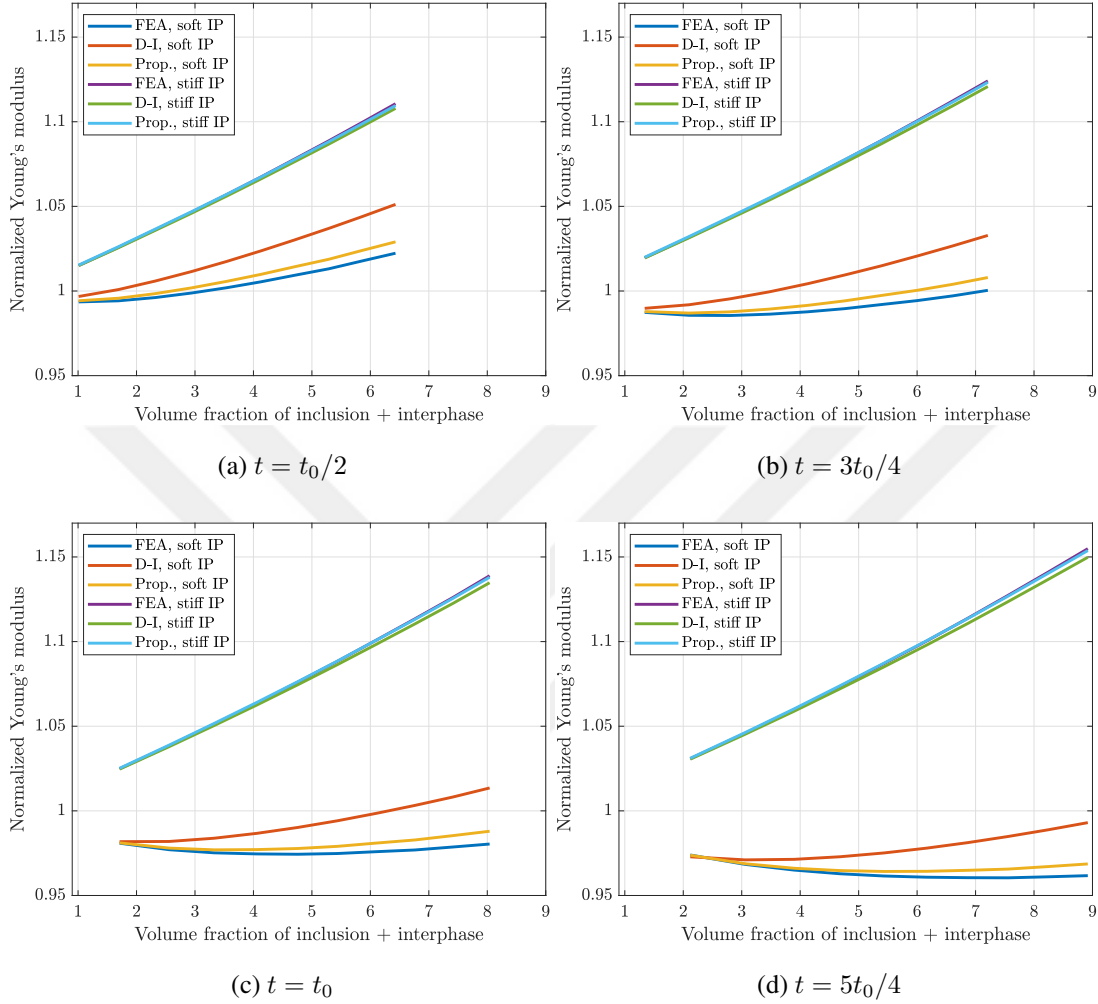


Figure 4.11: Effect of interphase thickness in two-dimensional problems. Comparison of the proposed method with the D-I method and the FEA

The proposed method is compared with the D-I method in terms of errors. Error calculations are made for assuming FEA results as the correct solution. The error of the proposed method is less than the error of the D-I method for every thickness of the interphase.

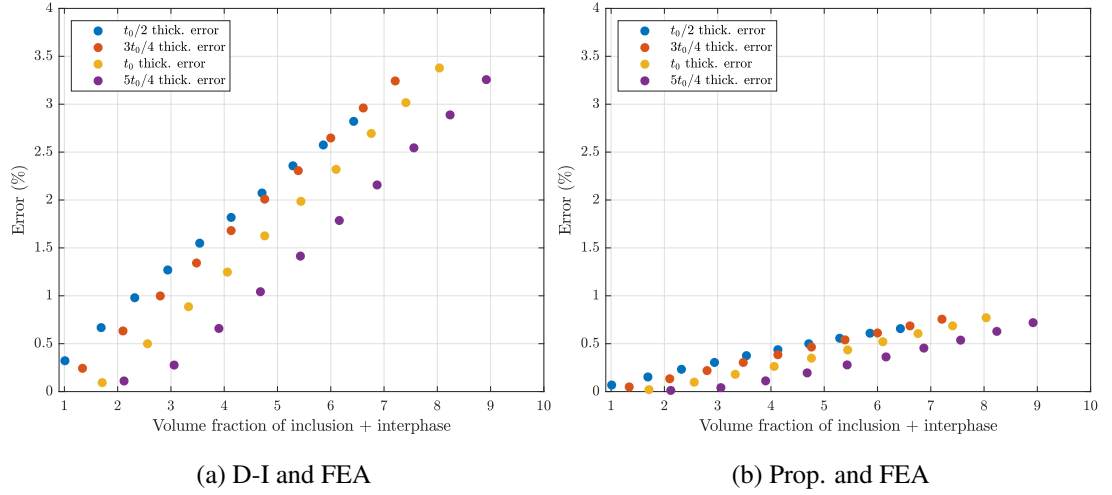


Figure 4.12: Variation of error for the D-I method and the proposed method with interphase thickness for two-dimensional problems. In (a)-(b) errors are plotted with respect to the volume fraction of inclusion and interphase

4.2.3 Dilute Limit Violation for Two-Dimensional Problems

The maximum volume fraction of inclusion plus interphase reaches up to 9% for all different thickness cases and the reference case as well. Dilute limit is defined as the limit that inclusions are far away from each other so that interactions between these particles can be negligible. However, a certain specific value cannot be specified, some researchers accept less than 1% even, some uses 5% as the dilute limit. In this study, the maximum volume fraction of inclusion is chosen as 5%, however, corresponding volume fraction of effective inclusion is more than that. Therefore, even in this range, results may be over the dilute limit. But in order to investigate the performance of the proposed method over the dilute limit, really high volume fractions of inclusion are chosen in this section. The dilute limit is violated also to show the performance of micromechanics based D-I model over the dilute limit.

In Figure 4.13, even though the total volume fraction of interphase and inclusion is well over 5% – 10%, the stiff interphase results of the proposed method show very good agreement with the Double-Inclusion model and the FEA results (reference). While for the soft interphase, it can be observed that over dilute limit, the D-I model

results diverge compared to the FEA (reference) results. But the proposed method still provides acceptable results over the dilute limit. Even though, the error increases with increasing volume fraction, the proposed method provides a remarkable improvement compared to the D-I method. Thus it seems that the model is not limited to low volume fractions only.

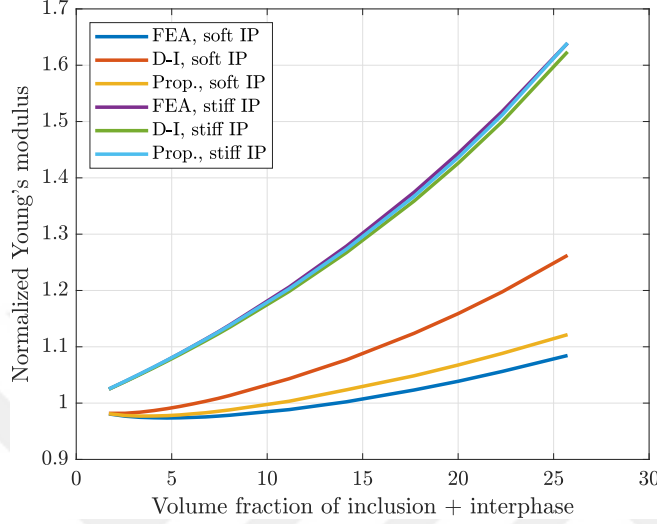


Figure 4.13: Dilute limit violation, for thickness, t_0

4.2.4 Poisson Ratio of Effective Inclusion for Two-Dimensional Problems

In the first level of homogenization, stress and strain tensors are obtained from Abaqus, then through a simple Python script to find the homogenized stress tensor. Afterwards, using the six loading cases, the elasticity tensor can be formed. This level is applied to the inclusion and the interphase to create the effective inclusion. Having found the effective inclusion's elasticity tensor the physical material properties can be determined as well. Since the obtained elasticity tensor shows the properties of isotropic material, the Young's modulus and the Poisson ratio can be calculated from the elasticity tensor of the effective inclusion. Although the inclusion and interphase have the same Poisson ratio, as shown in Table 4.3, the effective Poisson ratio of the effective inclusion is different than the common Poisson ratio value. This is not expected intuitively. It is found that the Poisson ratio of the effective inclusion is a function of the volume fraction of constituents as can be seen in Fig. 4.14. Similar

results regarding the change in Poisson ratio are obtained, and reported in [131] as well.

Table 4.3: Poisson ratio values of inclusion and interphase for effective inclusion

Phase	Poisson ratio ν [-]
Inclusion	0.3
Interphase	0.3

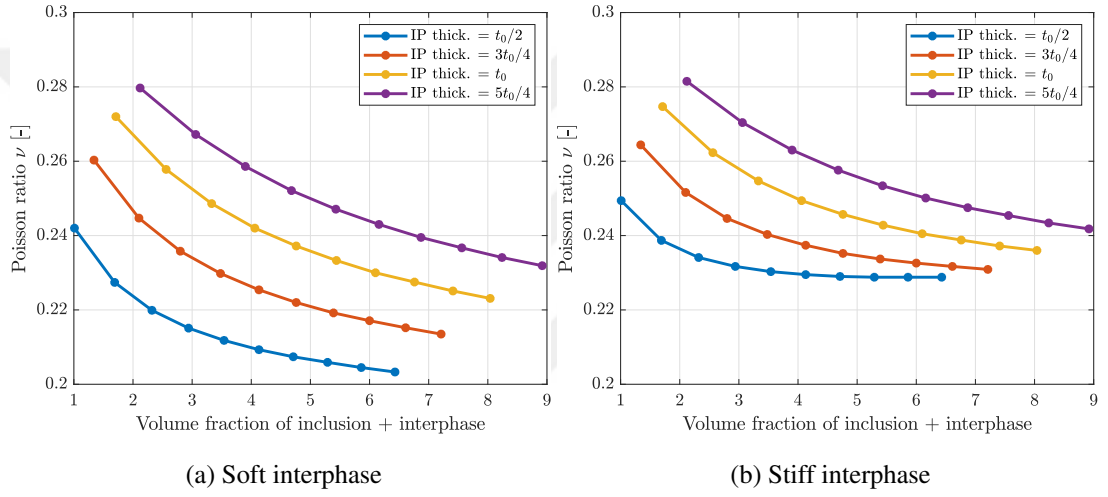


Figure 4.14: Variation of the Poisson ratio of effective inclusion with volume fraction for different thickness cases

Observing Fig. 4.14a and Fig. 4.14b, dependency of the Poisson ratio to volume fraction can be seen in soft and stiff interphase cases and for all different thickness cases. It seems that the thinnest interphase case creates the lowest bound. In both the soft and the stiff interphase cases as the interphase thickness increases, the Poisson ratio of the effective inclusion is higher. As seen in Fig. 4.14b, for thickness of $t_0/2$ case, it seems there is a lower bound for the Poisson ratio of effective inclusion. Similar characteristics can be seen for other thickness results as well but the convergence is obtained for greater volume fractions.

4.2.5 Comparison with Classical Homogenization Techniques for Two-Dimensional Problems

In Chapter 3, different homogenization techniques are summarized. Very basic methods such as the Voigt and the Reuss bounds and more sophisticated methods such as the Mori-Tanaka model are covered. In the proposed method the second level of the homogenization, a micromechanics-based Double Inclusion (D-I) model is utilized. However, the reason for choosing the D-I method is not explained. To this end different homogenization techniques are considered as the second level of the proposed methodology. All the models are created for soft interphase case only. In the first level FEA based homogenization is applied, while in the second level, the Voigt, the Reuss and the Mori-Tanaka methods are selected. Voigt and Reuss bounds are expected to form upper and lower bounds for a two-phase composite. Here the following convention is used in the naming of different two-level homogenization schemes. FEA+Voigt means that FEA based homogenization is used to find the elastic properties of the effective inclusion at the first level and the Voigt averaging is used to determine the overall elastic properties of the composite at the second level. The other schemes are named similarly. As can be seen in Fig. 4.15 when FEA+Voigt and FEA+Reuss are compared with FEA+M-T and FEA+D-I for different thicknesses and volume fractions, FEA+Voigt creates an upper bound and FEA+Reuss creates a lower bound. Furthermore, FEA+D-I and FEA+M-T results are very similar, so micromechanics-based methods are both promising. Here one thing should be highlighted, the M-T method has a closed form, explicit expression while the D-I method uses an iterative approach. This iterative nature of the D-I method causes a computational burden. However, as will be shown later in three-dimensional problems the D-I method yields better results. On the other hand, here in two-dimensions both micromechanics-based results are very similar. In Fig. 4.15, the three phase FEA (reference solution) is also presented. The reference solution seems outside of these bounds, created by FEA+Voigt and FEA+Reuss. In a two phase elastic composite Voigt and Reuss bounds create an envelope and results of every homogenization technique are inside this envelope. However, here the reference solution is not a two-phase composite and there is no replacement procedure to create effective inclusion. Therefore, to have the reference solution outside of these bounds is acceptable. Note

that, once the properties of the effective inclusion are found, the Voigt and the Reuss bounds are very easy to implement and therefore, these bounds can be used as well for rough estimates.

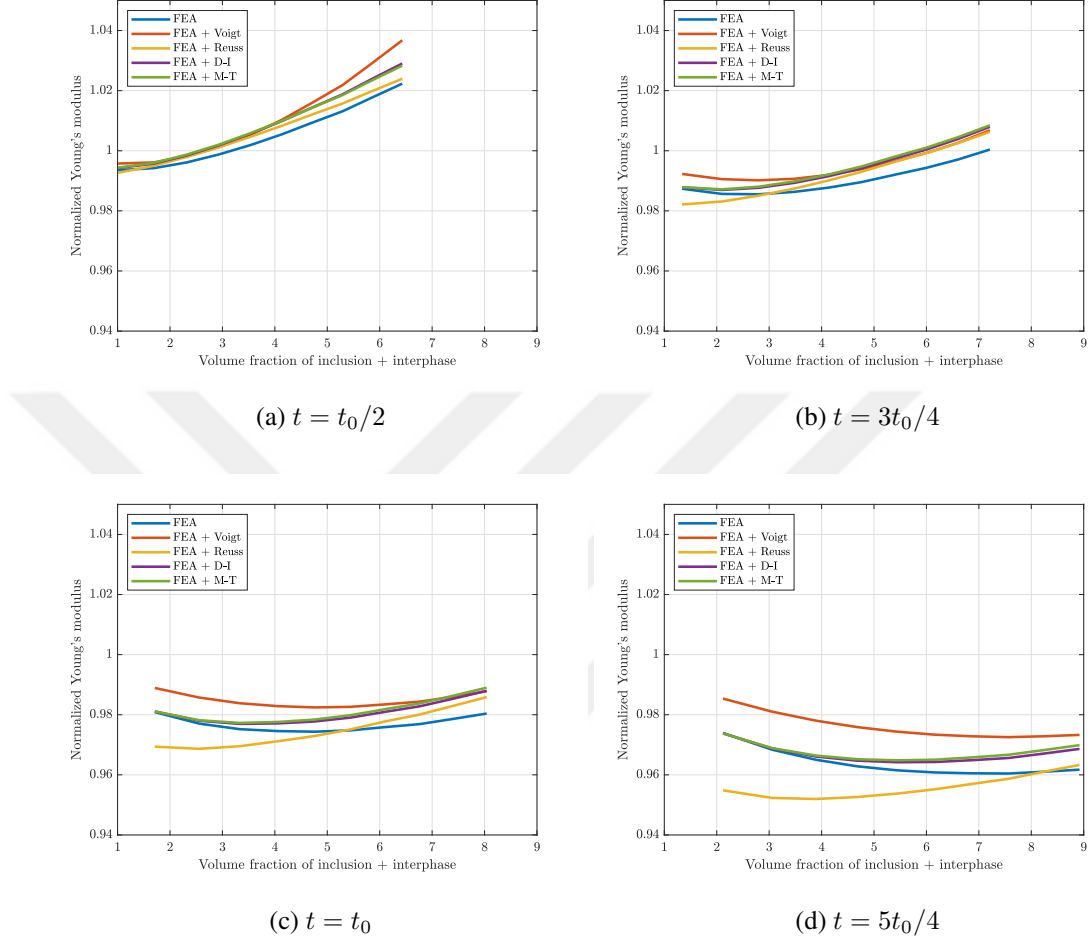


Figure 4.15: Comparison of different homogenization techniques for the second level of two-level proposed method. Only the soft interphase case is presented.

4.2.6 Comparison of Different Meshing Techniques for Two-Dimensional Problems

In three-phase models several cases having various volume fractions of inclusions and interphase thicknesses are considered. Throughout this study, for every case, local seed sizing is controlled with the total number of finite elements. Therefore, for

every case independent of the inclusion radius and the interphase thickness, the same number of finite elements are used. This is managed by using the same local seed along the thickness for every case. Here for comparison, the same mesh is created for all different interphase thickness cases instead of assigning local seeds along the thickness direction. For this purpose, a general model that consists of different layers of interphase thicknesses is created. Assigning the corresponding material properties to the thickness layers for the corresponding thickness values provides the same mesh for all the different thickness cases. This comparison is conducted only for one inclusion volume fraction. Using assigned mesh instead of assigned seed along the thickness gives the following results, for $\phi_{inclusion} = 2.5$. The mesh used for the assigned mesh case with different thickness' is also presented. In Table 4.4, the Young's modulus values for the assigned seed and reference mesh are compared. The Young's modulus values for both mesh models are almost same for four different interphase thickness cases. Therefore, reference mesh is chosen for the current study due to simplicity and avoiding computational burden. The corresponding total element numbers are tabulated in Table 4.5.

Table 4.4: Reference mesh (assigned seed along the thickness) and assigned mesh Young's modulus results

Interphase thickness	Assigned mesh E [GPa]	Reference mesh E [GPa]
$t_0/2$	2.5047	2.5048
$3t_0/4$	2.4692	2.4693
t_0	2.4358	2.4359
$5t_0/4$	2.4038	2.4038

Table 4.5: Total element numbers for specific sections, seed along thickness (reference) and assigned mesh comparison

Phase	Inclusion	Interphase	Matrix
$t_0/2$	1200	1600	6400
$3t_0/4$	1200	3200	4800
t_0	1200	4800	3200
$5t_0/4$	1200	6400	1600
Seed along thickness	1200	1600	1600

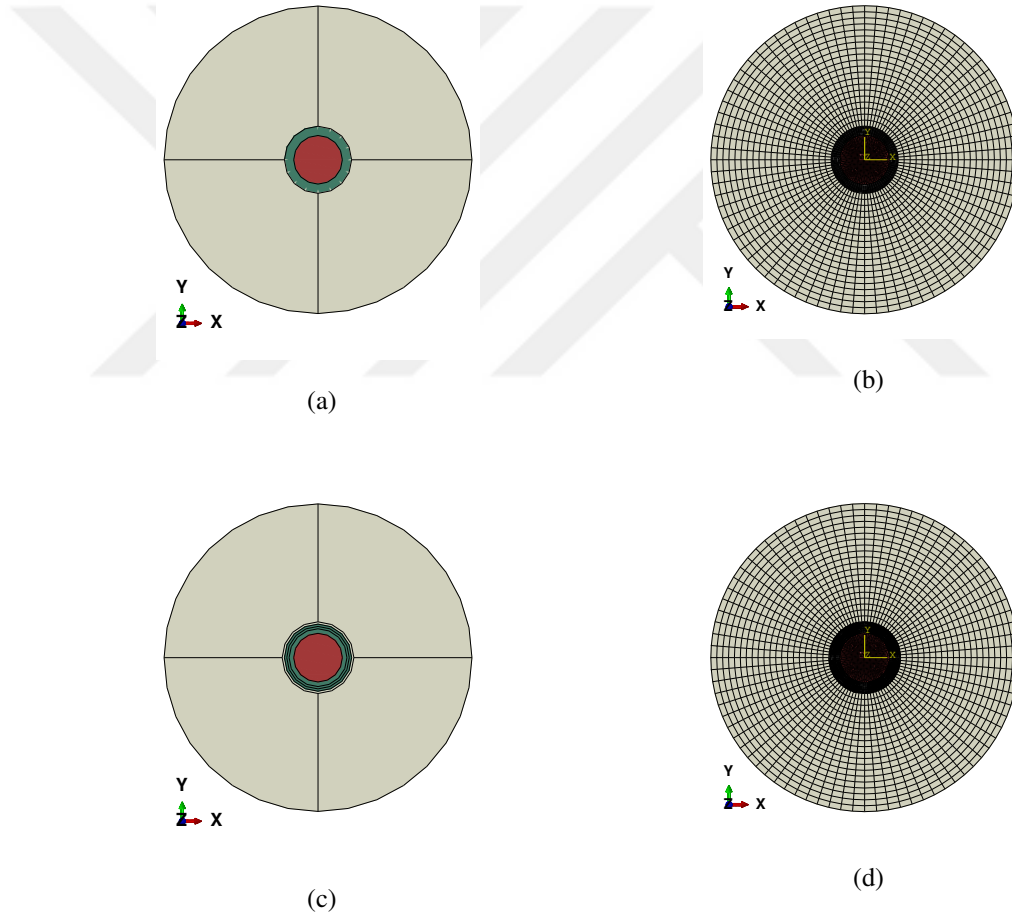
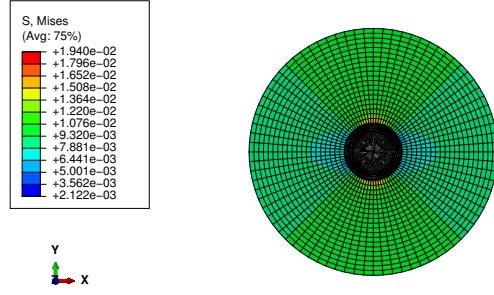
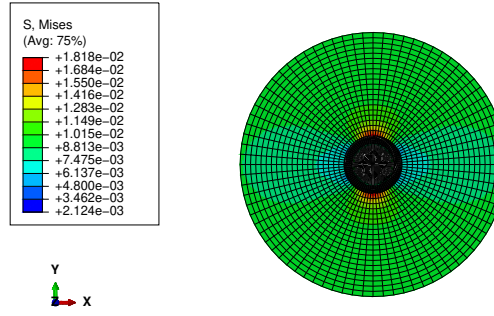


Figure 4.16: (a) Assigned local seed case geometry, (b) Assigned local seed case mesh, (c) Assigned mesh case geometry, (d) Assigned mesh case mesh, for IP thick. $= t_0$



(a)



(b)

Figure 4.17: (a) Under displacement boundary conditions, stress results assigned mesh for different thickness, (b) Under displacement boundary conditions, stress results assigned seed along thickness for different thickness

4.2.7 Three-Dimensional Results for Double-Inclusion Model

Until this point, results of two-dimensional problems are presented in the thesis. It is shown that the proposed method can be applied to the soft and the stiff interphase cases. For the soft interphase case, having a replacement procedure, forming the effective inclusion corrects the D-I results. Interphase thickness and resulting volume fraction studies are presented to understand the effect of interphase thickness. The proposed method is used well-over dilute limit to see if there is any limitations of volume fraction. In order to justify mesh structure used, mesh study of assigned seed versus assigned mesh is conducted as well. As a result of the first level homogenization, the Poisson ratio of the effective inclusion is shown and a dependency on volume fraction of constituents is observed. Furthermore, in the second level different homog-

enization techniques are employed and obtained results show that micromechanics-based methods yield promising results. In this section, these analyses are repeated for spherical, three-dimensional RVE in order to see the performance of the proposed method in three-dimensional problems.

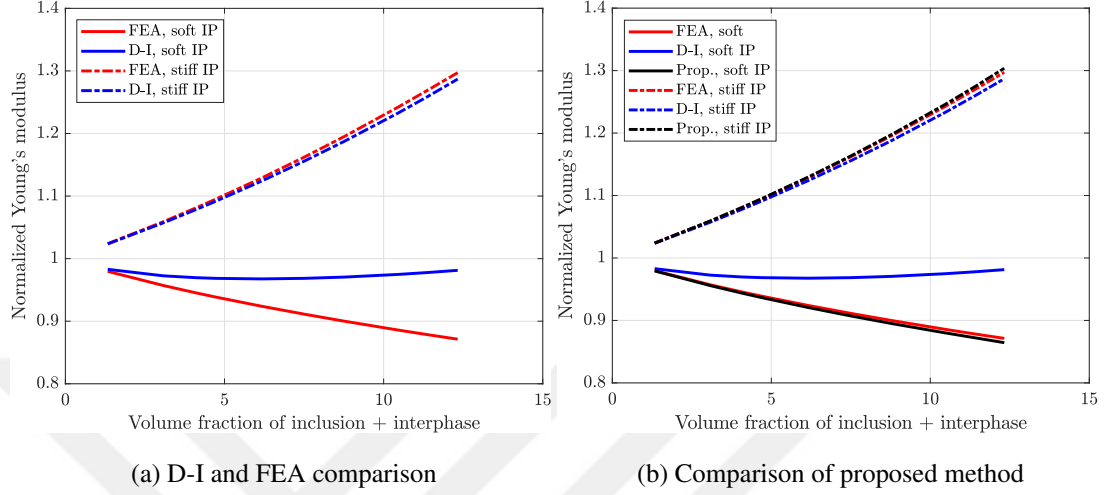


Figure 4.18: Three-dimensional reference results for thickness t_0 case

Fig. 4.18a proves that, when there is a stiff interphase, the micromechanics-based model is in a good agreement with the three-phase FEA (reference solution). However, when the interphase is softer than the matrix, these models do not match. The D-I model even shows an increasing trend for high volume fractions while the reference solution is monotonously decreasing. It shows that, even though the volume fraction of inclusion is getting higher, due to presence of soft interphase, the overall macroscopic elastic modulus decreases. Therefore, even the trend of the elastic modulus with the volume fraction is different for the D-I model and the reference FE solution. In order to overcome the stress shielding problem for soft interphase and eliminate this mismatch, proposed method is used for three-dimensional geometries as well. The comparison of the proposed method with the D-I method and the reference solution is given in Fig. 4.18b. It can be seen that the proposed method makes a more significant improvement in three-dimensional case, see Fig. 4.8b for two-dimensional results. The predictions of the proposed method is closer to the reference solution for the stiff interphase case as well. When Fig. 4.8b and Fig. 4.18b are compared, it can

be concluded that the proposed method works both in two- and three-dimensional problems. However, in three-dimensional problems the performance of the method is better.

In order to verify the mesh, a mesh study is conducted. The results are tabulated in Table 4.6 and presented in Fig. 4.19, the mesh with total number of 80000 elements is chosen.

Table 4.6: Mesh study results for three-dimensional problems

Total element number	C_{11}	C_{12}
16000	3.5654	1.7943
57088	3.5648	1.7941
80000	3.5646	1.7940
258648	3.5645	1.7939
432000	3.5644	1.7939

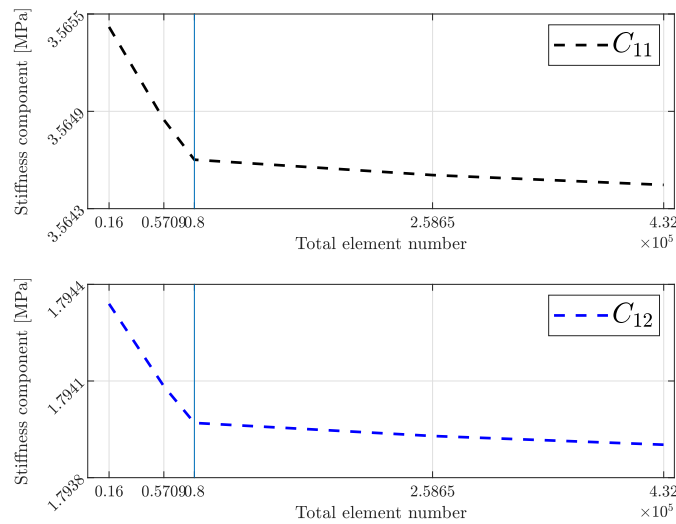


Figure 4.19: Mesh study for different stiffness components in three-dimensions

4.2.8 Variation of Interphase Thickness in Three-Dimensions

Fig. 4.20 represents the relation between the volume fraction of inclusion to the volume fraction of interphase for three-dimensional spherical inclusions. Four different thicknesses are investigated. The volume fraction of interphase is affected by the choice of thickness parameter. In Fig. 4.20, the reference line $x = y$ is plotted to compare the change in interphase and inclusion volume fractions.

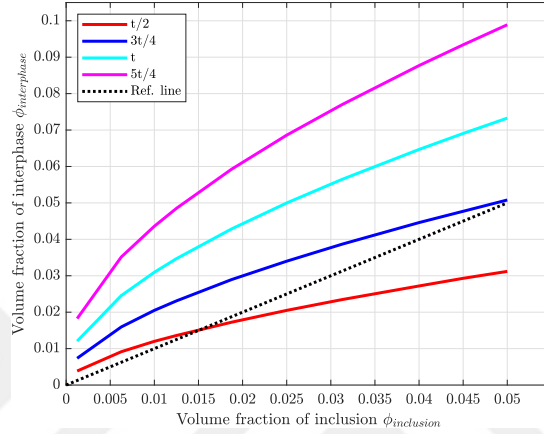


Figure 4.20: Variation of volume fraction with volume fraction of interphase and inclusion for different interphase thicknesses in three dimensions

Four different thicknesses are chosen as before, $t_0/2$, $3t_0/4$, t_0 and $5t_0/4$. Different from the two-dimensional cases, in three-dimensional models even the overall volume fraction of thinnest interphase case is well above the dilute limit. The total volume fraction of inclusion and interphase of the thinnest interphase case for three-dimensions is higher than the thickest interphase case in two-dimension. Similar to previous results, for the stiff interphase case three methods, the three-phase FEA (reference), the D-I method and the proposed method agree well, see Fig. 4.21. A few observations can be made for the soft interphase case. First except the thickest interphase $5t_0/4$ case the D-I method predicts that the Young's modulus increases with the volume fraction after some minimum volume fraction value. Most probably, this behavior exists for the thickest interphase $5t_0/4$ case as well, but it appears for volume fractions greater than 15%. Second, as the total volume fraction of inclusion and interphase increases, the gap between predictions of the D-I method and FEA

solution is opening. Similar observations can be made for the proposed model and FEA however, this gap is very small when compared to the results of D-I method. Finally, comparison of three-dimensional results (Fig. 4.21) with two-dimensional results (Fig. 4.11), show that the performance of the proposed method is better in three-dimensional problems.

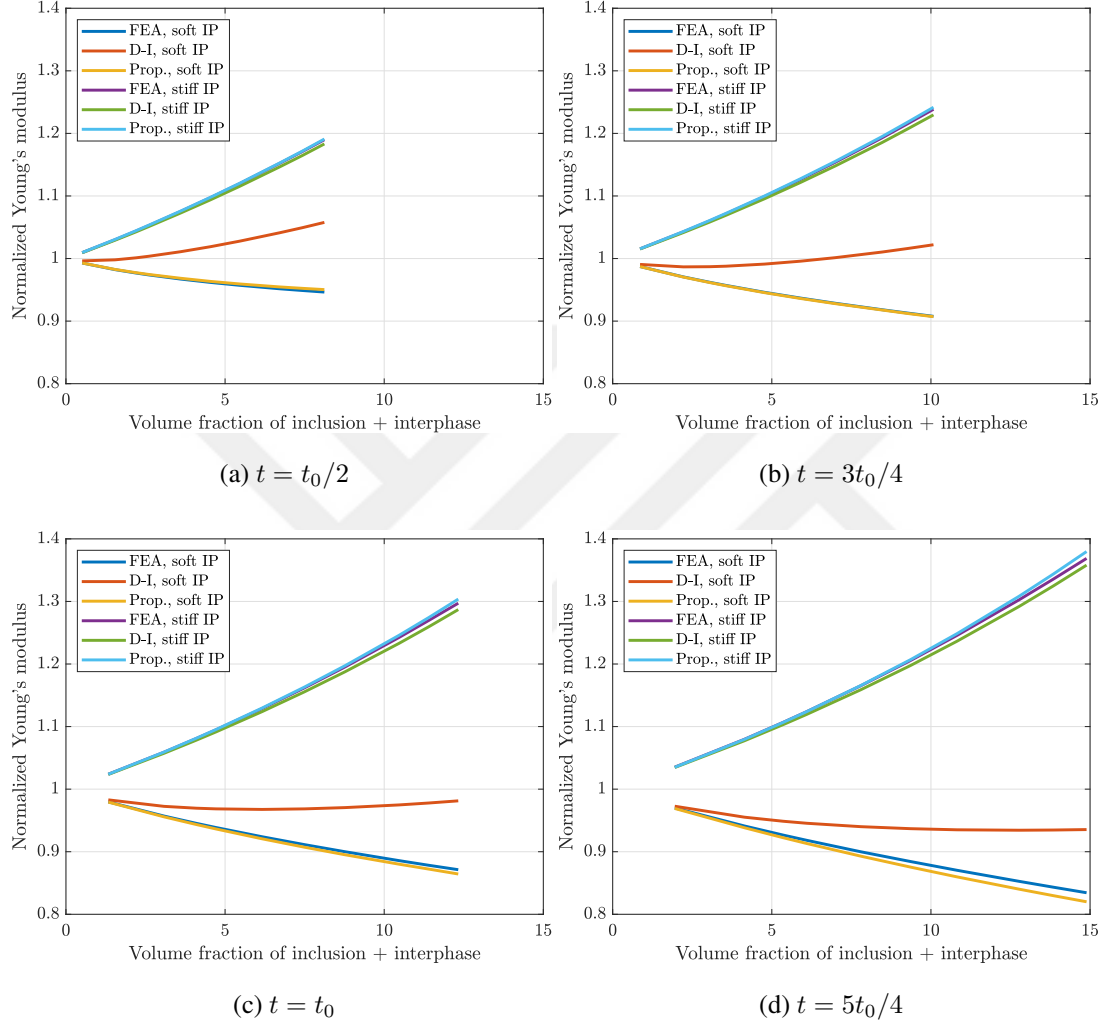


Figure 4.21: Effect of interphase thickness in three-dimensional problems. Comparison of the proposed method with the D-I method and the FEA

In order to understand, if the thickness of the interphase affects the error between D-I and FEA cases and proposed method and FEA cases, error is calculated and illustrated in Fig. 4.22. The error of the proposed method is less than the error of the D-I method for every thickness of the interphase.

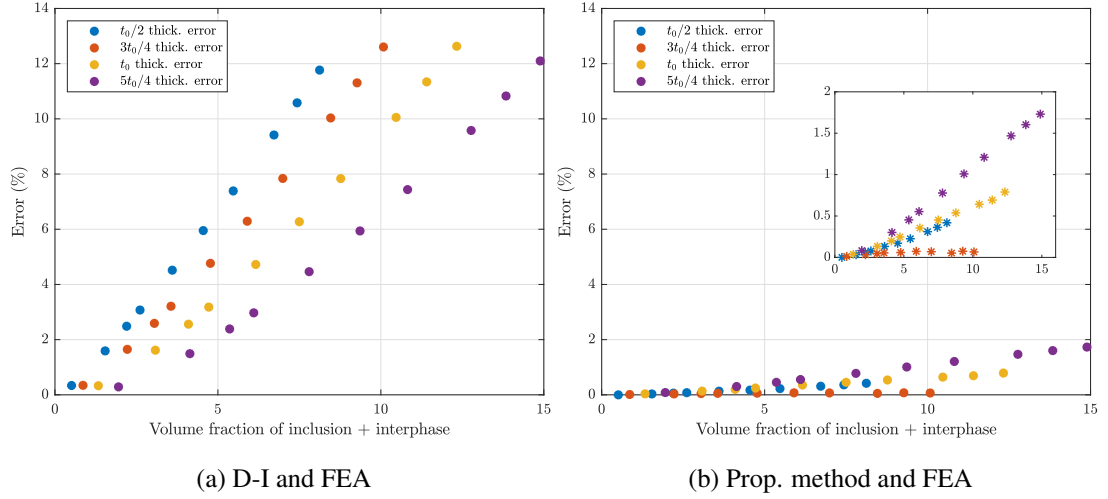
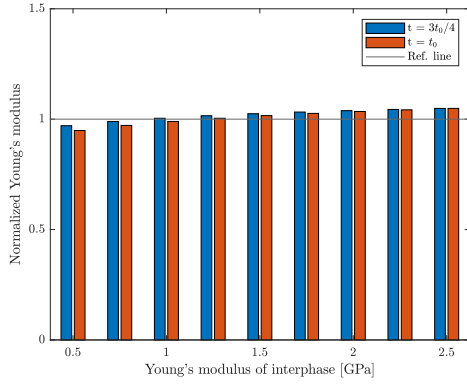


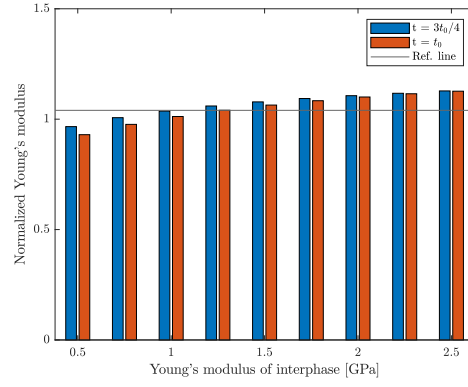
Figure 4.22: Variation of error for the D-I method and the proposed method with interphase thickness for three-dimensional problems. In (a)-(b) errors are plotted with respect to the volume fraction of inclusion and interphase.

Next a study is conducted to see whether there is a unique combination of interphase thickness and interphase Young's modulus to obtain a particular overall effective behavior. For this purpose the Young's modulus of the interphase is changed for two different thickness cases. For the thickness cases $t = t_0$ and $t = 3t_0/4$, several models have been created and analyzed in the range of interphase Young's modulus $[0.5; 2.5]$. Two volume fractions of inclusion are chosen, $\phi_{\text{inclusion}} = 0.02$ and $\phi_{\text{inclusion}} = 0.05$. In Fig. 4.23 the variation of normalized homogenized Young's modulus with interphase modulus is shown for two different interphase thicknesses and two different inclusion volume fractions. As can be seen from the figure different combinations of the interphase modulus and the interphase thickness may result in the same homogenized modulus for a given inclusion volume fraction. Therefore, it is clear that there is no unique combination of thickness and Young's modulus to obtain the same macroscopic property.

Fig. 4.24 illustrates the cases for which the interphase Young's moduli are set to 0 and ∞ . The first condition corresponds to the case where the load transfer between the matrix and the inclusion is completely prevented. The latter condition corresponds to a rigid interphase. As expected, the soft and the stiff interphase curves are between these limits.



(a) $\phi_{\text{inclusion}} = 0.02$



(b) $\phi_{\text{inclusion}} = 0.05$

Figure 4.23: Variation of normalized homogenized Young's modulus with interphase modulus for different interphase thicknesses and different inclusion volume fractions

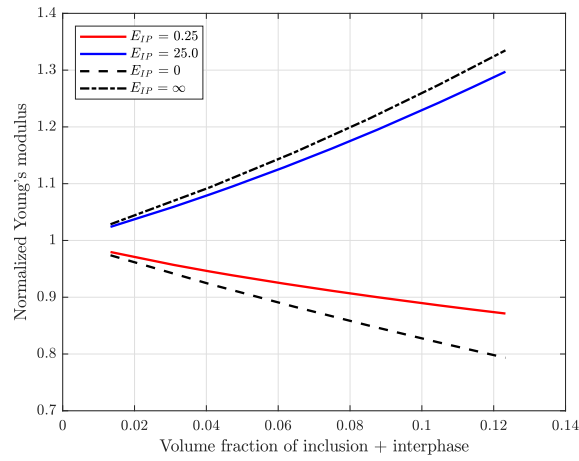


Figure 4.24: Comparison of the soft and the stiff interphase cases with limit cases.

4.2.9 Dilute Limit Violation for Three-Dimensional Problems

To prove the eligibility of the proposed method over dilute limit, higher volume fractions of inclusion and interphase is studied. Similar study is performed for the two-dimensional case and no limitation regarding the volume fraction is found. In Fig. 4.13 it is observed that for the stiff interphase case all three models are in good agreement, while for the soft interphase case, the proposed method performs remarkably better than the D-I method. Furthermore, Fig. 4.13 shows that as the total volume fraction of inclusion and interphase increases, the gap between the reference solution and the proposed method raises slightly opening. On the other hand, no dependency on the volume fraction is observed for the stiff interphase case. Fig. 4.25 indicates the opposite behavior in three-dimensional problem, i.e., the proposed model works well over dilute limit for the soft interphase case. The discrepancy between the reference solution and the proposed model is also slightly increases but compared to two-dimensional case it is negligible. Contrary to the two-dimensional results, the performance of the methods for the stiff interphase case shows a dependency on the volume fraction. It seems that over the dilute limit, the D-I model and the proposed method do not calculate the effective properties very well. It shows that the two-level homogenization technique may overestimate the homogenized properties of the multi-phase composite. It is known that the D-I and the M-T methods work better in the volume fraction range of 0% – 30%. For really high volume fractions micromechanics-based methods such as the D-I and the M-T methods are not very suitable. This may be an explanation for the discrepancy between the D-I method and the reference solution. However, interesting result here is that the proposed two-level homogenization scheme overestimates both the reference solution and the D-I solution over the dilute limit. In the stiff interphase case, first level's results, effective inclusion material properties are cause of the highly stiff behavior for high volume fractions. Fig. 4.25 demonstrates that for soft interphase with high volume fractions, proposed method can be performed and calculated effective properties are very close to reference solution. But for stiff interphase case, there may be an overestimation for D-I and proposed model, therefore it should be investigated carefully. Comparison with two-dimensions results also indicate that, for soft interphase, proposed method works better in three-dimensions as well.

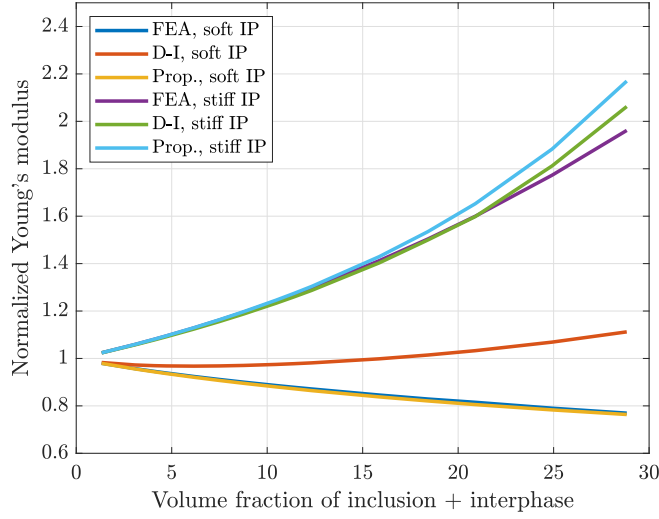


Figure 4.25: Dilute limit violation in three-dimensions, for thickness, t_0

4.2.10 Poisson Ratio of Effective Inclusion for Three-Dimensional Problems

The effective inclusion's material properties are extracted from the elasticity tensor, which is obtained at the end of the first level of homogenization. To recapture, the inclusion and the interphase have the same Poisson ratio, $\nu = 0.3$. However, the Poisson ratio of the effective inclusion is found to be different than the common value and depend on the volume fraction. Similar results with two-dimensions, A behaviour similar to two-dimensional results shown in Fig. 4.14 is obtained in three-dimensional case as depicted in Fig. 4.26. For the soft and the stiff interphase cases, the Poisson ratio shows a dependency on the volume fraction of constituents. The Poisson's ratio of the effective inclusion corresponding to thickest interphase is always the largest for all volume fractions. These characteristics are similar to two-dimensional case. To the best of our knowledge, this volume fraction dependence for a three-dimensional problem is shown for the first time in literature.

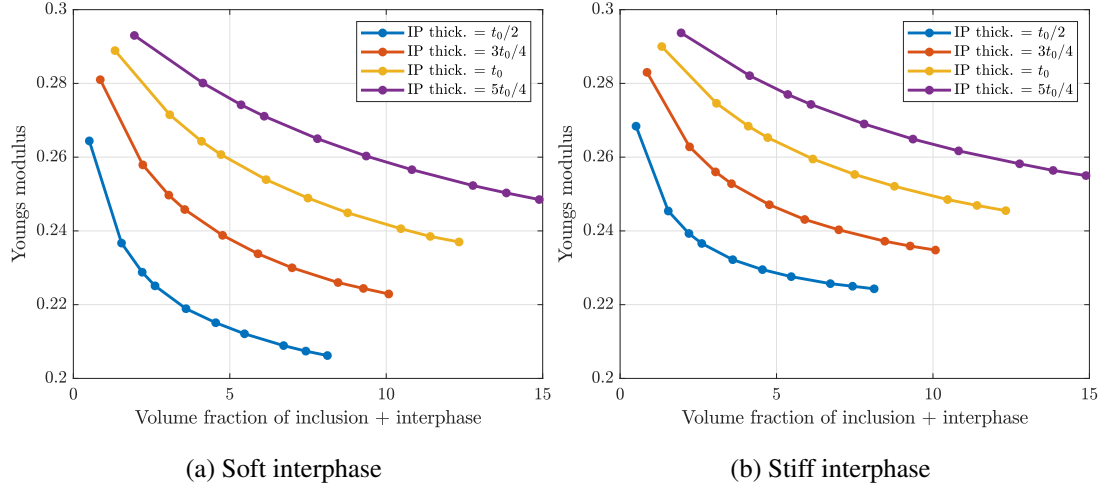
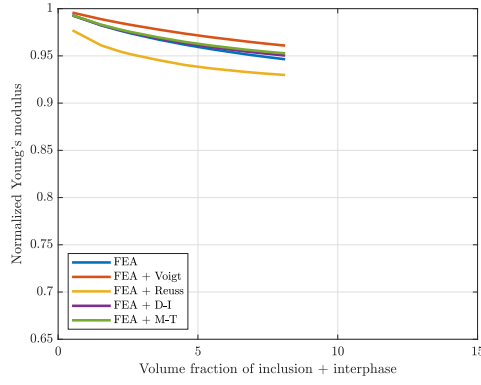


Figure 4.26: Variation of the Poisson ratio of effective inclusion with volume fraction for different thickness cases in three-dimensions

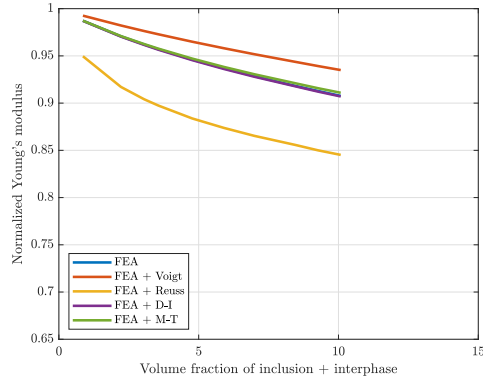
4.2.11 Comparison with Classical Homogenization Techniques for Three-Dimensional Problems

In this section different homogenization techniques are employed in the second level of homogenization.. The reference solution (direct finite element solution of three-phase composite), FEA+Voigt, FEA+Reuss, FEA+M-T (Mori-Tanaka) and the proposed model are compared in Fig. 4.27. Different from two-dimensional results, here when the Voigt and Reuss bounds are used in the second level of homogenization, they indeed create the expected bounds. In the two-dimensional case Fig. 4.15 demonstrates that, among two level homogenization techniques, the Voigt and Reuss averaging create upper and lower bounds, however, three phase reference solution does not completely lie inside of this envelope. However, in the three-dimensional case the reference FEA solution, FEA+M-T and the proposed method lie between FEA+Voigt and FEA+Reuss bounds. Another difference between two- and three-dimensional results is that FEA+D-I (Double-Inclusion) results, which is the proposed method and FEA+M-T results differ more in three-dimensional problem. For two-dimensional problems, those two bounds are almost equal to each other, while here FEA+D-I gives better correction for thickness of $t_0/2$, $3t_0/4$ and t_0 interphase cases. For the thickest interphase thickness, FEA+M-T agrees better with the pro-

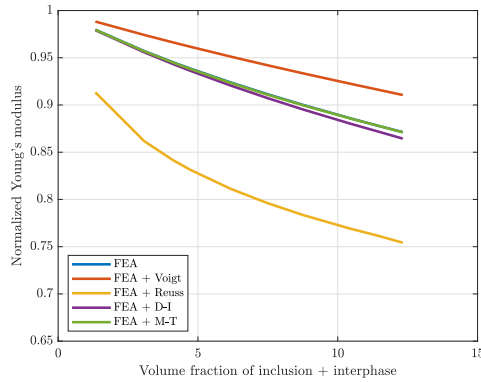
posed solution, and the proposed method slightly underestimates the reference solution. The Mori-Tanaka method uses an explicit expression and therefore, it is cheaper and easier to implement. To this end, it can be preferred over the D-I method, which has an iterative nature and is computationally expensive. In this thesis, for the second level the D-I method is suggested, but Fig. 4.27 shows that the M-T method is also suitable.



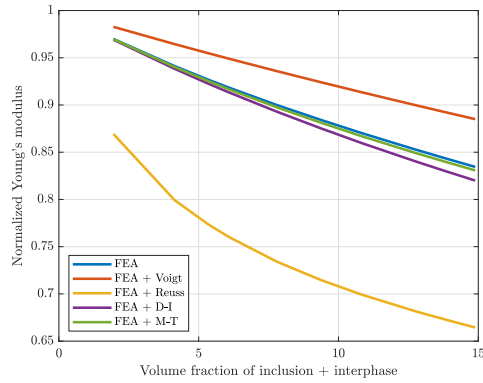
(a) $t = t_0/2$



(b) $t = 3t/4$



(c) $t = t_0$



(d) $t = 5t_0/4$

Figure 4.27: Comparison of different homogenization techniques for the second level of two-level proposed method. Only the soft interphase case is presented.

4.2.12 Extension to Non-Spherical Inclusions: A Short Fiber Reinforced Composite Example

Until this point, the representative volume element (RVE) is chosen as spherical in three-dimensional problems and circular in two-dimensional problems. Furthermore, the inclusion shapes are chosen similarly as spherical or circular. The response of these RVEs exhibit isotropy as long as constituents are isotropic. One of the main advantages of the D-I model is that it is not limited to spherical inclusions only, rather formulations are available for ellipsoidal inclusions as well. Here to demonstrate this capability a transversely isotropic example, an ellipsoidal inclusion in an ellipsoidal RVE is chosen to analyse. This example is analysed in order to show capability of the method to model different geometries. Since sphere is a special case of an ellipsoid, in which all the major and minor radii are the same ($a = b = c$), a general spheroid ($a = b < c$) case is modeled for this purpose. In micromechanics-based methods Eshelby tensor $\mathbb{S}$ is calculated differently depending on the aspect ratio, as explained earlier. In the case of the spherical inclusions, the formulation is simplified to (4.2). Here the components of the Eshelby tensor are presented for an ellipsoidal inclusion for an isotropic medium.

$$\begin{aligned}
 S_{1111} &= \frac{3}{8\pi(1-\nu)}a^2I_{11} + \frac{1-2\nu}{8\pi(1-\nu)}I_1 \\
 S_{1122} &= \frac{1}{8\pi(1-\nu)}b^2I_{12} + \frac{1-2\nu}{8\pi(1-\nu)}I_1 \\
 S_{1133} &= \frac{1}{8\pi(1-\nu)}c^2I_{13} + \frac{1-2\nu}{8\pi(1-\nu)}I_1 \\
 S_{1212} &= \frac{a^2+b^2}{16\pi(1-\nu)}I_{12} + \frac{1-2\nu}{16\pi(1-\nu)}(I_1 + I_2) \\
 S_{1112} &= S_{1223} = S_{1232} = 0
 \end{aligned} \tag{4.13}$$

In (4.13) it is assumed that $a > b > c$ where a , b and c are the semi axes of the

ellipsoid. Here I terms are defined as standard elliptic integrals as follows.

$$\begin{aligned}
I_1 &= \frac{4\pi abc}{(a^2 - b^2)\sqrt{(a^2 - c^2)}} [F(\theta, k) - E(\theta, k)] \\
I_3 &= \frac{4\pi abc}{(b^2 - c^2)\sqrt{(a^2 - c^2)}} \left[\frac{b\sqrt{(a^2 - c^2)}}{ac} - E(\theta, k) \right] \\
F(\theta, k) &= \int_0^\theta \frac{dw}{(1 - k^2 \sin^2 w)^{1/2}} \\
E(\theta, k) &= \int_0^\theta (1 - k^2 \sin^2 w)^{1/2} dw
\end{aligned} \tag{4.14}$$

where,

$$\begin{aligned}
\theta &= \arcsin \sqrt{\frac{a^2 - c^2}{a^2}} \\
k &= \sqrt{\frac{a^2 - b^2}{a^2 - c^2}}
\end{aligned} \tag{4.15}$$

Note that these elliptic integrals should satisfy the conditions given in (4.16).

$$\begin{aligned}
I_1 + I_2 + I_3 &= 4\pi \\
3I_{11} + I_{12} + I_{13} &= \frac{4\pi}{a^2} \\
3a^2 I_{11} + b^2 I_{12} + c^2 I_{13} &= 3I_1 \\
I_{12} &= \frac{I_2 - I_1}{a^2 - b^2}
\end{aligned} \tag{4.16}$$

Material properties of the soft interphase case are chosen for illustration, see Table 3.1. Thus the interphase is the softest of all materials in the system. Furthermore, the thickness is kept constant while the inclusion volume fraction changes from $\phi = 0.01$ to $\phi = 0.05$. Note that the corresponding combined volume fraction of the inclusion and the interphase is more than 0.12, which is far above the dilute limit. In order to model a composite system, a short fiber reinforced composite (SFRC) with polymer matrix is chosen. A unidirectional fiber alignment is considered and effects of orientation distribution are not investigated. Aspect ratio of fiber is chosen as 20. It is important to note that the thicknesses of the interphase along the longitudinal and the transverse directions are different and depend on the aspect ratio. Aspect ratio is

an important variable for fiber reinforced composites. Due to geometry of the fiber and problems related with the mesh generation, 20 is chosen in this study.

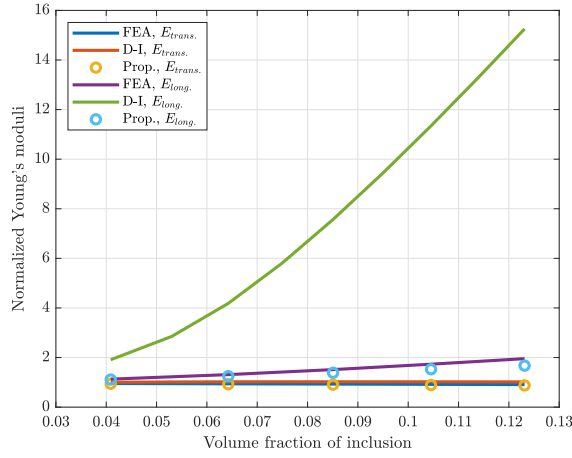


Figure 4.28: Longitudinal and transverse Young's moduli for single fiber reinforced composite. Comparison of the proposed method and micromechanics based D-I method with reference finite element solution.

Fig. 4.28 demonstrates that the Young's moduli predictions of the proposed method agrees very well with the reference finite element solution both in longitudinal and transverse directions. It is apparent that the prediction of the D-I method for the longitudinal modulus of the composite is very poor compared to the reference solution. The D-I method also slightly overestimates the transverse modulus and needs an improvement. The need for an improvement can be stated easily for the longitudinal Young's modulus results. However, close up observations demonstrate the overestimation of the D-I method for the transverse modulus as well, see Fig. 4.29b.

Other than two-level homogenization techniques, two-step homogenization techniques for systems having inclusions with different orientations were proposed by Naili et al. [132] for short fiber reinforced composites as well. They proposed a pseudo-grain homogenization technique and used FE homogenization for the first step. Then, in the second step they compared different techniques, such as Voigt, Reuss and M-T. In the first step they group different orientation of fibers as pseudo-grains and then homogenize the pseudo grains by means of FEA. Then these homogenized grains are homogenized by means of bounds and micromechanics-based method. They show

that their two-step homogenization technique is a promising way to calculate the effective properties of SFRCs.

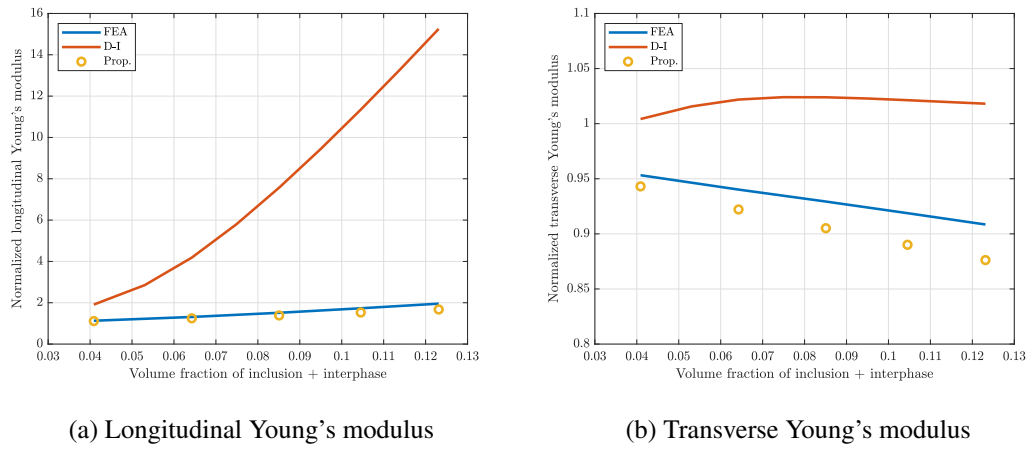


Figure 4.29: Comparison of the proposed method and micromechanics based D-I method with reference finite element solution.

Close up plots of Fig. 4.28 are shown in Fig. 4.29 for the longitudinal and the transverse moduli. As seen in Fig. 4.29a, the proposed method and the reference solution are in good agreement. By means of a replacement procedure and forming an effective inclusion, overestimation problem of the D-I method resulted due to the soft interphase is prevented. However, the proposed method still slightly underestimates the reference solution. This is also observed for the spherical inclusion case, see Fig. 4.18b, and therefore is not unexpected. This underestimation becomes more clear when the transverse modulus is compared, see Fig. 4.29b. But, the performance of the proposed model is still acceptable. As seen in Fig. 4.29b, the micromechanics-based D-I prediction of transverse modulus behaves very differently. The transverse modulus of the D-I method does not change monotonously with the volume fraction of the inclusion. Therefore, the characteristics of the transverse modulus of FEA is not followed in D-I model.

CHAPTER 5

TWO-LEVEL HOMOGEZATION METHOD FOR COATED INCLUSION PROBLEM IN VISCOELASTICITY

5.1 Homogenization Methodology for Viscoelasticity

5.1.1 Dynamic Correspondence Principle

In constitutive modeling of materials, there are different methods to model time-dependent material behavior. The differential approach uses linear springs and dashpots to model elastic and viscous behavior. For example, the Maxwell model uses a spring and dashpot in series, while the Kelvin model uses a spring and dashpot in parallel. A combination of these two models is known as the Burgers model. Burgers model is used to model **standard linear solid**. Another approach is based on the hereditary integrals. The hereditary approach relies on the concept of the superposition principle. When the strain history over time $[-\infty, t]$ is given, the stress at the current time step can be calculated using hereditary integrals. Integral equations and Stieltjes convolution are used to examine the time-dependent behavior in this approach. This is an iterative method and requires the variables from the previous step. Therefore, numerical calculations take a long time while modeling material behavior with integral equations. The solution of hereditary integrals and detailed formulations can be found at the reference [133].

These problems arising from time-dependent modeling can be solved by restating the problem in the Fourier space depending on the frequency. For this, the Dynamic Correspondence Principle is used; in this formulation, material behavior is modeled with a complex, dynamic modulus instead of elastic modulus [120, 134]. When first

proposed, it is used in modeling of linear viscoelasticity. Today, the Dynamic Correspondence Principle is used even in exceptional cases such as crack propagation when the material is functionally graded [135]. By means of the Dynamic Correspondence Principle, the problem is formulated in the frequency domain. The time-dependent change of stress, according to the Stieltjes convolution, is expressed as follows.

$$\sigma(t) = \int_{-\infty}^t G(t - \tau) \frac{d\varepsilon(\tau)}{d\tau} d\tau \quad (5.1)$$

$G(t)$ and τ correspond to the relaxation modulus and relaxation time, respectively. Constitutive equation for linear, isotropic viscoelastic material can be written as.

$$\begin{aligned} s_{ij}(x, t) &= \int_{-\infty}^t 2G(t - \tau) \frac{de_{ij}(x, t)}{d\tau} d\tau \\ \sigma_{kk}(x, t) &= \int_{-\infty}^t 3K(t - \tau) \frac{d\epsilon_{kk}(x, t)}{d\tau} d\tau \end{aligned} \quad (5.2)$$

In (5.2) s_{ij} and σ_{kk} are the deviatoric and the volumetric stress tensors depending on time and spatial position, respectively, e_{ij} , ϵ_{kk} are the corresponding strain tensors. $G(t)$ and $K(t)$ are time-dependent shear and bulk moduli of the material. As mentioned, these equations can be written in the frequency domain through the Dynamic Correspondence Principle. Time-dependent deformation is written harmonically under steady-state conditions as in (5.3). Variables expressed with an overline correspond to complex quantities.

$$\epsilon_{ij}(x, t) = \bar{\epsilon}_{ij}(x, w)e^{iwt} \quad (5.3)$$

Different tests are used to determine the time-dependent material behavior, such as creep, relaxation, and constrain-strain tests. The material is kept under constant strain in the relaxation test, and the corresponding stress is recorded. Stress-time and strain-time curves in a typical relaxation test are illustrated in Fig. 5.1. An applied strain may be tensile, compressive, or shear. The material's initial stress is due to its elastic behavior, and the material loosens over time due to its viscous nature. The resulting stress-time curve is used to understand the viscoelastic behavior of the material. The obtained stress-strain curve can be fitted to different models. For example, the Prony

series is a frequently used method in modeling viscoelastic materials in the time domain. In this method, the behavior is expressed as the sum of independent relaxations, as seen in (5.4).

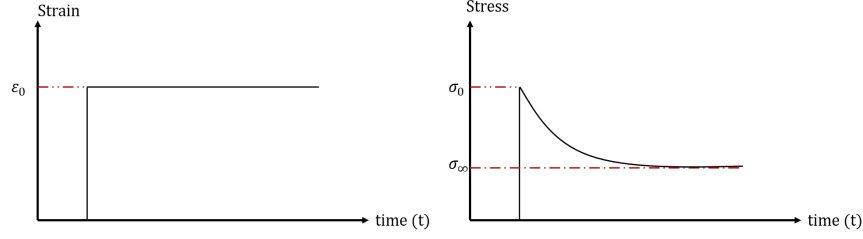


Figure 5.1: Stress and strain v. time curves for relaxation test

$$G(t) = G_\infty + \sum_{j=1}^N G_j e^{-\frac{t}{\tau_j}} \quad (5.4)$$

G_∞ given in (5.4) is the shear modulus that is found in fully relaxed state, $t = \infty$, G_i and τ_i are the terms of the Prony series. For every relaxation time τ_i , there is a corresponding relaxation modulus G_i .

Shear and bulk moduli in the frequency domain can be written in integral form as follows,

$$\begin{aligned} \bar{G}(w) &= \int_0^\infty G(t) e^{-iwt} dt \\ \bar{K}(w) &= \int_0^\infty K(t) e^{-iwt} dt \end{aligned} \quad (5.5)$$

Having inserted (5.3) and (5.5) in (5.2), deviatoric and volumetric stress terms can be written depending on the frequency and position.

$$\begin{aligned} \bar{s}_{ij}(x, w) &= 2iw\bar{G}(w)\bar{e}_{ij}(x, w) \\ \bar{\sigma}_{kk}(x, w) &= 3iw\bar{K}(w)\bar{e}_{kk}(x, w) \end{aligned} \quad (5.6)$$

Eqn. (5.6) consists of two terms, $iw\bar{G}$ and $iw\bar{K}$. They represent the material's complex dynamic moduli and can be divided into real and imaginary parts as storage and

loss moduli.

$$\begin{aligned} iw\bar{G}(w) = G^*(w) &= G'(w) + iG''(w) \\ iw\bar{K}(w) = K^*(w) &= K'(w) + iK''(w) \end{aligned} \quad (5.7)$$

The storage modulus defines the viscoelastic material's elastic character, and the loss modulus defines the viscous character. Moreover, the storage and loss moduli can be defined in the frequency domain as given in (5.8). These equations are obtained by half-sided Fourier transformation of (5.2).

$$\begin{aligned} G'(w) &= G_\infty + \sum_{i=1}^n \frac{G_i(w\tau_i)^2}{1 + (w\tau_i)^2} \\ G''(w) &= \sum_{i=1}^n \frac{G_i w \tau_i}{1 + (w\tau_i)^2} \end{aligned} \quad (5.8)$$

Integral equations that represent the viscoelastic behavior in the time domain can be reduced to linear elasticity equations in the frequency domain by the Dynamic Correspondence Principle. All quantities now depend on the frequency and expressed as complex numbers. Therefore, analytical or numerical solutions developed for elasticity problems can be used in viscoelasticity. In this chapter, homogenization procedures are discussed in a viscoelastic framework using this principle. Micromechanics-based Double Inclusion (D-I) method and FEA homogenization for coated inclusion problem are extended to viscoelasticity. The equations obtained for linear elasticity will be used to model the viscoelastic behavior in the frequency domain.

5.1.2 Double-Inclusion Model for Viscoelasticity

The double Inclusion (D-I) model is a popular method proposed by Nemat-Nasser and Hori in 1993 for obtaining the effective properties of multi-phase composites [8]. In Chapter 4, the detailed formulation of the model is given. In the viscoelastic case, the elements of the elasticity tensors are composed of complex numbers that depend on frequency. Since the Eshelby tensor is a function of aspect ratio and Poisson ratio, the components of the Eshelby tensor must also be complex numbers. Apart from

this, the Double Inclusion model equations obtained for elasticity can be used in the same way. The quantities expressed with superscript * are complex numbers.

The elasticity tensor of multiphase viscoelastic composite

$$\mathbf{C}^* = \mathbf{C}^{*\text{inf}} : [\mathbf{I} + (\mathbf{S}^* - \mathbf{I}) : \Lambda^*] : [\mathbf{I} + \mathbf{S}^* \Lambda^*]^{-1} \quad (5.9)$$

$$\Lambda^* = \sum_{i=1}^n \phi_i \Lambda_i^* \quad (5.10)$$

For a uniform constant elasticity of phase

$$\Lambda_i^* = [(\mathbf{C}^{*\text{inf}} - \mathbf{C}_i^*)^{-1} : \mathbf{C}^{*\text{inf}} - \mathbf{S}^*]^{-1} \quad (5.11)$$

Instead of the D-I method, the effective modulus can also be determined using the Mori-Tanaka approach. In this case the effective composite modulus of elasticity for two-phase viscoelastic material is given by Brinson and Lin [4].

$$\mathbf{C}^* = \mathbf{C}_m^* : (\mathbf{I} - \phi_i [\mathbf{S}^* \phi_m + \phi_i \mathbf{I} + (\mathbf{C}_i^* - \mathbf{C}_m^*)^{-1} \mathbf{C}_m^*]^{-1})^{-1} \quad (5.12)$$

In (5.12), $\mathbf{C}_m^*$ and $\mathbf{C}_i^*$ correspond to elasticity tensors of matrix and inclusion. ϕ_m and ϕ_i are the volume fraction of matrix and inclusion, respectively. $\mathbf{S}^*$ and $\mathbf{I}$ are the fourth order complex Eshelby and identity tensor. The Mori-Tanaka method is used by different researchers and reported in literature [3, 107, 124].

5.1.3 Homogenization with Finite Element Method for Viscoelastic Problems

Boundary value problems can also be solved by using the finite element method through the Dynamic Correspondence Principle. The main difference in the viscoelastic homogenization approach with the homogenization of the linear elasticity problem is that the quantities are complex numbers. The displacement vector can be

expressed as given in (5.13).

$$\mathbf{u}^* = \begin{bmatrix} u'_1 + iu''_1 \\ u'_2 + iu''_2 \\ u'_3 + iu''_3 \end{bmatrix} \quad (5.13)$$

The problem can be solved like an elasticity problem after making the necessary modifications. Instead of storing these complex numbers as a whole, complex quantities are reallocated as real and imaginary parts. This problem can be solved by doubling the degrees of freedom at each node. In this case, obviously the number of unknowns doubles at each node. The components of the displacement vector, the stress tensor, and the strain tensor are complex quantities in the viscoelastic formulation. Thus, each component is separated into real and imaginary parts,

$$\begin{aligned} \mathbf{u} &= \begin{bmatrix} u'_1 & u'_2 & u'_3 & u''_1 & u''_2 & u''_3 \end{bmatrix}^T = \begin{bmatrix} \mathbf{u}' & \mathbf{u}'' \end{bmatrix}^T \\ \boldsymbol{\sigma} &= \begin{bmatrix} \boldsymbol{\sigma}' & \boldsymbol{\sigma}'' \end{bmatrix}^T \\ \boldsymbol{\epsilon} &= \begin{bmatrix} \boldsymbol{\epsilon}' & \boldsymbol{\epsilon}'' \end{bmatrix}^T \end{aligned} \quad (5.14)$$

The vectors $\boldsymbol{\sigma}'$, $\boldsymbol{\sigma}''$, $\boldsymbol{\epsilon}'$ and $\boldsymbol{\epsilon}''$ in (5.14) are defined as

$$\begin{aligned} \boldsymbol{\sigma}' &= \begin{bmatrix} \sigma'_{11} & \sigma'_{22} & \sigma'_{33} & \sigma'_{12} & \sigma'_{23} & \sigma'_{13} \end{bmatrix} \\ \boldsymbol{\sigma}'' &= \begin{bmatrix} \sigma''_{11} & \sigma''_{22} & \sigma''_{33} & \sigma''_{12} & \sigma''_{23} & \sigma''_{13} \end{bmatrix} \\ \boldsymbol{\epsilon}' &= \begin{bmatrix} \epsilon'_{11} & \epsilon'_{22} & \epsilon'_{33} & \epsilon'_{12} & \epsilon'_{23} & \epsilon'_{13} \end{bmatrix} \\ \boldsymbol{\epsilon}'' &= \begin{bmatrix} \epsilon''_{11} & \epsilon''_{22} & \epsilon''_{33} & \epsilon''_{12} & \epsilon''_{23} & \epsilon''_{13} \end{bmatrix} \end{aligned} \quad (5.15)$$

Conservation of linear momentum is used to derive the weak form of the governing equation. For the static problems, the balance equation can be written as

$$\nabla^T \boldsymbol{\sigma} + \mathbf{b} = \mathbf{0} \quad (5.16)$$

The material model of the linear elasticity reads

$$\boldsymbol{\sigma} = \mathbb{C} : \boldsymbol{\epsilon} \quad (5.17)$$

For the viscoelastic material model, it can be arranged as follows. The stress, the strain, and the elasticity tensors are complex quantities, as seen in (5.18).

$$\begin{aligned}\boldsymbol{\sigma}^* &= \mathbb{C}^* : \boldsymbol{\epsilon}^* \\ \begin{bmatrix} \sigma' \\ \sigma'' \end{bmatrix} &= \begin{bmatrix} \mathbb{C}' & -\mathbb{C}'' \\ \mathbb{C}'' & \mathbb{C}' \end{bmatrix} \begin{bmatrix} \epsilon' \\ \epsilon'' \end{bmatrix}\end{aligned}\quad (5.18)$$

Since the elasticity tensor in (5.18) is a complex quantity, it is restated as a matrix. Any complex number is expressed as a $(a + bi)$ matrix as follows.

$$\begin{bmatrix} a & -b \\ b & a \end{bmatrix}$$

Similarly the elasticity tensor is divided into real and imaginary parts for a viscoelastic material and expressed as follows in the matrix form.

$$\mathbb{C} = \begin{bmatrix} \mathbb{C}' & -\mathbb{C}'' \\ \mathbb{C}'' & \mathbb{C}' \end{bmatrix}\quad (5.19)$$

The strain-displacement relation can be expressed in the matrix form

$$\boldsymbol{\epsilon} = \nabla \boldsymbol{u}\quad (5.20)$$

where the three-dimensional strain operator ∇ can be expressed as follows.

$$\nabla = \begin{bmatrix} \frac{\partial}{\partial x_1} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{\partial}{\partial x_2} & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\partial}{\partial x_3} & 0 & 0 & 0 \\ \frac{\partial}{\partial x_2} & \frac{\partial}{\partial x_1} & 0 & 0 & 0 & 0 \\ 0 & \frac{\partial}{\partial x_3} & \frac{\partial}{\partial x_2} & 0 & 0 & 0 \\ \frac{\partial}{\partial x_3} & 0 & \frac{\partial}{\partial x_1} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\partial}{\partial x_1} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{\partial}{\partial x_2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial x_3} \\ 0 & 0 & 0 & \frac{\partial}{\partial x_2} & \frac{\partial}{\partial x_1} & 0 \\ 0 & 0 & 0 & 0 & \frac{\partial}{\partial x_3} & \frac{\partial}{\partial x_2} \\ 0 & 0 & 0 & \frac{\partial}{\partial x_3} & 0 & \frac{\partial}{\partial x_1} \end{bmatrix} \quad (5.21)$$

Eqn. (5.16) is multiplied with an arbitrary test function w and then integrated on the region where the problem is defined

$$\int_{\Omega} \left(\nabla \sigma \cdot w + b \cdot w \right) d\Omega = 0 \quad (5.22)$$

Using the partial integration, (5.22) can be arranged as

$$\begin{aligned} \int_{\Omega} \left(\nabla(\sigma \cdot w) - \nabla w \cdot \sigma + b \cdot w \right) d\Omega &= 0 \\ \int_{\Omega} \left(\nabla w \cdot \mathbb{C} : \nabla u \right) d\Omega - \left[w t \right]_{\Gamma} &= \int_{\Omega} b \cdot w d\Omega \end{aligned} \quad (5.23)$$

where the constitutive relation, (5.18) is inserted in the second step. Choosing the same approximation functions for u and w leads to Galerkin approach. Following the Galerkin approach the displacement field and the test function are approximated

as

$$\begin{aligned}\mathbf{u} &= \sum_{i=1}^8 N_i \mathbf{u}_i \\ \mathbf{w} &= \sum_{i=1}^8 N_i \mathbf{w}_i\end{aligned}\tag{5.24}$$

Inserting (5.24) into (5.23), the following result is obtained.

$$u_i \int_{\Omega} \frac{\partial N_i}{\partial \mathbf{x}} \mathbb{C} \frac{\partial N_j}{\partial \mathbf{x}} d\Omega = \left[\mathbf{w} \mathbf{t} \right]_{\Gamma} + \int_{\Omega} N_j \mathbf{b} d\Omega \tag{5.25}$$

Eqn. (5.25) is similar to finite element formulation for a linear elastic problem. However, the definitions of the stress and the strain and the elasticity tensors are different from the elastic formulation.

The algorithmic chart for the proposed methodology is given as follows.

Algorithm 2: Proposed methodology for viscoelastic problem

Result: Effective storage and loss material properties of three-phase polymer nanocomposite

- 1 Create the geometry with Abaqus for specific volume fraction of inclusion $\phi_{\text{inclusion}}$;
 - 2 Obtain the node, element, connectivity and boundary information via Python script from Abaqus input file (*.inp);
 - 3 Apply six load cases, boundary conditions for different frequencies ω in Matlab;
 - 4 Solve the finite element problem with doubled degrees of freedom that is derived for viscoelastic homogenization in Matlab;
 - 5 Perform the following homogenization algorithm via Matlab;
 - 6 **while** $j \leq \text{load cases}$ **do**
 - 7 **while** $i \leq n$ (*total number of elements*) **do**
 - 8 $\bar{\sigma} = \frac{\sum_{i=1}^n \sigma_i V_i}{\sum_{i=1}^n V_i}$;
 - 9 $\bar{\epsilon} = \frac{\sum_{i=1}^n \epsilon_i V_i}{\sum_{i=1}^n V_i}$;
 - 10 **end**
 - 11 $\overline{\mathbb{C}}(,j) = \frac{\overline{\sigma}(,j)}{\overline{\epsilon}(,j)}$;
 - 12 **end**
 - 13 Place the effective $\overline{\mathbb{C}}$ into the viscoelastic Double-Inclusion method script in Matlab and calculate the effective $\overline{\mathbb{C}}$ of the composite with an iterative solution;
 - 14 Post-process the material properties according to whether the obtained result shows isotropy or not
-

5.2 Results

5.2.1 Verification of D-I and Finite Element Homogenization

In this section, two verification studies are first presented to see the capabilities of the Mori-Tanaka method and the FE method in viscoelastic homogenization. Matlab is

used for micromechanics-based calculations. The performance of the proposed model for linear elastic problems was demonstrated using Abaqus in Chapter 4. However, for the solution of viscoelastic problems, an in-house finite element code is written in Matlab for two- and three-dimensional analyses. Thus, in order to see whether these codes are working correctly, a verification is needed. For this purpose, the results given by Brinson and Lin are compared [4]. The material properties are taken from the reference article. There are two imaginary materials, one is stiff, and another one is soft. They are modeled with a Prony series approach, and the terms of the Prony series are given in Table 5.1. The material properties are created so that the storage modulus values of soft and stiff materials never intersect for any frequency. It is explained that, in the Prony series approach, the behavior of material is expressed as the sum of independent relaxations, as seen in (5.4). The shear and bulk moduli of the soft and stiff materials are expressed using Prony series, as follows

$$\begin{aligned} G(t) &= G_{\infty} + \sum_{j=1}^N G_j e^{-\frac{t}{\tau_j}} \\ K(t) &= K_{\infty} + \sum_{j=1}^N K_j e^{-\frac{t}{\tau_j}} \end{aligned} \quad (5.26)$$

Using Half-sided Fourier transforms, terms in (5.26) are defined in frequency domain as the components of the storage and loss moduli.

$$\begin{aligned} G'(w) &= G_{\infty} + \sum_{i=1}^n \frac{G_i (w\tau_i)^2}{1 + (w\tau_i)^2} \\ G''(w) &= \sum_{i=1}^n \frac{G_i w\tau_i}{1 + (w\tau_i)^2} \\ K'(w) &= K_{\infty} + \sum_{i=1}^n \frac{K_i (w\tau_i)^2}{1 + (w\tau_i)^2} \\ K''(w) &= \sum_{i=1}^n \frac{K_i w\tau_i}{1 + (w\tau_i)^2} \end{aligned} \quad (5.27)$$

As seen in Table 5.1, the elastic bulk modulus, and the shear modulus for the viscoelastic materials are given. When the bulk and the shear moduli are known, the elasticity tensor can be constructed for an isotropic material. Since the shear and the

Table 5.1: Material constants used in the Prony series

Stiff material shear modulus		Soft material shear modulus		Bulk and asymptotic mod.
τ_i^1	G_i^1	τ_i^2	G_i^2	
3	3.162	0.032	2.512	Stiff mat.
10	17.783	0.100	10.000	$\tau_1^1 = 10000$
32	100.000	0.316	56.234	$K_1^1 = 40000$
100	316.228	1.000	316.228	$K_\infty^1 = 8000$
316	1000.000	3.162	1000.000	$G_\infty^1 = 100.00$
1000	5623.413	10.000	199.526	
3162	10000.000	31.623	50.119	
10000	562.341	100.000	19.953	Soft mat.
31623	141.254	316.228	12.589	$\tau_1^2 = 100$
100000	56.234	1000.000	2.512	$K_1^2 = 3000$
316228	17.783	3162.278	1.698	$\tau_2^2 = 316.228$
1000000	5.623	10000.000	1.202	$K_2^2 = 100$
3162278	3.162	31622.777	1.148	$K_\infty^2 = 200$
10000000	1.778	100000.000	1.096	$G_\infty^2 = 3.162$

bulk moduli have real and imaginary parts, the resultant elastic moduli should be derived separately for the real and the imaginary parts, which correspond to the storage and the loss moduli. Homogeneous isotropic linear elastic materials have their elastic properties uniquely determined by any two moduli. Thus, given any two, any other of the elastic moduli can be calculated. In [4], given material constants are the shear and bulk moduli. The Young's modulus and the Poisson ratio formulas are given as

$$\begin{aligned} E^* &= \frac{9K^*G^*}{3K^* + G^*} \\ \nu^* &= \frac{3K^* - 2G^*}{2(3K^* + G^*)} \end{aligned} \quad (5.28)$$

In (5.28), the bulk modulus (K^*) and the shear modulus (G^*) are complex numbers. The storage Young's modulus and the loss Young's modulus are written as (5.29) and the storage Poisson ratio and the loss Poisson ratio are written as (5.30). K_{stor} , K_{loss} correspond to the storage bulk modulus and the loss bulk modulus. G_{stor} , G_{loss} correspond to the storage shear modulus and the loss shear modulus.

$$\begin{aligned} E_{\text{stor}} &= \frac{(9G_{\text{loss}}K_{\text{stor}} + 9G_{\text{stor}}K_{\text{loss}})(G_{\text{loss}} + 3K_{\text{loss}})}{((G_{\text{loss}} + 3K_{\text{loss}})^2 + (G_{\text{stor}} + 3K_{\text{stor}})^2) - \frac{(9G_{\text{loss}}K_{\text{loss}} - 9G_{\text{stor}}K_{\text{stor}})(G_{\text{stor}} + 3K_{\text{stor}})}{(G_{\text{loss}} + 3K_{\text{loss}})^2 + (G_{\text{stor}} + 3K_{\text{stor}})^2}} \\ E_{\text{loss}} &= \frac{(9G_{\text{loss}}K_{\text{loss}} - 9G_{\text{stor}}K_{\text{stor}})(G_{\text{loss}} + 3K_{\text{loss}})}{((G_{\text{loss}} + 3K_{\text{loss}})^2 + (G_{\text{stor}} + 3K_{\text{stor}})^2) + \frac{(9G_{\text{loss}}K_{\text{stor}} + 9G_{\text{stor}}K_{\text{loss}})(G_{\text{stor}} + 3K_{\text{stor}})}{(G_{\text{loss}} + 3K_{\text{loss}})^2 + (G_{\text{stor}} + 3K_{\text{stor}})^2}} \end{aligned} \quad (5.29)$$

$$\begin{aligned} \nu_{\text{stor}} &= -\frac{(2G_{\text{loss}} - 3K_{\text{loss}})(2G_{\text{loss}} + 6K_{\text{loss}})}{4((G_{\text{loss}} + 3K_{\text{loss}})^2 + (G_{\text{stor}} + 3K_{\text{stor}})^2)} - \frac{(2G_{\text{stor}} - 3K_{\text{stor}})(2G_{\text{stor}} + 6K_{\text{stor}})}{4((G_{\text{loss}} + 3K_{\text{loss}})^2 + (G_{\text{stor}} + 3K_{\text{stor}})^2)} \\ \nu_{\text{loss}} &= \frac{(2G_{\text{loss}} + 6K_{\text{loss}})(2G_{\text{stor}} - 3K_{\text{stor}})}{(2G_{\text{loss}} + 6K_{\text{loss}})^2 + (2G_{\text{stor}} + 6K_{\text{stor}})^2} - \frac{(2G_{\text{loss}} + 6K_{\text{stor}})(2G_{\text{loss}} - 3K_{\text{loss}})}{(2G_{\text{loss}} + 6K_{\text{loss}})^2 + (2G_{\text{stor}} + 6K_{\text{stor}})^2} \end{aligned} \quad (5.30)$$

For the first verification, two three-dimensional spherical RVEs are created with homogeneous soft and homogeneous stiff material properties. Furthermore, by applying six different load cases explained before, the loss and the storage Young's modulus are calculated back. Since RVEs are homogeneous, the original material properties should be obtained back. Fig. 5.2 displays the estimated homogenized properties of the soft and the stiff material and the given material properties in the article [4]. As expected, both curves coincide for all frequencies considered.

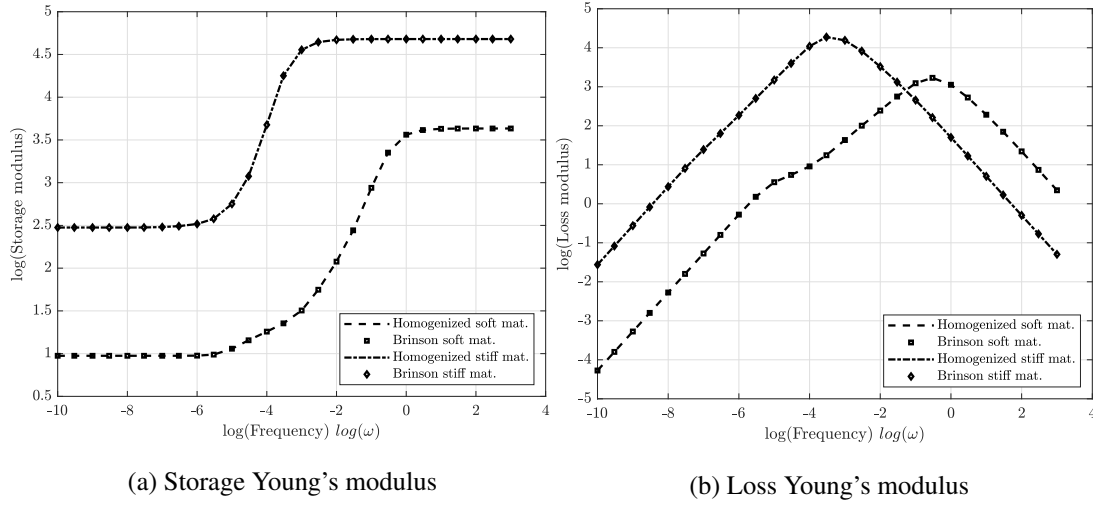


Figure 5.2: Verification study of FE based viscoelastic homogenization in three-dimensional spherical RVE

Another verification study is done to see whether the Mori-Tanaka method and the viscoelastic FE homogenization are capable to solve the problem. For this purpose, an example with a high volume fraction of inclusion is chosen, $\phi_{\text{inclusion}} = 0.5$. It is a two-phase composite example, a matrix with soft material properties and an inclusion with stiff material properties. The model is solved as a two-dimensional plane strain problem since, originally, a transverse modulus of a fiber-reinforced composite is modeled. In the article [4], a two-phase micromechanics-based Mori-Tanaka method was used. However, for generality in the current study, a multi-phase framework is coded. Having the thickness of the third phase (interphase) as 10^{-6}m , the multi-phase model practically boils down to a two-phase material. In Fig. 5.3, material properties of the matrix and the inclusion are shown as well. It shows that results of the current study (the multi-phase Mori-Tanaka method) is in good agreement with the results of [4].

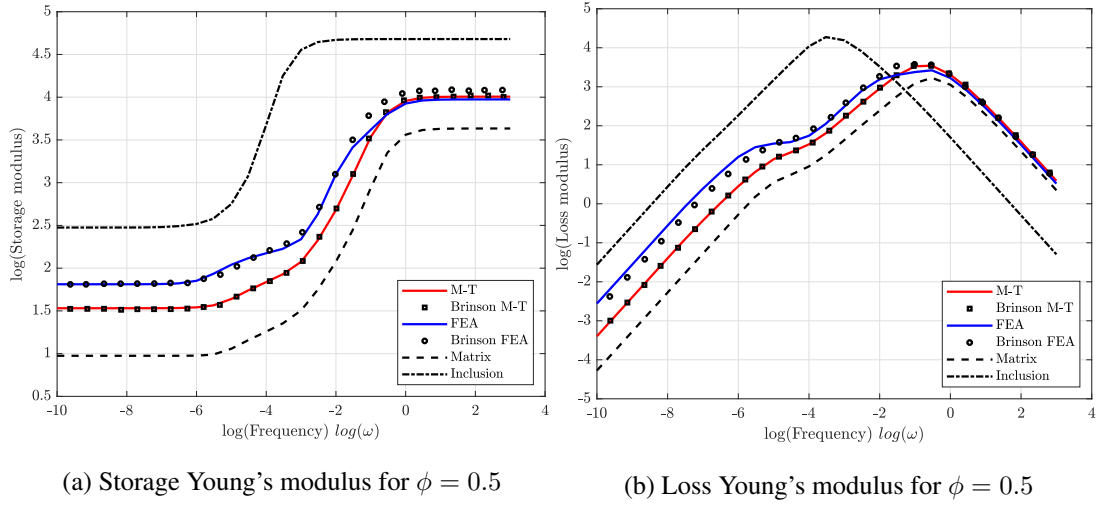


Figure 5.3: Verification study for viscoelastic homogenization with M-T and FEA for two-dimensional circular RVE (stiff inclusion)

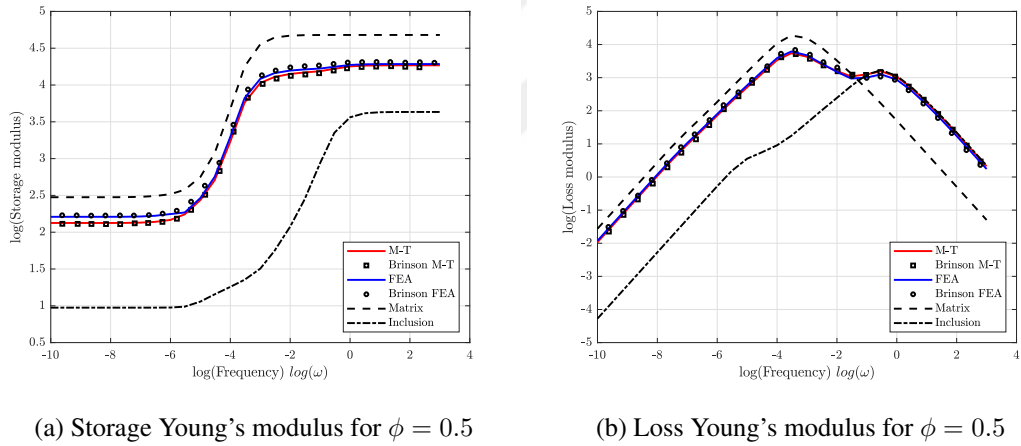


Figure 5.4: Verification study for viscoelastic homogenization with M-T and FEA for two-dimensional circular RVE (soft inclusion)

For the verification of finite element based viscoelastic homogenization, a different problem with the same volume fraction of inclusion and material properties is chosen. There are two different RVEs in the reference article: one is a square array, and the other is a hexagonal array. In Fig. 5.5, the first two RVEs are from the reference article, and the third circular RVE is chosen in this study. Brinson and Lin [4] use

square/rectangular matrix and circular inclusions. In the thesis, both the RVE and the inclusion are chosen as circles, see the last picture in Fig. 5.5.

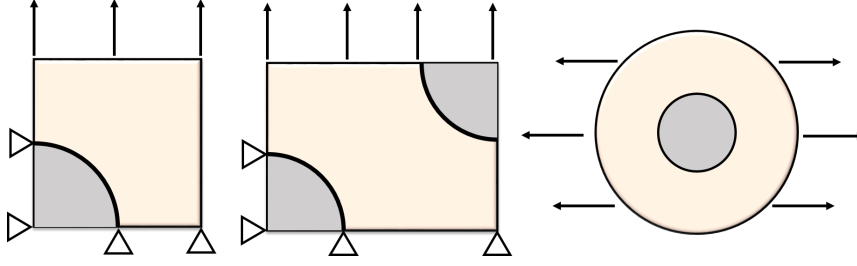


Figure 5.5: Different RVEs compared in the verification study, square array, hexagonal array proposed by Brinson and Lin [4], and circular RVE used in this study

Brinson and Lin [4] observed that the calculated storage and loss moduli change with sequencing. They showed that the square array leads to higher values than the hexagonal array for the same volume fraction. In both cases symmetrical boundary conditions were used such that the quarter of the actual geometry is modeled, and a displacement in the form of $\bar{u} = u + 0i$ was applied to the top surface in the vertical direction. Furthermore, the displacements of the nodes on the right surface were iterated such that the average normal stress on this surface becomes zero. The effective transverse Young's modulus and Poisson's ratio were calculated with the resulting displacement and the initial length. In the circular RVE (the current study), boundary conditions are different than the reference article. Here three separate macroscopic strains are applied, and the components of the elasticity tensor are obtained. The elastic modulus is then derived from the elasticity tensor assuming plane strain conditions.

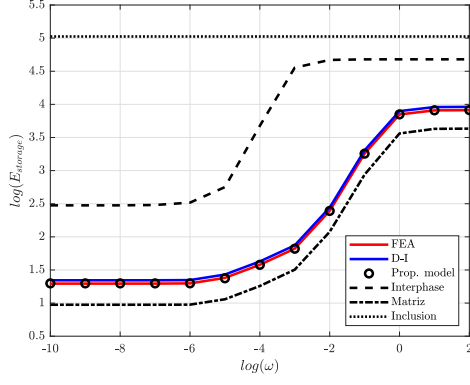
5.2.2 Two-Dimensional Results for Double-Inclusion Model

After validation of the micromechanics-based and FE-based viscoelastic homogenization techniques in the previous section, a new two-level homogenization method that combines these two approaches is proposed. Even though the Mori-Tanaka method is shown for comparison, the Double Inclusion (D-I) method is used in the proposed method. The approach proposed for linear elastic materials in the previ-

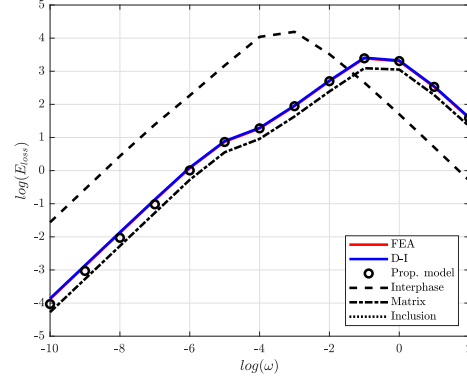
ous chapter is extended to viscoelasticity. In Chapter 4, it was demonstrated that the micromechanical models cannot accurately predict effective composite properties of elastic materials when the interphase is soft. The researchers [124], [3] have reported a similar modeling problem for viscoelastic materials.

A two-level viscoelastic homogenization approach is proposed. In this method, each phase can behave elastic or viscoelastic; there is no limitation. At the first level, inclusion and interphase are homogenized with FEA, and consequently the effective inclusion is obtained. Then, with the micromechanics-based homogenization (the D-I method) the effective inclusion and matrix problem is solved for two-phase composite. At the end of the second level, the homogenized storage and loss moduli can be determined.

The first example, a two-dimensional plane strain problem, is created for validation of the proposed method, where the volume fraction of inclusion is $\phi_{\text{inclusion}} = 0.3$ and interphase is $\phi_{\text{interphase}} = 0.1$. The inclusion is assumed to be elastic, the matrix and the interphase are viscoelastic [5], [124]. The imaginary material proposed in [4] is used. The stiff interphase case corresponds to a softer matrix case, and the soft interphase case corresponds to a stiffer matrix. The inclusion is always the stiffest of all three phases in both cases. In the elastic framework, it is observed that in the presence of a stiff interphase, three-phase FEA reference solution, and the D-I method agree very well, and elastic modulus values are quite similar. The increasing volume fraction of the total inclusion and interphase may cause a slight gap. However, in general, a two-level homogenization scheme is not needed. First, the stiff interphase case is considered. Fig. 5.6 demonstrates that the reference solution and the D-I results are consistent for the storage and the loss moduli values. The proposed method estimates the storage and the loss moduli quite well.



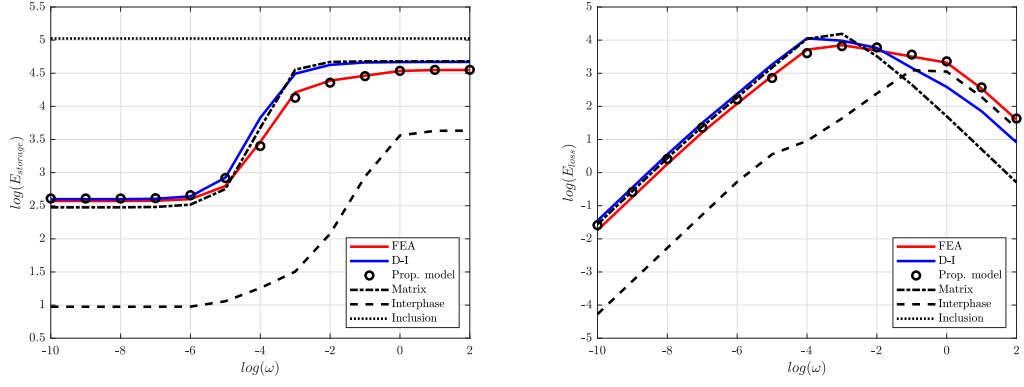
(a) Storage Young's modulus for $\phi_{\text{interphase}} = 0.1$



(b) Loss Young's modulus for $\phi_{\text{interphase}} = 0.1$

Figure 5.6: Comparison of three phase reference viscoelastic FE homogenization solution, the D-I method and the proposed method (stiff interphase)

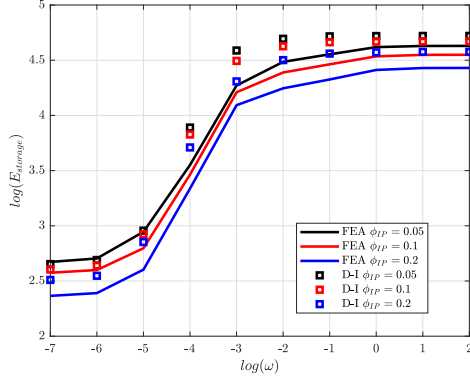
The method proposed in the thesis is expected to calculate the effective composite properties more accurately than the classical Double Inclusion model when the interphase is softer than the matrix. Fig. 5.7 reveals a difference between the reference solution and the D-I model. The D-I model's behavior is dominated by the interphase material, especially for the storage modulus and the low-frequency loss behavior. Since it is plotted in the logarithmic scale, the difference between the reference solution and the D-I model is not negligible. Fig. 5.7 indicates that the results of the proposed model, two-level homogenization method, agrees very well with the reference solution.



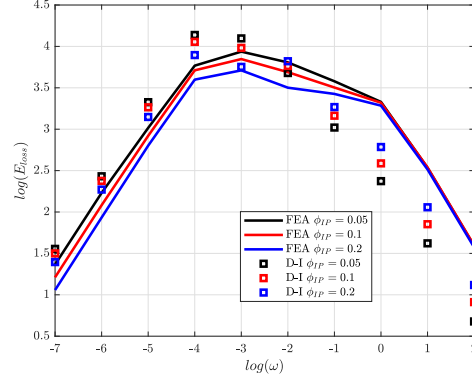
(a) Storage Young's modulus for $\phi_{interphase} = 0.1$ (b) Loss Young's modulus for $\phi_{interphase} = 0.1$

Figure 5.7: Comparison of three phase reference viscoelastic FE homogenization solution, the D-I method and the proposed method (soft interphase)

Fig. 5.7 confirms that the reference solution and the D-I estimate different Young's modulus values for that example. Various interphase volume fractions are investigated to comprehend how different reference solutions and D-I models are. It can be seen that in Fig. 5.8, the micromechanical model predictions are stiffer than the reference results and as the volume ratio increases the discrepancy also increases. This situation is explained by the fact that the load transfer between the matrix and the inclusion through the interphase is not modeled correctly for viscoelastic material. Friebel et al. [3] proposed a two-step homogenization technique to model the coated inclusion problem properly. They extended the interpolative double inclusion model to viscoelastic material behavior. In the first step, pseudo-grains are homogenized with interpolative D-I method, and in the second step, the Voigt bound is used. They reported that in the first step, different homogenization techniques can be applied. They presented improved results for the soft interphase problem proposed by Fisher and Brinson [124] by means of their two-step homogenization technique.



(a) Storage Young's modulus for $\phi_{\text{interphase}}$



(b) Loss Young's modulus for $\phi_{\text{interphase}}$

Figure 5.8: Comparison of three phase reference models with the D-I model for soft interphase with different volume fractions of interphase, $\phi_{\text{inclusion}} = 0.3$

Fisher and Brinson reported [124] the same problem with the stiff interphase case; they investigated different micromechanics-based methods and FEA. In the article, they used the Benveniste solution [87] and the Mori-Tanaka method for comparison. It is a coated inclusion problem, and phases are not all viscoelastic; the inclusion is expected to behave elastically. However, for the stiff interphase case, all three models agree with each other and the FEA method. However, there is a discrepancy among all three models for the soft interphase case. It was reported that interphase properties dominate the Benveniste solution. The Benveniste solution cannot model the stress transfer through interphase correctly and overestimates the storage and the loss moduli.

When Fig. 5.7 is examined closely, it is seen that in the case where the interphase is softer than the matrix, the reference FEA solution and D-I results are well separated. Especially in the transition region from the rubbery (where the frequency is low) to the glassy (where the frequency is high), the D-I model overestimates the reference solution results. The two models' results in the rubbery region are close; a reasonable estimate can be made with micromechanics-based homogenization methods. However, the glassy region's storage and loss moduli are quite different from the FEM results, which are accepted as reference. The proposed two-level viscoelastic homogenization method gives similar results to the reference FEA results; the asymptotic

behavior of the storage modulus is captured by the proposed method. If the logarithmic scale of the vertical axis is neglected, it can be claimed that the micromechanical model also predicts the results well. However, when the results are quantitatively evaluated, the D-I model compared to the reference solution gives the error values of 20%, while the proposed method predicts the glassy asymptotic behavior with 0.5% error.



5.2.3 Variation of Interphase Thickness in Two-Dimensions

An interphase thickness study is performed for two-dimensional problems. For the same volume fraction of inclusion, ($\phi_{\text{inclusion}} = 0.3$) three different interphase thicknesses ($t = t_0/2, t_0, 2t_0$) and corresponding three different volume fractions are studied. Here thickness t_0 is chosen as the thickness corresponding to interphase volume fraction of $\phi_{\text{interphase}} = 0.1$. Fig. 5.9 shows that the proposed method predicts well for different interphase thicknesses. The D-I model predicts the loss modulus at the glassy state poorly; for the storage modulus, it seems that the D-I model overestimates at the glassy state but predicts well at the rubbery state. However, in general the performance of the micromechanics-based D-I model is significantly poorer than the proposed two-level homogenization approach.

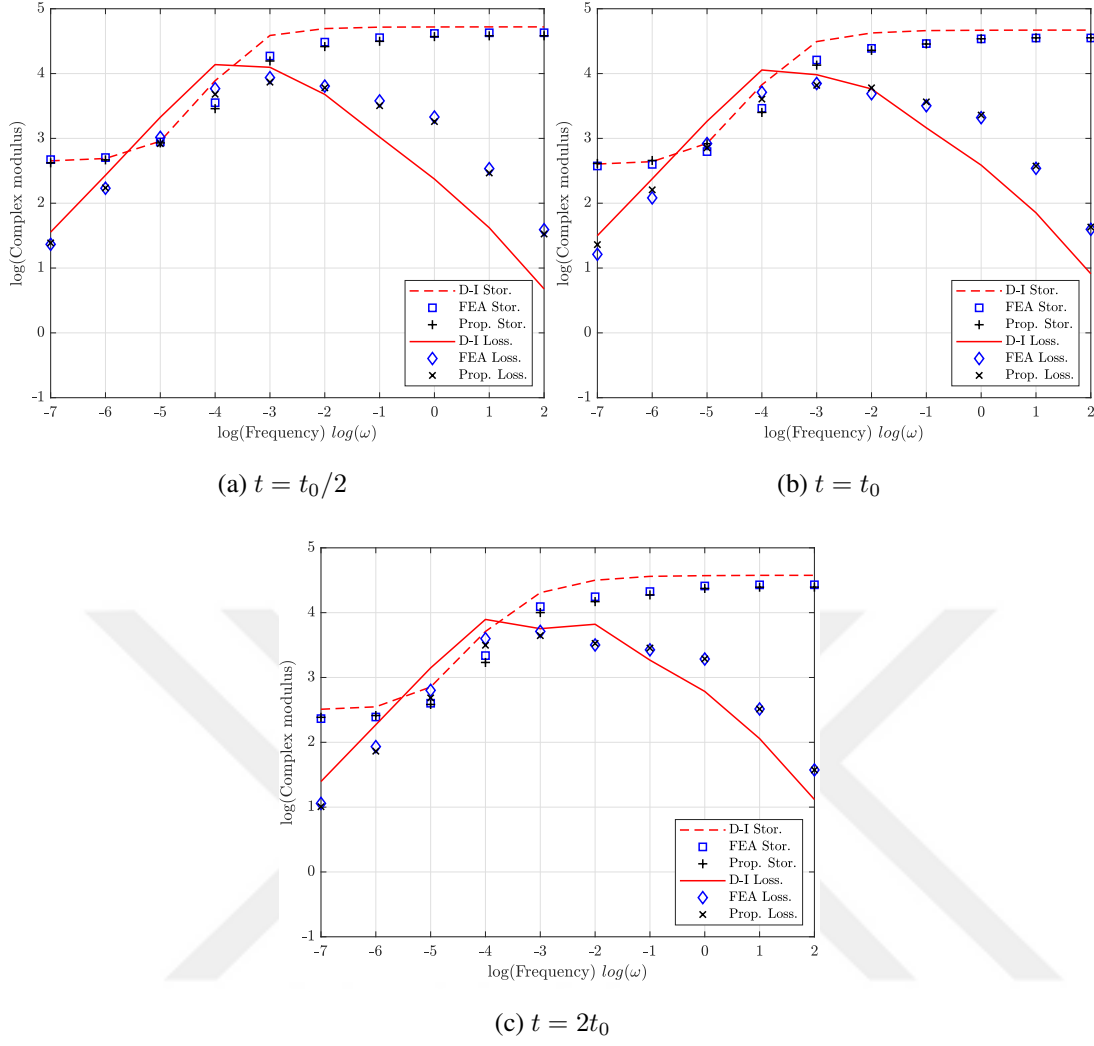


Figure 5.9: Effect of interphase thickness in two-dimensional problems. Comparison of the proposed method with the D-I method and the FEA

5.2.4 Variation of Interphase Thickness in Three-Dimensions

A similar interphase thickness study for three-dimensional problems is also performed to understand how well the proposed model works. Similar to the two-dimensional study, the volume fraction of inclusion is chosen as $\phi_{\text{inclusion}} = 0.1$ and three different thickness cases are investigated, $t = t_0/2, t_0, 3t_0/2$. The thickness of t_0 is chosen as half of the thickness of inclusion radius in $\phi_{\text{inclusion}} = 0.1$. In the two-dimensional study, the thickest interphase is chosen as $t = 2t_0$. However, this choice leads to a

very high total volume fraction of interphase and inclusion in the three-dimensional case. Therefore, $t = 3t_0/2$ is chosen as the thickest interphase. Fig. 5.10 demonstrates that a two-level homogenization model can be applicable for coated inclusion problem in polymer matrix nanocomposites.

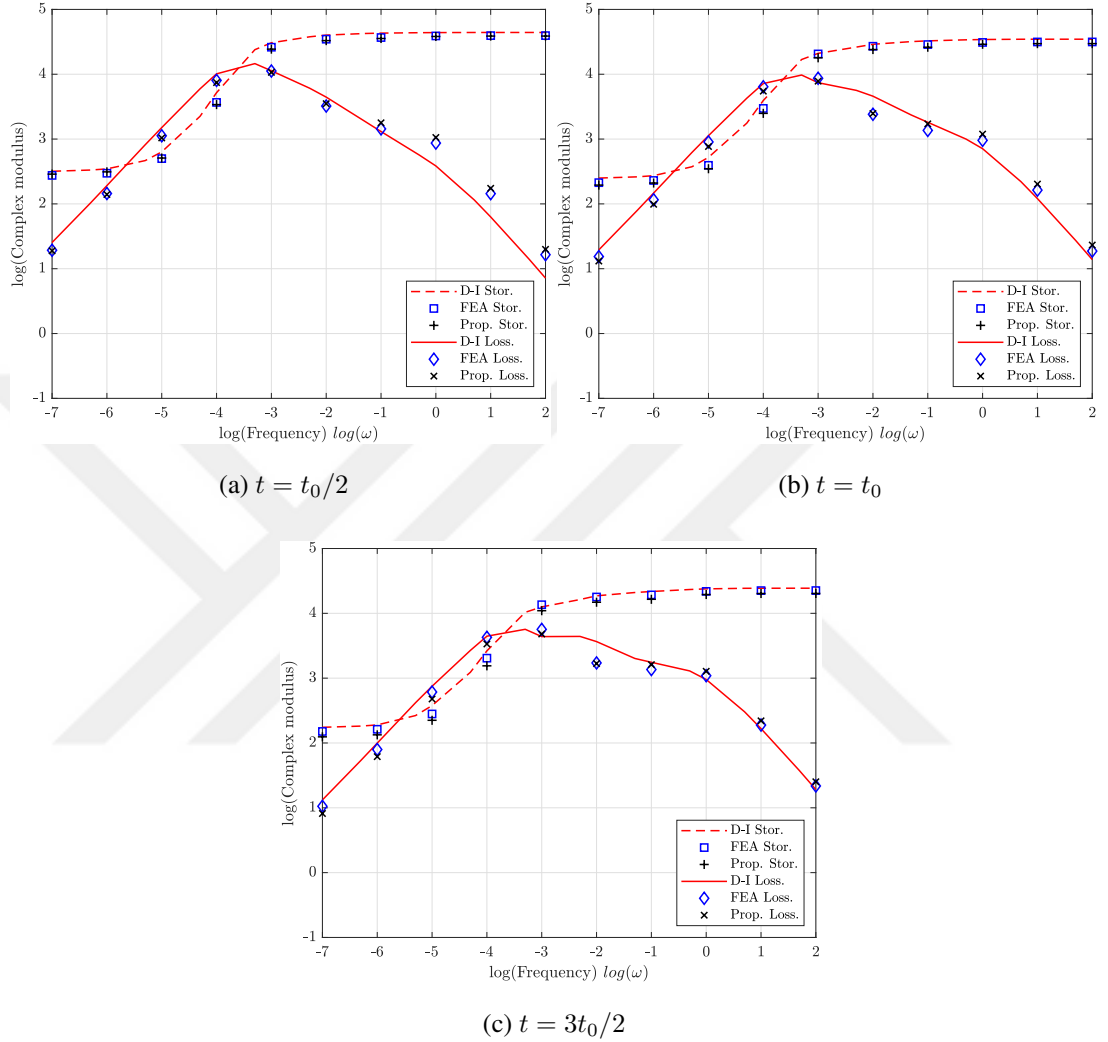


Figure 5.10: Effect of interphase thickness in three-dimensional problems. Comparison of the proposed method with the D-I method and the FEA

5.2.5 Experimental Validation

Cruz et al. [5] compared micromechanics-based methods with experimental data for PET/Glass Beads. Cruz et al. [5] performed dynamic mechanical tests of PET at dif-

ferent temperatures. They obtained the master shear modulus curves for amorphous PET at the reference temperature of 70 C°. In order to use the shear storage and shear loss moduli values in the current study, these master curves are digitized as a function of frequency. For the bulk modulus of PET, the volumetric behavior of matrix is assumed to be purely elastic and it shows a similar trend to the storage shear modulus. Following empirical relation for the bulk modulus was proposed in [5].

$$K^*(\omega) = K' = K_m^{T=90} + \alpha(\omega)(K_m^{T=70} - K_m^{T=90})$$

$$\alpha(\omega) = \frac{G'(\omega) - G'(\omega_{\min})}{G'(\omega_{\max}) - G'(\omega_{\min})} \quad (5.31)$$

In (5.31), following values are used, $K_m^{T=90} = 2.59 \times 10^9 \text{Pa}$, $K_m^{T=70} = 4.23 \times 10^9 \text{Pa}$, $G'(\omega_{\min}) = 1.1 \times 10^6 \text{Pa}$ and $G'(\omega_{\max}) = 6.8 \times 10^8 \text{Pa}$. These parameters are obtained by means of dynamic mechanical testing.

In [5], the Mori-Tanaka results and the self-consistent method results were presented. The composite system was assumed to be a two-phase composite, i.e., the inclusion and the matrix. The matrix was assumed to have viscoelastic properties, while the inclusion was assumed to be elastic. Both micromechanics-based methods showed a discrepancy with experimental results. In [5], they suggested that this can be explained with the **confinement effect**. They discussed that there might be another region around the inclusion other than the matrix and the inclusion, with reduced molecular mobility.

Diani et al. [122] showed a similar discrepancy between experimental results and Christensen and Lo's self-consistent predictions for Rubber/Carbon Black composites with different volume fractions. They attributed this discrepancy to the existence of interphase region with reduced molecular mobility, which mainly affected rubbery behavior in the low-frequency range. Moreover, they suggested a relation for the interphase properties based on the viscoelastic matrix properties.

$$G_i(w) = G_{mg} + \chi(G_m(w) - G_{mg}) \quad (5.32)$$

Here G_{mg} corresponds to the glassy state shear modulus while G_m corresponds to the

matrix shear modulus depending on the frequency. χ is a parameter in the range $[0,1]$ that is using for tuning here. In order to model the interphase the relation in (5.32) was proposed by Diani et al. [122]. Interphase, a region with reduced molecular mobility, should be observed at the rubbery state. Because it is expected that the interphase effects are not present in the glassy state but rather at the rubbery state. Therefore, as χ goes to 1, this corresponds to the interphase having matrix properties, while χ goes to 0, which means the interphase acts like it is at the glassy state.

In the article by Cruz et al. [5], a two-phase composite was modeled with different micromechanics based techniques and a discrepancy between experimental results and micromechanics based techniques was found. In the current study, the Mori-Tanaka results for two different volume fraction, $\phi_{\text{inclusion}} = 0.15$ and $\phi_{\text{inclusion}} = 0.27$ are presented in Fig. 5.11. The storage shear and loss moduli curves are same with the results in [5].

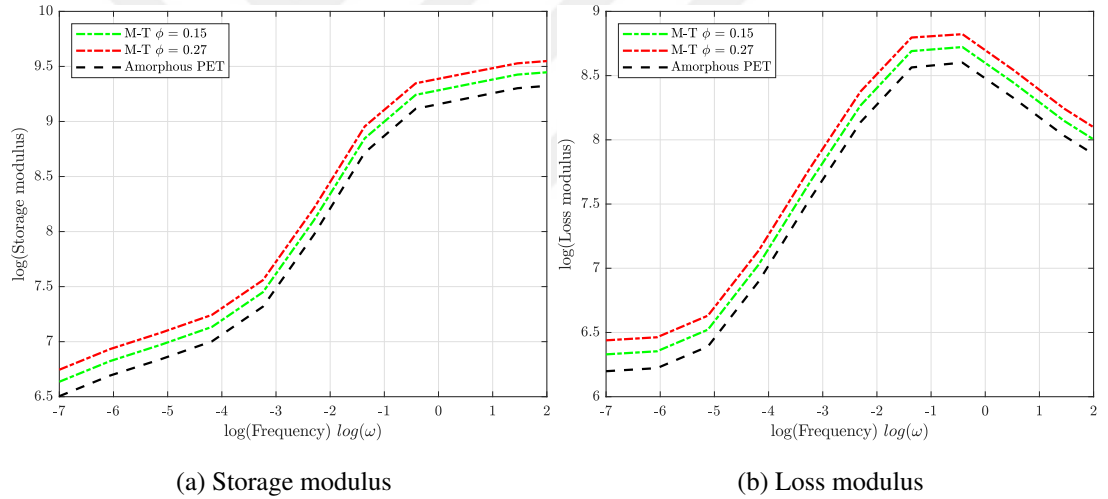


Figure 5.11: Verification study for [5], the Mori-Tanaka method for given volume fractions and bulk amorphous PET

In [5], experimental results were compared with the micromechanics based techniques. In current study, FE viscoelastic homogenization is also employed. Same composite system (PET/Glass beads) are modeled in two-dimensions and three-dimensions. The micromechanics-based Mori-Tanaka method is dominated by viscous matrix material, especially in storage modulus behavior. Any of these methods are not capable

of capturing the experimental results. Results of all three methods underestimate the experimental values. Note that Fig. 5.13 show the storage Young's modulus and the loss Young's modulus.

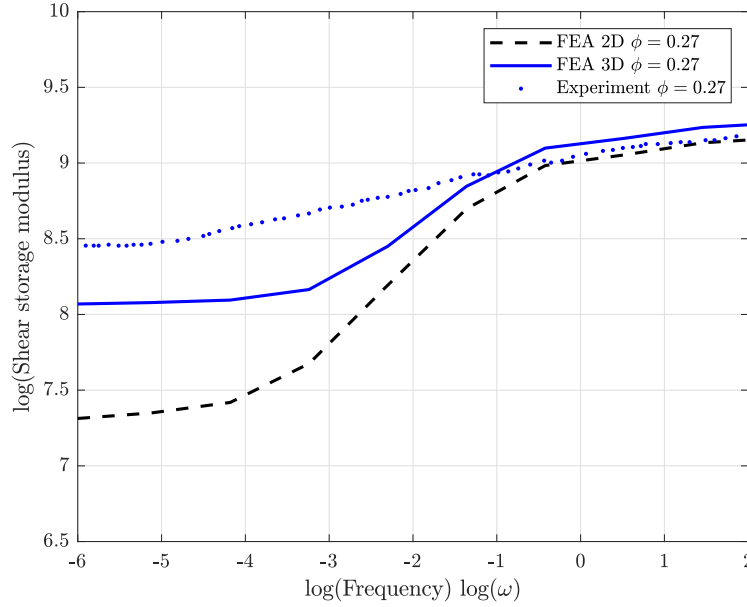


Figure 5.12: Comparison of two- and three-dimension viscoelastic FE homogenization results for $\phi = 0.27$

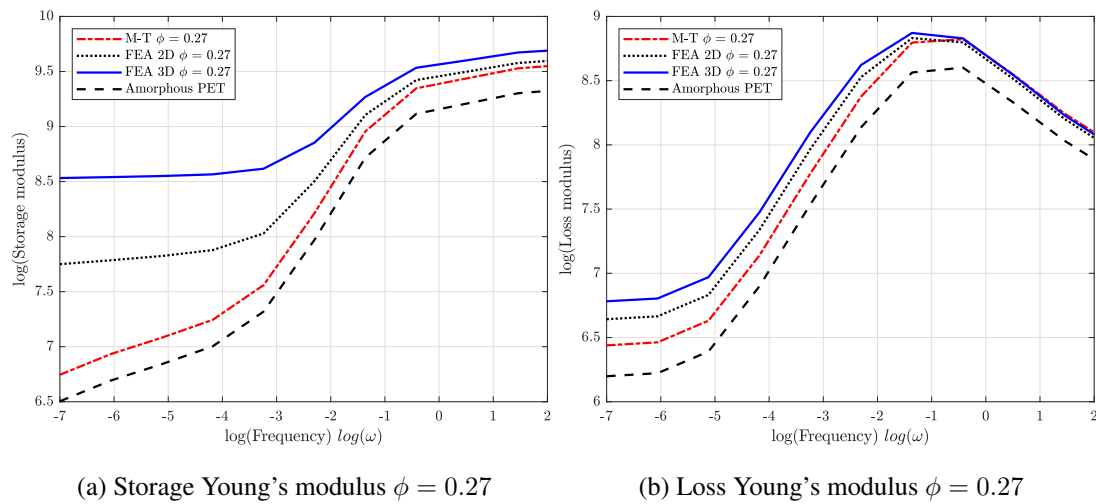


Figure 5.13: Comparison of two- and three-dimension viscoelastic FE homogenization results and the Mori-Tanaka method for $\phi = 0.27$

The loss and the storage Young's modulus underestimate the experimental values; this can be explained with the presence of a third, stiffer than matrix phase in the model. The interphase should be taken into account and in order to model the interphase (5.32) is used. Different χ values are chosen and the results are presented in Fig. 5.14.

Chen et al. [6] used the same experiment to validate their method. Their proposed method is a micromechanics-inspired novel homogenization method for particle reinforced composites in the time domain. For $\phi = 0.15$, their method underestimates the experiment, but for $\phi = 0.27$, their results seems better than the Mori-Tanaka method, and the results are close to experimental data. In Fig. 5.14, methods are compared for $\phi = 0.27$.

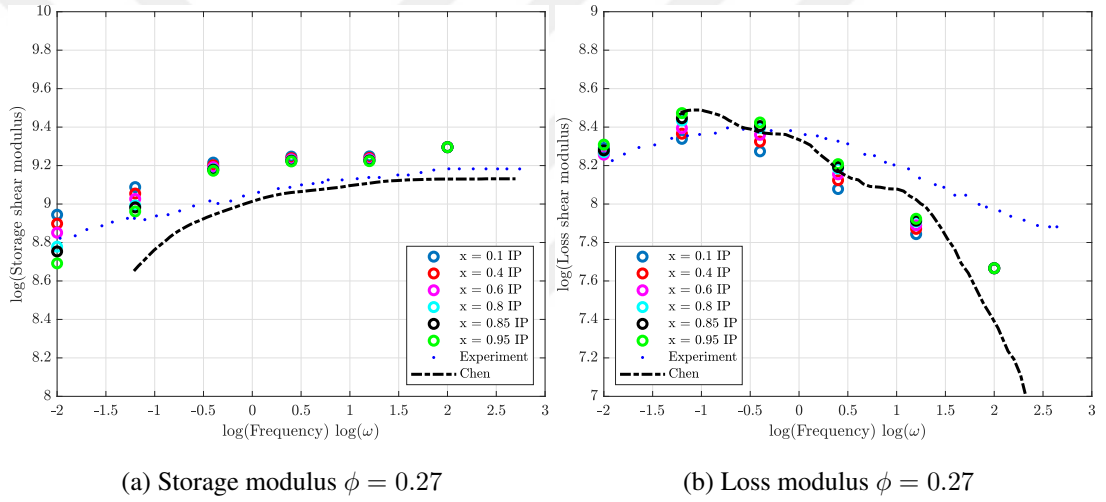


Figure 5.14: Comparison of experimental results from literature with the proposed method and the method of Chen et al. [6] for $\phi_{\text{inclusion}} = 0.27$

The experiments were conducted for a wider frequency range, but Chen et al. [6] reported between $[10^{-2}, 10^2]$. It seems that their approach underestimates the storage shear and the loss shear modulus. Especially for the lower frequency range, the discrepancy is getting higher for storage modulus. Furthermore, the gap is opening for the loss modulus in the high-frequency range. A similar trend for the loss modulus is observed when the proposed two-scale homogenization approach is used. For the storage modulus, Chen et al. reported results [6] seem quite consistent with

experimental results. Nevertheless, the storage modulus of Chen et al. [6] in the low-frequency range is getting lower drastically. Thus, outside of this range, predictions of Chen et al. [6] would probably be even worse, according to trend. In order to understand how the presence of interphase affects the overall composite modulus, different χ values are tested for a wider frequency range. Obtained results are given in Fig. 5.15.

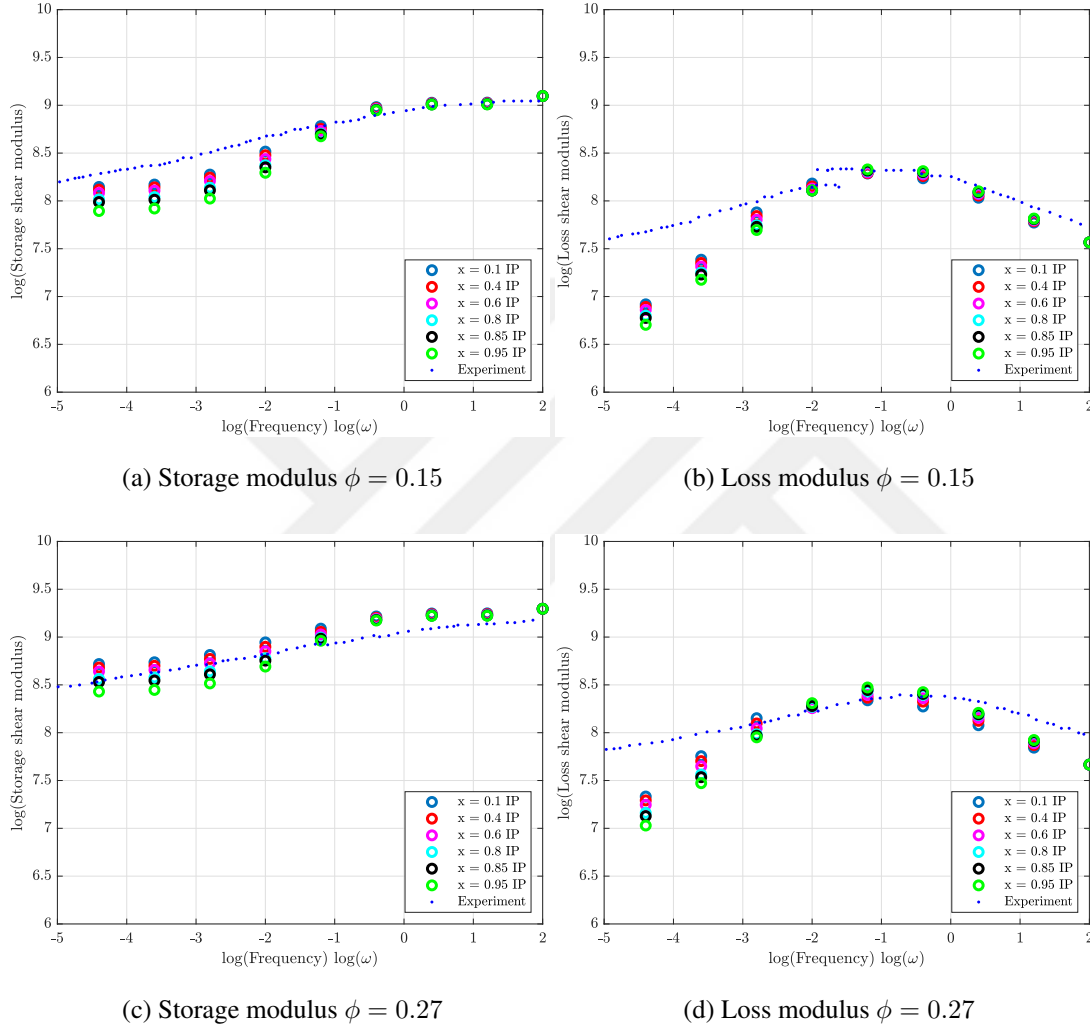


Figure 5.15: Comparison of different χ values for interphase modeling

A volume fraction of $\phi_{\text{interphase}} = 0.1$ is chosen for $\phi_{\text{inclusion}} = 0.27$ case, and the corresponding thickness is used for $\phi_{\text{inclusion}} = 0.15$ case as well. Here the interphase thickness is assumed to be constant and not scaled with the inclusion radius. In Fig. 5.15 the responses for different χ values are depicted. Looking at the storage modu-

lus, it seems for both volume fractions, the presence of interphase makes a significant improvement in the model. The choice $\chi = 0.1$ gives the highest value in each case. A constant χ does not capture the experimental results very well for this example. When the loss modulus is examined, there is a bigger discrepancy with experiment and the proposed results. Especially in a lower frequency range, it seems that the presence of interphase does not result in good agreement. The experimental loss modulus values seem quite high, and the proposed two-scale homogenization method cannot predict them well with the selected thickness and interphase properties. Improvement may be achieved by changing the interphase thickness or considering a graded interphase instead of a uniform one.





CHAPTER 6

CONCLUDING REMARKS

In the thesis, a two-level homogenization method for polymer nanocomposites with coated inclusions is proposed. First of all importance and formation of interphase on polymer nanocomposites are presented. Different experimental techniques are discussed to characterize the interphase. Depending on the thickness of the interphase, interphase volume fraction may correspond to a significant portion; hence interphase modeling is essential for polymer nanocomposites. However, interphase characterization becomes a challenging task. Generally, AFM and nanoindentation tests give information about nanocomposites' local properties, specifically the interphase region. These observations and measurements show that, in general, interphase has graded characteristics instead of exhibiting uniform material properties such as that stiffness, conductivity, density change through the thickness. Other vital characteristics, such as interfacial shear strength, toughness, and change in thermal properties, are investigated through testing. Since nano-scale experiments are complicated and difficult, modeling polymer nanocomposites with coated inclusions is a valuable alternative.

Micromechanics-based homogenization schemes are fast and usually easy to implement. However, these techniques may have some deficiencies, as stated in the thesis. In the thesis, it is demonstrated that the well-known Double-Inclusion method cannot model the stress transfer between matrix and inclusion through soft interphase. While the interphase is stiffer than the matrix, micromechanics-based estimations are in close agreement with the three phase reference finite element solution. Since no experimental study is performed in the scope of the thesis, the reference solution is obtained from a three-phase finite element solution.

Homogenized stress and strain values are used to compute the homogenized elasticity tensor. It is demonstrated that when the interphase is softer than the matrix, micromechanics-based methods may have some problems arising from load transfer mechanisms. Here proposed model utilizes a replacement procedure to form an effective inclusion from the inclusion and the interphase. For this replacement procedure, strain-controlled FE analyses are performed to obtain the elasticity tensor of the effective inclusion. Later, the proposed two-level homogenization scheme uses the simplicity and convenience of a micromechanics-based method for a two-phase composite. By means of the proposed method, the effective moduli corresponding to the soft interphase case are estimated very close to the reference solution. One critical remark needs to be stated here; all of the imaginary examples in Chapter 4 are for a very stiff inclusion and a soft matrix case. The difference between the matrix and the inclusion is very high, while the interphase is the softest of all phases. Thus, the interphase stiffness is a crucial parameter here, and if the interphase stiffness is not as low as the considered example, the micromechanics-based D-I model may estimate better compared to the reference solution. The interphase thickness is also another variable that should be considered. Depending on the interphase's thickness, the corresponding interphase volume fraction may be very high, which can be overestimated in micromechanics-based methods. However, results show that the proposed method makes a significant improvement to the D-I method for the soft interphase case. It seems for the stiff interphase cases; the D-I method confirms the reference FE solution.

Since the matrix material in polymer nanocomposites exhibit generally viscoelastic behavior in the matrix, an extension to include viscoelastic effects is critical. To this end, a homogenization scheme in the frequency domain is proposed for viscoelastic polymer nanocomposites. For this purpose finite element formulation for linear elasticity is extended to account real and imaginary variables of materials. The Dynamic Correspondence Principle allows using complex variables and complex moduli instead of real variables and classical elastic moduli. This principle is applied to micromechanics-based homogenization models and standard finite element formulation of linear elasticity. However, separating real and imaginary parts of complex variables causes some modifications and complexity in formulation and code. By

means of the proposed method, the effective moduli corresponding to the soft interphase case are estimated very close to the reference solution. the D-I method cannot estimate the reference FE solution, similar to elastic problem.

- This framework can be extended to functionally graded materials in the future since the interphase usually has graded properties. AFM observations prove that the interphase has graded Young's modulus distribution. The micromechanics based D-I model can take this effect into account. Functionally graded materials are studied quite extensively in the literature. Therefore, including gradual property changes to the proposed model may be an essential step to model polymer nanocomposites more realistically.
- In Chapter 4, an example of non-spherical geometries are discussed. SFRC example demonstrated the capability of the framework to non-spherical inclusions. However, a detailed study for the limit cases and different aspect ratios are not performed in the thesis. In order to model different nanocomposite systems, extension to different geometries are critical.
- The proposed framework is solely limited to elasticity and viscoelasticity. Fracture is not discussed in the thesis. But other than the interphase, the interface plays an important role for polymer nanocomposite systems. Debonding of the interface is an important phenomena.
- The proposed framework can be extended to large deformations. The current study is based on the small deformation theory. The micromechanics based methods such as the Mori-Tanaka is extended for finite strain modeling [136]. By means of these extensions and finite element homogenization scheme in large deformations, the proposed framework can be extended to the large deformations.



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