Adhesion and Adhesives: Fundamental and Applied Aspects

INTERFACE/ INTERPHASE IN POLYMER NANOCOMPOSITES

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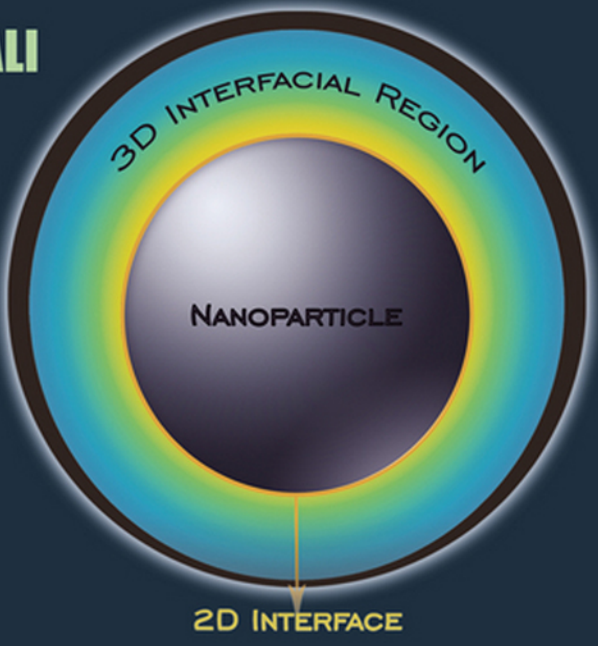

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Adhesion and Adhesives: Fundamental and Applied Aspects

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Preface

Polymer composites are made of two components: polymer or matrix (continuous phase) and filler or reinforcement (discontinuous phase) to obtain properties that cannot be achieved by a single component alone. The specific tensile properties of fiber reinforced composites are excellent because of their low density and high mechanical properties. Over the past few decades such composites have replaced metals in many applications from aerospace to sports gears, from automobiles to wind turbines, and from circuit boards to civil structures such as bridges and buildings. With composites impacting every part of our lives they have become ubiquitous. Over the past 2-3 decades the fillers or reinforcing elements used in composites have become smaller and smaller to their current nanosize. Using nanoparticles or nanofibrils in polymers or resins provides significant advantages. Hundreds of studies have shown that only a small weight percent (loading) of nanoparticles can significantly alter the stiffness, strength and fracture strain as well as electrical, thermal or other functional properties of polymers because of their high surface-to-volume ratio. However, such benefits can be derived only if the particle dispersion is uniform and no clustering occurs. It is also universally accepted that the nanoparticle/resin interface and the interphase region in nanocomposites play a critical role in enhancing their properties. With better understanding of interface and interphase characteristics it should be possible to predict as well as design polymer nanocomposites with desired properties and performance. This book brings together several experts and leading researchers in this field to present their cutting edge research in understanding, modifying and controlling interfacial interactions between various nanofillers and a host of polymer matrices.

The book is divided into two parts; Part 1: *Nanocomposite Interfaces/Interphases* with 6 chapters and Part 2: *Techniques to Characterize/Control Nanoadhesion* with 5 chapters. In chapter 1 Schadler and coworkers define and discuss the two phases of polymer nanocomposites: polymeric matrix phase and inorganic nanofiller phase. Efforts have been made to improve the intrinsic properties of both the matrix and the nanofiller to enhance

the overall performance of polymer nanocomposites. Accordingly, this chapter discusses the thermodynamic mechanisms governing nanofiller dispersion. The thermodynamic matrix/filler interactions also influence the structure and properties of the interfacial region, which can be significantly different from the bulk material. Examples of such structural modifications in semicrystalline and thermoset polymer nanocomposites are presented. In chapter 2 Pegoretti and colleagues discuss engineering of interphase with nanofillers in fiber-reinforced polymer composites. The first part of the chapter surveys recent advancements in the interphase engineering of fiber-reinforced polymer composites using different nanofillers. The second part of the chapter discusses strategies followed for stress transfer improvement or adding functionality to the interphase. The chapter also includes state-of-the-art knowledge on the characterization and modelling of the interphase. In the last 'Outlook' section some challenges and perspectives in the engineering of fiber/matrix interphase are summarized. The third chapter by Kim and colleagues discusses formation and functionality of interphase, a distinct region between the two phases in polymer nanocomposites. This chapter presents fundamental issues on the formation of interphase between carbon-based nanofillers, such as carbon nanotubes, graphene, carbon black, and polymer matrices. Special emphasis is placed on illustrating the role of interphase in governing the mechanical, electrical, thermal and other functional properties of nanocomposites. Based on the progress made so far, some suggestions are proposed for designing the interphase with specific structures for intended applications of nanocomposites. In chapter 4 D'Souza and colleagues examine the effects of crystallization on the interface in polymer nanocomposites. Crystallization in polymer nanocomposites is influenced by the nature of the polymer, the percentage of nanoparticles present and their dispersion and interparticle distance. This chapter presents the effect of montmorillonite nanoclay on the interfacial crystallization in three polymers: nylon, poly (ethylene terephthalate) and poly (ethylene naphthalate). The effect of crystallization on the permeability of all three systems is also examined. Chapter 5 by Zaldivar and Kim discusses a new class of Graphite Nanoplatelets (GnPs) based nanocomposites that have unique electrical and thermal properties. To obtain the highest possible properties, the nanoparticle/resin bonding needs to be improved. The chapter discusses how the nanoparticle surface can be optimally functionalized using Split Plasma Method. The sixth and the final chapter of Part 1 by Pissis and associates is devoted to the experimental investigation of interfacial effects in polymer nanocomposites using calorimetric studies for the glass transition and dielectric techniques for the segmental dynamics. After discussing the

experimental techniques briefly, the authors focus on proper evaluation of the measurements to extract maximum information from the data. The authors also present methods and equations used to evaluate the results in terms of interfacial characteristics, in particular polymer fraction in the interfacial layer (the fraction of polymer with modified properties) and thickness of the interfacial layer. The chapter provides an overview of the state-of-the-art in the field from the materials point of view simply by using various methods to characterize several selected polymer nanocomposites.

Part 2 of the book spans chapter 7 to chapter 11. In chapter 7 Liu describes the recent progress in theoretical and experimental aspects of interfacial adhesion in nanostructured carbon materials based polymer nanocomposites and summarizes the common methods utilized to characterize the interfacial properties in nanocomposites. The next chapter by Sain and colleagues discusses chemical and physical techniques for surface modification of nanocellulose reinforcements. The polarity of cellulose fibers due to the abundance of hydroxyl groups is responsible for poor wetting of natural fibers by non-polar resins. Furthermore, a large difference in surface free energy levels between resins and natural fiber reinforcements is responsible for poor interfacial bonding. The chapter discusses the most recent surface treatment techniques being employed to develop high-performance nanocomposites. In chapter 9 Park and colleagues discuss a unique electro-micromechanical technique developed as an efficient nondestructive evaluation (NDE) method for sensing and determination of micro-damage at the filler/epoxy interface in nanocomposites. This 'self-sensing' method has also been used to evaluate interfacial damage in fiber reinforced polymer matrix nanocomposites. Among the advantages of this new NDE method, compared to other evaluation methods, include better stability, lower cost and its relative simplicity. Bhattacharyya and colleague discuss particulate incorporation, interphase generation and evaluation by nanoindentation in polymeric biocomposites in chapter 10. This chapter provides an overall perspective on the development of composites containing bio-based reinforcements, e.g., biochar. The properties and governing factors of the biochar composites are explained, which is followed by a discussion of the suitability of nanoindentation technique for determining nano-sized particle/resin interfacial properties. Finally, several studies involving nanoindentation on the nano-sized interfacial regions of composites are reviewed and critically discussed. In the 11th and the final chapter Pasquinelli and colleagues demonstrate the use of molecular dynamics (MD) simulations to quantify filler-matrix adhesion and nanocomposite mechanical properties. They also illustrate how MD simulations can predict the mechanical properties of polymer nanocomposites as a function

of the chemical and structural composition of these materials. Other prospects for MD simulations include calculating other physical properties, improving the structure-property prediction through advancements in hardware architecture and software development, and connecting through multiscale modeling the nanoscale/microscale details from MD simulations to the macroscale characteristics.

The book should be of interest to researchers in academia, in government research labs and R&D personnel in a host of industries (e.g. aerospace, automotive, biomedical, composites, dentistry, fibers, medical, microelectronics, packaging, plastics, textiles) who are interested in designing and improving the properties of polymers and composites by the addition of nanoparticles. Industries such as aerospace and automotive where lightweighting of each component is critical and an ongoing effort, improved properties through scientific understanding of nanocomposites could be very advantageous. Anyone working in plastics/polymers and composites industries should find this book of great interest and very useful.

It is our great pleasure to thank those who made this book possible. First and foremost, we are profusely thankful to the contributing authors for their sustained interest, enthusiasm and cooperation and for investing their valuable time in sharing their knowledge and cutting edge research (in the form of chapters) with the interested community. This book would not have been possible without their hard work. The unwavering interest and support of Martin Scrivener (Scrivener Publishing) in this book project and for giving this book a body form is also very much appreciated.

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Part 1

NANOCOMPOSITE INTERFACES/INTERPHASES

1

Polymer Nanocomposite Interfaces: The Hidden Lever for Optimizing Performance in Spherical Nanofilled Polymers

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Abstract

Polymer nanocomposites consist of at least two phases: a polymeric matrix phase and an inorganic nanofiller phase. To enhance the overall performance of polymer nanocomposites, efforts have been made to improve the intrinsic properties of both the matrix and the nanofiller. A hidden lever for performance optimization, however, lies in understanding and tailoring the matrix/filler interface. Depending on the dispersion state of the nanofiller and the interface area, the resulting interfacial region can be a critical component in polymer nanocomposites. Generally, uniform nanofiller dispersion, which maximizes interface area and therefore the volume of the interfacial region, is desirable. This chapter will first briefly discuss the thermodynamic mechanisms governing nanofiller dispersion. The thermodynamic matrix/filler interactions also influence the structure and properties of the interfacial region, which can be significantly different from the bulk material. Examples of such structural modification in semicystalline and thermoset polymer nanocomposites will be given. Deviations in polymer properties, such as the

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change in molecular mobility in the interfacial region, influence the macroscopic mechanical and dielectric properties of the polymer nanocomposite. However, measuring these properties is a challenge because of the hidden nature of the interfacial region. The measurement techniques can be broadly divided into direct and indirect methods. The direct methods rely on the use of probes to directly measure the local properties at the interface while indirect methods deduce the interface properties by analyzing differences in the measurements from bulk composites and the neat matrix.

***Keywords*:** Nanocomposite, interface, thermodynamics, dielectric relaxation, viscoelasticity

1.1 Introduction

Understanding the structure and properties of the 2D nanofiller/matrix interface and the resulting 3D interfacial region or "interphase" (used interchangeably in this chapter) that develops is the lynchpin to controlling and optimizing the properties of polymer nanocomposites (Figure 1.1). The 2D interactions are critical because:

1. The nanofiller/matrix interfacial interactions determine the dispersion state of the filler particles and the amount of interfacial area.
2. These 2D interactions impact the structure and properties of the 3D interfacial region.

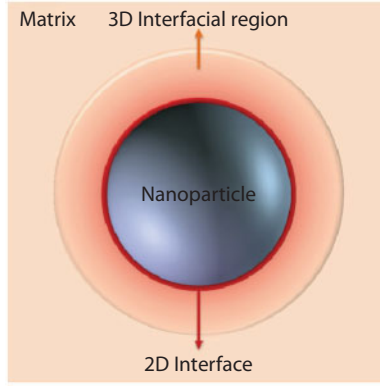

Figure 1.1 An illustration of a 2D nanofiller/matrix interface and the resulting 3D interfacial region.

The 3D interfacial region is a region with properties different from the bulk polymer matrix. Due to the large interfacial area to volume ratio in nanocomposites, this region may constitute a significant portion of the bulk. For example, in a polymer nanocomposite filled with 5 vol% monodisperse 10 nm spherical nanoparticles, even if the thickness of the interfacial region is as small as 5 nm, the volume fraction of this interfacial region can be as high as 35 vol%. As the nanofiller loading level increases, this becomes an even more significant volume fraction of the composite. The 3D region controls nanocomposite performance in two key ways:

1. The changes in structure or chemistry in this region can drastically change bulk composite structure (e.g. average cross-link density, crystalline morphology).
2. The changes in mobility (e.g. changes in relaxation time spectra) strongly impact the composite bulk properties, in particular, the mechanical and dielectric properties.

To model and/or predict the properties of a nanocomposite, it is essential to include the properties of the interfacial region. This inclusion needs to occur in a spatially specific way and not as a volume averaged property because of the role of percolation, stress concentrations, and defects on composite bulk properties. However, we do not yet have a full understanding of how to control the structure and properties of the interfacial region, which reduces the impact of polymer nanocomposites in high-end applications. This lack of understanding and control of the interfacial region is attributable, in part, to the challenge of measuring the structure and properties of the interfacial region because of its small size and embedded nature.

This chapter will address the impact of the 2D interface on the propensity for nanofiller dispersion in quasi-equilibrium conditions in detail, briefly touch upon its role under kinetic processing conditions, and provide a summary of what is currently known about the structure of the 3D interfacial region. Further we discuss three key approaches to determining interface properties including: dynamic mechanical analysis to understand thermomechanical and relaxation processes, dielectric spectroscopy to understand permittivity changes as well as dielectric relaxation processes, and the role materials informatics plays in developing an in-depth quantitative understanding of interfacial interactions.

1.1.1 Dispersion Control

To optimize the amount of interfacial area, the nanoparticles need to be well distributed and well dispersed [1, 2]. It is well known that even in the

athermal limit (no attraction or repulsion between matrix and particle), there could be entropically driven depletion forces that encourage the agglomeration of nanoparticles [3]. As the particle-particle attraction increases, this driving force increases. This interaction can be mitigated by attaching surface ligands to the nanoparticles that alter the enthalpic and entropic interfacial interactions [4–6]. The attached surface ligands can be broadly categorized into short molecules or polymer brushes. Short molecules primarily impact the enthalpic interactions with the matrix [7], while polymer brush ligands introduce a large entropic component and therefore complicate the thermodynamic interaction between the filler and matrix. The approaches to ligand engineering for dispersion control and the prediction of nanofiller dispersion based on interfacial thermodynamics models will be presented in Section 1.2.

1.1.2 Interface Structure

As the thermodynamic interactions are tuned between the nanofiller and the matrix, the structure of the resulting interfacial region changes. For example, in thermosetting and elastomeric matrices, the degree of chemical/physical cross-linking can be impacted by the presence of nanoparticles with a modified surface [8, 9]. In semicrystalline thermoplastic polymer matrices, the particle surface can impact matrix crystallization [10–12], and during crystallization the alignment of matrix polymer chains can cause or prevent agglomeration of nanoparticles [13, 14]. In the case of polymer brush grafted nanoparticles dispersed within amorphous polymers, depending on the graft density and the length of the brush, the matrix can penetrate the brush (wet brush) or be repelled from the brush (dry brush) [15], which, in turn, determines the structure of the interfacial region. Section 1.3 will focus on the current understanding of interface structure.

1.1.3 Interface Properties

The scientific and technological significance of interface structure studies primarily lies in their implications for tailoring interface properties. To be noted, the mobility of the matrix and/or brush polymer chains in the interfacial region with a defined structure has led to significant discussion in the literature [16–18]. Short molecules, typically used to create compatibility, can contribute to changes in properties [19]. For example, short ligands can repel, attract, or bond with matrix chains, and modify matrix chain mobility [20]. The morphology of grafted long polymer brushes also impacts the polymer chain mobility in the vicinity of particle surface as well as the

ability to transfer stress from the matrix to the particle. In addition, adding a highly polar molecule can lead to significant changes in dielectric permittivity or dielectric breakdown strength [21–23]. Other surface ligands can introduce ions to the interface, alter the band structure, act as traps or scattering sites for charge carriers, *etc.* [24, 25]. The first part of Section 4 will focus on changes in mobility due to the 2D interface.

1.1.4 Measuring and Modeling the Interface

A key to understanding interfacial structure and properties is the ability to measure them. The second part of Section 1.4 will focus on measuring the dielectric and viscoelastic properties of the 3D interfacial region. There are two broad methods for determining the properties of the interface: direct and indirect measurements. Direct measurements use a local probe with nanoscale resolution to "see" the interface or measure the properties directly. For example, nano Dynamic Mechanical Analysis (nano DMA) has been used to measure local viscoelastic properties with nanometer resolution [26]. The challenge with probes such as Atomic Force Microscopy (AFM) and intermodulated AFM is that the impact of the surface on the measured properties is difficult to separate out [27]. Indirect methods can also be a powerful approach for estimating interface properties. In this case, the changes in bulk properties are monitored as a function of particle loading or systematic change to the nanoparticle surface ligands, and the changes in properties are ascribed to the interfacial region. For example, photoluminescence spectroscopy can provide useful information on charge trapping and transfer at the interface [28]. Thermally stimulated depolarization current measurements are useful for characterizing slow relaxation processes especially those associated with space charge separation and propagation [29, 30]. Using an inverse problem approach, finite element models that explicitly include the matrix and filler properties can be used to handle nanofiller dispersion explicitly, and then tune the interface properties to match experimental results. Using this indirect approach, interface properties can be inferred. One powerful approach that is being developed for understanding the interface and designing nanocomposites is materials informatics. Informatics combines both empirical and first principles models, data mining, targeted experimental validation, and ultimately processing parameters. By combining informatics with finite element models (FEMs), interface properties may be inferred. Once the relationships between interface chemistry and properties are developed, informatics can be used to create a design loop that should lead to faster introduction of polymer nanocomposite materials into the marketplace.

1.2 Dispersion Control through Interfacial Modification

1.2.1 Introduction

Nanosized inorganic particles possess unique features compared to chemically identical materials on a larger size scale, and can be used to significantly alter the properties of polymers. However, the dispersion of nanoparticles (NPs) into polymeric matrices, which determines the distribution and amount of interface present in the nanocomposite, is a significant challenge that requires an in-depth understanding of both entropic and enthalpic driving forces [7, 31, 32]. For the case of zero enthalpic mismatch, even though the ideal translational entropy favors dispersion of NPs, excluded-volume effects and depletion attractions between the NPs can lead to NP aggregation [33, 34]. When the NPs are sufficiently small, the enthalpic driving force for inorganic NP agglomeration is mainly determined by van der Waals (vdW) core-core attractions [33]. It is well-known that a strongly bound surface layer of matrix-compatible ligands markedly diminishes the interfacial tension between modified NPs and the matrix and suppresses agglomeration. These ligands can be classified into two types based on their size. Short ligands are found to tailor the enthalpic compatibility at the interface, and long polymer chains tune the enthalpic as well as entropic interactions [7, 35]. While this functionalization has been found to alter the proclivity to aggregate, it also simultaneously alters the interface characteristics (Section 1.3). In this section, we focus primarily on the effect of interfacial thermodynamics on NP dispersion. The aforementioned approaches to ligand engineering are discussed in further detail. Predictive thermodynamic models are then introduced to shed light on the unique morphology-structure-property relations of inorganic/organic nanocomposites.

1.2.2 Short Ligands

The short organic compounds used for modifying NPs include thiols, carboxylic acids, amines, silanes, and phosphonates, which can react with NP surface atoms via covalent, electrostatic, or hydrogen bonding interactions and act as reactive anchors (Figure 1.2) [36]. Dithioesters or trithiocarbonates have been reported to directly attach to gold substrates as anchoring groups [36]. Carboxylic acids are routinely used to stabilize metal oxide NPs upon their synthesis, with oleic acid being the most commonly utilized ligand. The oleic acid prevents surface oxidation of the metal oxide and due to its long alkyl chain, improves the dispersibility of the nanoparticles

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