High-Pressure Study of Bio-inspired Multi-Functional Nanocomposites Using Atomic Force Microscopy Methods

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To my family,

Thanks for the continuous support, encouraging me to pursue my goals and thank you for teaching me the value of education.
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Abstract of Dissertation

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Bioinspired design has been crucial in the development of new types of hierarchical nanocomposites. Particularly, the nacre-mimetic brick-and-mortar structure has shown excellent mechanical properties as well as gas barrier properties and optical transparency. Along with these intrinsic properties, the layered structure has been designed to serve as sensing devices. Here we expand the multi-functionality of nacre-mimetics by designing an optically transparent and electron conductive coating that reacts to high-pressure based on PEDOT:PSS and nanoclay. The main objectives of this project are: (i) to develop a multifunctional nanocomposite and evaluate the effect of high-pressure applied at the surface and (ii) to establish protocols for the morphological and structural characterization, and electro-mechanical testing of the nanocomposites based on a combination of atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmittance spectroscopy.

The synthesis of the nanocomposite, containing PEDOT:PSS (conductive polymer) and nanoclay, was achieved using the self-assembly of core/shell platelets. Two different types of nanoclay, Cloisite Na+ and Laponite RD, are used and their properties compared. The reduction of thickness in PEDOT:PSS has been shown to increase the light transmittance across a film. Similarly, the thickness of the nanocomposite was reduced and compared to PEDOT:PSS. The measured optical transmittance for both nanocomposites is comparable to the bare polymer, demonstrating that the addition of the nanoclay does not affect the transparency of PEDOT:PSS.
significantly. The layered structure of the nanocomposites is investigated by imaging the fracture surface with SEM. The fracture surface of the Laponite RD based nanocomposite is much flatter than the Cloisite Na+ nanocomposite, since the particle size in Cloisite Na+ is about 10 times larger than Laponite RD. The characterization of electro-mechanical properties of the nanocomposites was performed using the correlation of conductive atomic force microscopy and contact resonance force microscopy to measure the local variations. The analysis shows that in thin and transparent films, there is segregation in the response of Cloisite Na+ based nanocomposites compared to the bare polymer or Laponite RD nanocomposite, hence the investigation focuses on Laponite RD.

For Laponite RD, we investigate the 3-D distribution of nanoclay in the coating. The distribution of nanoclay at the surface is elucidated by mapping the dissipative and conservative interactions between tip and sample in bimodal AFM. Measuring the strain produced by the tip, the 3-D structure is inferred using models for mechanical properties of nanocomposites. Single platelet measurements are used to infer the inter-platelet distance. It is known that the free amplitude of the higher eigenmode can be modulated to produce large forces in bimodal AFM. The pressure estimated for the typical cantilever parameters used are in the range 1.2-3.3 GPa, which is used to apply high-pressure to the subsurface structure of the nanocomposite.

We show that the tip-surface interaction modifies the subsurface morphology of the nanocomposite and results in changes of the out-of-plane current. Also, the structural modification caused by the bimodal AFM treatment results in local changes in mechanical properties. This behavior is obtained for the Laponite RD nanocomposite, but it is not observed for the Cloisite Na+ nanocomposite or the bare polymer. Laponite RD has a platelet size similar to the tip, while Cloisite Na+ is much larger leading to a reduction in pressure. By modelling the transmission
probability of electrons, geometrical changes in the structure are examined and shown to modify the tunneling of the electrons through the coating. Specifically, parallel compression of the nanoclay (modelled as barriers for electrons) leads to a change in the transmission probability of the electrons. Depending on the kinetic energy of the electrons, the transmission probability could either increase or decrease.
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Chapter 1: Objectives and Scope

1.1 Overview

Bioinspired design has been crucial in the development of new types of hierarchical nanocomposites. The origin of one family of nanocomposites is traced back to nacre, a naturally occurring composite material with impressive mechanical properties [1]. Particularly, the nacre-mimetic brick-and-mortar structure has been synthesized by using hard particles embedded in soft polymers. Using the self-assembly of polymer and clay nanoplatelets (1 nm thick) have produced highly ordered nanocomposite films [2]. Besides the enhancement of the mechanical properties (nanocomposite compared to bare matrix), several functional properties have been attributed to the so-called brick-and-mortar structure that results from the layering of individual components. For example, an intrinsic property of the brick and mortar structure is that it creates a tortuous path for the diffusion of gas molecules, serving as a gas barrier and as a flame-retardant material [3]. By design, other functional properties have been achieved. High optical transparency can be obtained by minimizing structural and surface defects, in addition to selecting proper materials. Also, stimuli-response behavior has been measured. The stimuli interact mainly with the polymeric phase of the nanocomposite. Thus, the morphological alteration (e.g. change in polymer swelling) produces a measurable change (e.g. color change) in the nanocomposite [4]. It is important to broaden the multifunctionality of the nanocomposites, since it creates new opportunities for application.

Recently, basic characterization of a PEDOT:PSS/nanoclay composite was performed [5]. The nanocomposite exhibited improved mechanical properties, as expected, and the electrical conductivity is comparable to the bare polymer. PEDOT:PSS is a newly introduced member to the conducting-polymer family. To improve the processability of PEDOT, a polyelectrolyte solution
(PSS) is added, and this results in an aqueous dispersion. Thus, PEDOT:PSS is a polymer blend in which PEDOT is conductive, hydrophobic and positively charged, and PSS is hydrophilic and negatively charged. It has been shown that after drop casting a PEDOT:PSS solution, quasi-metallic PEDOT particles are formed and separated by layers of PSS, and are randomly oriented. The conductivity highly depends on the resulting morphology of the polymer. High-pressure studies can help elucidate relations between changes in morphology and the electron transport across the nanocomposite thickness. Thus adding potential new applications to the PEDOT:PSS/nanoclay brick-and-mortar structure for new generation of advanced multifunctional materials. Recently, there has been much interest in understanding how nanocomposites achieve their striking properties and in expanding their potential applications.

AFM is a family of techniques where a nanometer-sized tip attached to a cantilever interacts with a surface measuring different characteristics in a static [6] (contact), dynamic [7] (non-contact or intermittent contact) or combined fashion. Advanced AFM methods have demonstrated their strength for localized characterization by investigating the structure and mechanical properties of nacre [8, 9]. Also, nanoscale mechanical [10–12], electrical [13, 14], and magnetic [15] properties of nanocomposites have been widely studied using AFM methods. An specific advanced AFM technique is called bimodal AFM [16]. In this method, two eigenmodes of the cantilever are excited simultaneously producing an increased material contrast, sensitivity, penetration depth or applied force [17]. As a result, AFM provides a platform for localized characterization, high-pressure testing and investigation of the material response with high resolution. For example, individual nanoclay platelets (down to 25 nm) can be resolved using AFM methods. Also, by implementing different methodologies, a smooth transition between applying the pressure stimuli and measuring the response is possible in-situ.
1.2 Objectives

The main objectives of this project are: (i) develop a transparent multifunctional nanocomposite composed of PEDOT:PSS and nanoclay (ii) evaluate the effect of high-pressure applied at the surface and (iii) to establish protocols for the morphological and structural characterization, and electro-mechanical testing of the nanocomposites based on atomic force microscopy (AFM) to complement SEM and transmittance spectra analysis.

This project leverages from the brick-and-mortar structure in combination with the current capabilities of AFM methods, new ways of interpreting AFM observables and performing sequential experiments for characterization of functionality. More specifically, a combination of AFM methods are used to investigate the bio-inspired, PEDOT:PSS/nanoclay, composite electro-mechanical response (nanoscale out-of-plane current and mechanical properties) to an applied high-pressure. Besides the high-pressure study, structure and morphology are also important. The significance of this project is bifocal: (i) physical insight about effects of localized high-pressure is obtained and (ii) a combination of advanced AFM methods developed for modification and characterization is established with possible future implementations to any sample system. The experimental rationale presented throughout is generalizable and the findings are inherently related to the fundamental structure of the sample system studied. To accomplish the objectives several developmental stages are required. The scope at each stage is discussed in the following sections.

1.3 Development of AFM Methodologies

AFM is a technique that makes possible the measurement of several features, from topography to electrical characterization, of the investigated material. Conductive-AFM and contact resonance force microscopy (CRFM) are established techniques that characterize electrical and mechanical properties, respectively. Electro-mechanical response of the nanocomposite can
be measured by implementing a combination of these techniques. Bimodal AFM has proven to enhance material contrast and to increase the peak forces between tip and sample. The key parameter that will be investigated is the free amplitude for the higher eigenmode. A methodology for the characterization of conservative and dissipative interactions with highest contrast possible is required for investigating the distribution of nanoclay near the surface. To develop this method, dissipated energy and virial are calculated for different free amplitudes and the contrast is compared. Also, it is needed to test the ability of bimodal AFM to modify a functional sample by applying high-pressure. For that purpose, surface agglomerates in polymer solar cells are modified by high-pressure to provide evidence that support the usage of the method at the surface. Finally, it is important to implement all the AFM schemes in a systematic way, so that they can function sequentially without tweaking the system in-between experiments.

1.4 Synthesis and Characterization of PEDOT:PSS/nanoclay Composite

The starting point is to synthesize the nanocomposite films. The experimental approach is to use the previously introduced core/shell platelet self-assembly method by controlled water removal. By comparing two different types nanoclays, Laponite RD and Cloisite Na+, differences in behavior of the nanocomposite caused by the hard phase are investigated. Optical transparency has been of great interest when developing bio-inspired nanocomposites. The effect of thickness on the light transmittance for coatings on glass slides is studied for nanocomposites consisting of both types of nanoclay and compared to the bare polymer. Also, electrical and mechanical properties of the three materials are compared using conductive-AFM and CRFM. This analysis yields the intrinsic differences that arise from the addition of the nanoclay to the polymeric matrix. Finally, the surface of failure is imaged using SEM and compared to AFM images of the cross-section to obtain the surface profile. To break the samples, they are frozen with liquid nitrogen to
hinder the deformation of the polymer. The expected outcome of this section is to objectively decide in which of the two types of nanoclay focus the structure and high-pressure study.

1.5 Structure, High-pressure, and Response of the Nanocomposite

This section will focus on the high-pressure effects on the structure and electro-mechanical properties of the nanocomposite. Several studies are performed to characterize the structure of the nanocomposite. The distribution of nanoclay near the surface is obtained by using a developed method based on bimodal AFM. High-pressure is applied to the surface by means of bimodal AFM. First, the strain of the nanocomposite is calculated by comparing the thickness of the film before and during the application of high-pressure. By varying the concentration of nanoclay, an experimental response of strain versus concentration can be obtained for the material, this data can then be fitted and compared to different models available for nanocomposites. The inter-nanoclay distance is calculated by measuring the thickness of individual core/shell platelets and comparing it to the exfoliated nanoclay (1 nm). By increasing the penetration of the tip into the individual nanoplatelet, the presence of polymer can be confirmed. The electro-mechanical response of the material to high-pressure is measured by scanning an area with bimodal AFM and then switch to conductive and CRFM. Also, the effect of pixel density is investigated because it is related to the compression of the polymer in-between nanoclay. It is expected that the polymer will show a change in conductivity once the pressure is applied, since the conductivity of PEDOT:PSS greatly depends on its morphology. The electro-mechanical response to the stimuli is measured to assess the effect of the local modification of the embedded nanoclay. The discussion focuses in the mechanism behind the change in conductivity by theoretical formalisms.
Chapter 2: Introduction to Bio-inspired Nanocomposites

Bioinspired material designs have been at the forefront of artificial nanocomposites development [18]. Complex architectures in bone [19, 20], mollusk shells [21, 22], fish scales [23, 24], among other biological systems, result in enhancement of intrinsic properties when compared to individual constituents. Particularly, nacre has received much attention due to its remarkable mechanical properties and convoluted structure. The main experimental approach to produce artificial nacre is to create organic-inorganic multi-layered structures; so called brick-and-mortar structures [25, 26]. Several interesting properties have been obtained from bio-inspired nanocomposites, but recently the focus has shifted towards extending to stimuli-responsive functionality [27]. This chapter contains an introduction to bio-inspired materials with a specific focus on nacre’s structure, functionality and the inception of polymer/nanoclay composites.

2.1 Hierarchical Structure of Nacre and its implications

Nacre is an organic-inorganic composite material produced by some mollusks as an inner shell that serves as protection. Nacre is composed of 95% layered aragonite (a crystal form of calcium carbonate) platelets separated by 5% organic matter [1]. Figure 1 shows the hierarchical structure displayed by nacre that spans several lengthscales (from molecular to microscopic features). The multiscale nature of the material gives rise to the interesting properties found in nacre. In the centimeter range, the actual mollusk shell is shown. Zooming into the micrometer range, the so called “brick and mortar” structure is observed. Moving towards the nanoscale, there are several structures that have been observed for different types of mollusk. The precise orientation of the aragonite “tiles” can be either columnar or sheet nacre [28], which means that the tiles are concentrically stacked of randomly distributed along an horizontal plane, respectively. Also, mineral bridges that form a link between tiles have been discovered. Among other
structures, polygonal nanograins (3–10 nm) have been measured on the aragonite tiles using transmission electron microscopy.

![Hierarchical structure of nacre](image)

**Figure 1. Hierarchical structure of nacre** [29]. At least six structural levels are revealed by SEM spanning several length scales. At 100 µm, the so-called brick-and-mortar structure is visible.

The fascination with nacre relies on the mechanical properties that result from the hierarchical structure. The most attractive mechanical property of nacre is its tensile strength along the direction of the tiles and the fracture toughness [30]. Several mechanisms have been discussed [29] and are shown in Figure 2. Mainly, the cause for the toughening of nacre has been reported to be the highly tortuous path for crack growth to occur (Figure 2a), but the high amount of energy dissipation obtained cannot be explained by just considering the brick-and-mortar structure. Some secondary mechanisms (Figure 2b) that have been reported are:

i. The existence of mineral bridges that reinforce the weak interfaces.

ii. The nanoasperities on the surface of the tiles that act as a source for shear resistance.

iii. The interlocking of platelets due to their shape or waved surfaces.
iv. The viscoelastic, organic material that glues the *tiles* together. It is worth mentioning that the dissipation coming from the organic material is not in effect in the case of dry nacre, thus humidity plays an important role when determining nacre’s mechanical properties.

v. The rotation and deformation of the aragonite nanograins.

The effect of all these dissipation mechanisms results in a work of fracture 3000 times larger in nacre compared to the bare aragonite [31].

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**Figure 2.** *Mechanisms involved in the toughening of the nacre structure (a) by crack propagation and (b) via interplatelet interactions* [18]. *The brick-and-mortar structure deflects the direction of the crack growth. Interplatelet structures serve as link between them, thus reinforcing the structure.*
2.2 Synthesis of nacre-inspired composites

The structure–function harmony of nacre and other hard biological tissues has inspired a large class of biomimetic advanced materials and organic/inorganic composites [32]. Biomimicking refers to the attempt of reproducing naturally occurring structures, such as nacre, in a laboratory environment. Different strategies have been used in the pursuit of replicating nacre’s architecture. A few of the synthesis procedures available for nacre-inspired materials are highlighted below.

Freezing casting was developed in 2006 [33] to build homogeneous, layered and porous scaffolds by taking advantage of the physics of ice formation. During the freezing process of dilute suspensions, a critical particle size exists where, above the critical value, suspended particles are trapped by the moving water–ice front. Furthermore, the hexagonal ice crystals have strong anisotropic growth kinetics [1]. The experimental setup precisely controls the freezing kinetics considering the critical particle size and the anisotropic growth. Directional freezing of alumina slurries was possible by applying a parallel temperature gradient to freezing front. This method results in particles being trapped in between the ice dendrites. Subliming the ice by freeze drying results in a structure that contains surface roughness and ceramic bridges between layers, such as the nanoasperities and mineral bridges of nacre. Adjusting the experimental conditions the freezing kinetics change, thus the thickness of layers could be controlled from 1 mm to 200 mm. Aragonite tiles in nacre are approximately 0.5 mm [31].

Electrophoresis deposition (EPD) is a simple, cost-efficient, and scalable technology that can rapidly produce films over large areas [34]. EPD is usually carried out in a two-electrode cell. By applying an external electric field, charged nanoparticles well dispersed in suspension move toward the working electrode. The charged particles migrate, deposit and grow on the electrode.
This method has been used to produce polymer-clay structures similar to nacre with improved mechanical properties compared to the individual components [35].

Layer-by-layer (LBL) assembly is a versatile and simple technique for fabricating structured and functional thin films by alternately immersing a clean substrate into two solutions of oppositely charged materials. The process is repeated until a multilayered structure is obtained [36]. The driving forces mainly include electrostatic interaction, hydrogen bonding, charge transfer, covalent bonding, and hydrophobic interactions [37]. The adsorption time for each layer varies from seconds to hours, which is a drawback because to obtain a practical thickness many deposition steps are required. Therefore, this technique could be time-consuming. LBL can be used to combine hard inorganic species with soft organic phase. Also, it allows for accurate control over materials’ structure and it is capable of incorporating high loading of inorganic fillers in hybrid materials [1]. To overcome part of the limitation presented by LBL, Almqvist et al. [38] introduced the concept of mechanical assembly. Basically, several macroscopic mechanical processes including sedimentation, centrifugation, vacuum filtration, doctor blading, slip casting, extrusion, roll compaction, among others, have been optimized to fabricate nacre-like composites, rapidly and economically, using organic/inorganic materials.

Organisms utilize a bottom-up approach to produce the structure of nacre. In situ biomineralization is an experimental technique in which the crystallization of minerals takes place in vitro from supersaturated solutions in the presence of organic macromolecules that influence the size, type and morphology of the crystals and act as templates for their nucleation [37]. The idea is to use a proper organic phase as a template for the growth of the inorganic phase. Ideally, the organic template should influence the nucleation sites, orientation and the shape of the inorganic phase growth [39]. Also, self-assembly methods have shown to produce nacre-like
structures using, for example, silica particles and an organic material [40]. Relying on evaporation during dip-coating, a solution of silica, surfactant, and organic monomers induce the formation of organized structures. Moreover, evaporation induced self-assembled nanocomposites have been obtained from poly-(triethylene glycol diacrylate) and indium–tin–oxide layers [37].

2.3 Polymer and Nanoclay Composites

Polymers and nanoclay are the most common organic/inorganic materials used to produce nacre’s structure [25, 41–44]. The synthesis of this type of nanocomposite leverage from self-assembly processes [2]. Nylon 6 and polyvinyl alcohol (PVA) are some of the most used polymers for polymer/nanoclay composites. The nanocomposites exhibit properties dominated by the interfacial interactions between the polymer and nanoclay. For example, physical properties of nylon 6 are largely governed by strong hydrogen bonds. This results in three different crystalline forms that coexist at different percentages depending on the processing conditions. The addition of the nanoclay serves as nucleating agents for the crystallization of the matrix at low concentrations [45]. In higher concentrations, although there are more nucleation sites, it retards the polymer crystal growth.

![Figure 3. Schematic of Laponite RD nanoclay [46]. The chemical structure of the nanoclay is shown left. Three layers form each individual platelet. In solid state, the individual sheets are separated by sodium cations that get dispersed when in water.](image-url)
Nanoclays, Laponite RD [46] and Cloisite Na+ [47], are of 2:1 phyllosilicate where the two external surfaces are identical tetrahedral sheets and the middle has an octahedral coordination, an schematic for Laponite RD is shown in Figure 3. The difference between the mentioned nanoclays is the elements in the middle sheet. Stacks are formed from negatively charged platelets separated by sodium cations. These stacks aggregate into micro-sized particles (micro-sized powder is commercially available). When exfoliated in deionized water, the stacks separate dispersing negatively charged platelets (1 nm in thickness) and Na+ ions. Also, these platelets are non-polar, thus hydrophobic in the dispersion. The exfoliation process is mainly caused by shear forces that break apart the agglomerates. Depending on the exfoliation degree and order of the nanoclays in the matrix, several types of nanocomposites are identified and shown schematically in Figure 4. Completely delaminated nanoclays, distributed homogeneously and well oriented in the polymer (intercalated) is the morphology that more closely resembles nacre’s structure.

Recently, Walther et al. [25] introduced an experimental procedure to produce fully intercalated nanocomposites. The method is fast, easy to implement and scalable. Also, the process is environmentally friendly and economic. The basic principle of the method is to use core/shell nanoplatelets, formed by adsorption of soft polymers onto hard nanoclays. The resulting core/shell nanoplatelets undergo concentration induced self-assembly on a macroscopic-length scale during water removal. The resulting structure is characterized by maximum exfoliation and order of the inorganic reinforcements. Figure 5 shows schematically a summary of this process. Generally, the nanoclay is dispersed in deionized water and stirred vigorously, thus resulting in the separation of the individual 1 nm layers. Same procedure is used with the polymer, if it is not already in dispersion. Then, both dispersions are mixed producing the core/shell nanoplatelets. Finally, controlled evaporation of the solvent achieves the desired nacre-like structure.
Figure 4. Schematic illustration of different types of nanoclay-based composites depending on the nanoclay size and organization [45].

Figure 5. Schematic representation of the self-assembly process used to produce nacre inspired nanocomposites. In this example, PVA (polymer) and different aspect ratio nanoclays are shown.
The polymer and nanoclay are mixed in dispersion, thus forming the core/shell platelets as an intermediate step. Finally, the brick and mortar structure is obtained by solvent evaporation [2].

2.4 Multifunctionality of polymer/nanoclay composites

Polymer/nanoclay composites have been designed to include a wide range of functions. As expected, the mechanical properties of the matrix improve when the proper aspect ratio and quantity of the filler is used. For PVA-nanoclay composites, the Young’s modulus has been increased by up to 100 times compared to the bare PVA. Also, the tensile strength has been shown to increase beyond the values typically obtained for nacre [2]. It is important to mention that the mechanical properties of the polymer/nanoclay composite significantly vary when the humidity increases. The moisture content inside the films interact with the polymer reducing the stiffness and increasing the ductility (in some cases).

As shown schematically in Figure 2, nacre structure contains secondary strengthening mechanisms, such as interplatelet interactions and crack growth deflection. Several attempts to include those mechanisms in the synthesis of self-assembled nanocomposites have been made [48], [49]. As previously mentioned, there are sodium ions in the dispersion that contain the nanoclay. These Na\(^+\) ions serve as anchor between the nanoclay surface and the polymer chains of in between polymer chains. Using a solution that contained a stronger ion, Cu\(^{2+}\) in this case, it was possible to infiltrate and exchange the Na\(^+\) ions for the Cu\(^{2+}\) ions. This resulted in an enhanced mechanical response of the material in the presence of high humidity. Also, using self-healing polymers as the matrix, stiffer and tougher assemblies were achieved. The polymer chain contains a side group that will form a chemical bond with the nearest polymer chain containing the proper side group for the bond to occur. As stress is applied this secondary interaction will break and reform many times, improving the mechanical properties. For a similar nanocomposite, it was demonstrated that the
enhancement of the mechanical properties could be switched on and off by using light to control 
the chemical bond formed by the side groups [50]. Another important dissipation mechanism in 
nacre is the rotation of the nanograins [51]. Theoretical studies of hard fillers embedded into a soft 
matrix have found that in the presence of an externally applied stress, the hard particles move 
based on the deformation of the matrix [52]. The movement of the hard phase dissipates energy.

Besides mechanical applications, polymer/nanoclay composites also serve as barriers. The 
oxygen permeability of the nanocomposites decrease compared to the bare matrix [2]. Also, the 
aspect ratio of the nanoclays used plays a role. The oxygen barrier property is important for many 
applications, particularly, it has a direct impact on food science [53]. The nanocomposite is useful 
to help prevent oxygen and other gases from affecting packaged food. Basically, the addition of 
the nanoclays creates a difficult path for the gas molecules to move through the film, shown 
schematically in Figure 6. A consequence of the gas barrier property, it also serves as a fire 
retardant material [54]. The nanoclay prevents the diffusion of oxygen, thus the flame dies out. In 
aqueous electrolyte environments, the nanocomposites have shown to prevent corrosion, when 
painted on cold rolled steel, acting as a chemical barrier [55].

![Figure 6. “Tortuous diffusion path” in polymer/clay nanocomposite [44]. The ordered brick-and-mortar structure reduces the diffusion of species across the material.](image-url)
The optical properties of the nanocomposites are also important. To extend the usability of the nanocomposite full optical transparency is desired, thus any surface could be coated without a visual impact. For full transparency, irregularities must be prevented to reduce detrimental light scattering within the film. At the same time, the surface must be of high quality containing minimum roughness to avoid surface scattering. Also, exfoliation and orientation is desired \[2\]. Nacre-mimetics fulfill most criteria to the best possible extent. PVA-nanoclay nanocomposites have shown to have up to 97% of light transmission \[2\]. Different combinations of polymers and nanoclay have also proven to be highly transparent \[37\].

Historically, electrically conductive nanocomposites have been designed using nonconductive matrix (polymer) filled with a carbon-based material, e.g. graphene \[56, 57\], carbon nanotubes \[58, 59\], forming an electrically conductive network which can be used for a wide-range of applications (examples available in next section). Nowadays, conductive polymers are designed as coatings or free-standing films achieving high conductivity \[60\]. Recently, Walther et al. \[5\] introduced a new electrically conductive nanocomposite based on nanoclay and PEDOT:PSS (a conductive polymer). The material integrates high stiffness and strength with electrical conductivity close to the bare polymer. The integration of the nacre-like structure with the electrical properties of the polymer highlights the addition of relevant functionalities into a stiff and tough architecture. Properties beyond mechanical performance can be interweaved for the design of advanced multifunctional nanocomposites using nacre as inspiration.

2.5 Applications of nacre-inspired composites

The focus of designing bio-inspired materials has shifted towards extending the functionality of nanocomposites to designing of stimuli-responsive systems \[27\]. The most basic sensing application of nanocomposites is strain measurements. Using carbon nanotubes embedded
in a non-conductive polymer, strain sensing is possible [59]. Carbon nanotubes are added to the matrix until electrical percolation is obtained. The carbon nanotubes should be close enough to each other, so the electrons can tunnel between them. When stress is applied, the nanotubes move and the distance between them change. Thus, the tunneling barriers between individual nanotubes increase or decrease depending on the stress. The electrical current change across the material is proportional to the applied stress.

A similar system comprised of aligned nanotube structure and polymer has shown the capability of chemical vapor sensing [58]. The nanotubes are grown out of the polymeric substrate plane using chemical vapor depositions techniques. The flexible thin film device works by monitoring conductivity changes caused by the charge-transfer interaction with gas molecules and/or the distance change between nanotubes induced by polymer swelling via gas absorption. It showed changes in conductivity when exposed to THF, ethanol and cyclohexane. Also, graphene-based chemical sensors have been introduced [56, 57] where the same basic principle rules the sensing, the polymer reacts to the change in environment thus affecting the original graphene orientation.

![Figure 7](image)

**Figure 7.** Schematic representation of change of structure with external stimuli [30]. The organic layer reacts to the stimuli, thus producing a change in the overall sample structure.

For nacre-inspired materials containing nanoclay, the same working principle applies. External stimuli reorganize the organic phase morphology (schematically shown in Figure 7) and
as a result a measurable change is obtained [30]. Using layer by layer deposition, multiresponsive films containing nanoclay and poly(N-iso-propylacrylamide) have been designed [4]. The assemblies respond to temperature, pH, and salt concentration variations via changes in their swelling ratio and permeability characteristics to various solutes. These multiresponse features of clay-containing films make them promising candidates for applications in sensing, actuation, and controlled delivery. Similar layer by layer deposited structures have been developed as photonic crystals [61]. Their optical properties are tuned by changing the number of layers, incident angles, and the thickness of the layers, but also they are responsive to water vapor by reversible full-color switching. Layer by layer fabrication with double hydroxide nanoparticles and poly(N-iso-propylacrylamide) ultrathin films demonstrated switchable electrocatalytic performance in response to temperature stimuli [62]. All these cases use the layer by layer assembly to produce the ordered structure. Also, the organic material is the phase that reacts to the stimuli by changing the local morphology. Tracking thickness changes or color changes is not a straightforward measurement in application where there is no direct access to the sensing unit.

Another strategy for piezoelectric sensors use polyvinylidene difluoride (piezoelectric polymer) and nanoclay electrospun fibers for sensing a voltage response to loading while maintaining good flexibility with applications as smart clothing [63]. As mentioned in section 1.3, the added nanoclay serves as nucleation sites for the crystallization of the polymer. In the case of the piezoelectric polymer, the combination of adding the nanoclay and the manufacturing process yields the formation of β-phase. The β-phase is the crystalline structure in polyvinylidene difluoride that produces a high piezoelectric response. The full-fiber sensor showed notable piezoelectric properties with good response speed and reproducibility. The addition of nanoclay serves as a control for the polymer morphology, which at the end is what controls the deformation-
voltage relationship. The sensing applications have not focused on the fact that hard particles move when stress is applied [52], what reacts to the stimuli is always the organic phase of the nanocomposite.

2.6 Summary

The discovery of the hierarchical structure of nacre originates a new family of nanocomposites. Different attempts into synthesizing the nacre-like structures resulted in the development of self-assembly of core/shell platelets via solvent evaporation for polymer/nanoclay composites. Besides the improved mechanical properties, the polymer/nanoclay structure achieved many other functional properties. Some functional properties of polymer/nanoclay composites are: gas and chemical barrier, fire retardancy, transparency and electrical conduction. A common application for the bio-inspired nanocomposites is as sensing devices for humidity, chemicals, strain, among others. The basic working principle is that the polymer phase interacts with the stimuli causing a measurable response.
Chapter 3: Atomic Force Microscopy

Contact or static atomic force microscopy (AFM) was introduced in 1986 [6] as a method for imaging surfaces, either electrically conductive or insulative, at the nanoscale. In contact-mode AFM, a tip (typically 5-10 nm radius) attached to a cantilever is raster-scanned across the surface while maintaining a constant deflection as feedback. Given the continuous contact between the tip and sample during the raster scan, soft materials can be subjected to permanent surface damage. To overcome this intrinsic issue in contact mode AFM, dynamic AFM was introduced [7]. In the so-called amplitude modulation AFM (AM-AFM), the cantilever is excited at or near its resonance frequency with constant drive amplitude. AM-AFM has been used to image soft materials, such as polymers or biological specimens. The engaged oscillation amplitude is used as the feedback signal for a control loop to track the surface topography. There are two observables associated with AM-AFM, which are amplitude and phase. The response amplitude signal is the feedback error signal and the phase lag between the excitation and response of the cantilever is related to material properties. However, phase contrast is only observed when there are tip-sample dissipative interactions [64].

In 2004, Rodríguez and Garcia [16] proposed that by exciting two eigenmodes of the cantilever simultaneously, compositional mapping could be performed reliably. This work was the inception of a family of AFM techniques called multifrequency AFM, more specifically bimodal AFM in the case of two excited eigenmodes. In bimodal AFM, the first or fundamental eigenmode is reserved for topographical acquisition and the higher mode is reserved for material contrast. The most common bimodal AFM scheme is called amplitude modulation-open loop (AM-OL) where the first eigenmode oscillation amplitude is modulated as in AM-AFM while the second eigenmode has no feedback loop. The second or higher eigenmode is excited at constant frequency.
and amplitude resulting in two extra data channels, amplitude and phase for the second eigenmode. Several attempts have been made to optimize the contrast obtained from bimodal AFM. The free amplitude of the higher mode [65, 66] and its excitation frequency [67] have been independently optimized for phase, dissipated energy (mapping of dissipative interactions) and virial (mapping of conservative interactions) contrast; acquiring the sharpest possible image (with high signal-to-noise ratio). It is known that for multifrequency AFM there is an enhancement in the penetration (indentation) of the tip into the sample. More advanced multifrequency techniques have been used to image subsurface structures embedded in polymers [17]. Other AFM-based methods have expanded the capabilities from topography imaging to the measurement of mechanical [10–12], electrical [13, 14], or magnetic [15] properties of materials at the nanoscale. AFM have become a multiuse tool for characterization of materials.

This chapter contains an introduction to the basics of AFM. It starts by describing the theory behind the simplest AFM methods, and then covers more advanced topics related to functional characterization. Also, developments in AFM techniques for the specific purpose of the high-pressure study of multi-functional nanocomposites are described ahead and the reasoning behind using the combination of these techniques for this work.

3.1 Tip-Surface Interaction Forces

As implied by the name of the technique, the apparatus’ principle of operation relies on the force exerted by the tip on the surface. Different schemes of AFM operate at distinctive tip-sample interaction forces. The tip-sample interaction depends on their relative distance and their geometry. In air, the dominant forces are: van der Waals interactions, short-range repulsive interactions, adhesion and capillary forces [68].
The van der Waals forces have their origin in electric dipole interactions. These dipoles could be either permanent or induced. In AFM, van der Waals forces results in attraction between the tip and the sample surface. Over-simplifying the geometry of the tip-sample system, it is possible to describe the attractive force between the two using a sphere-flat approximation. The van der Waals force in this case is given by:

\[ F_{vdW} = -\frac{HR}{6d^2} \]  

where \( H \) is the Hamaker constant, \( R \) is the radius of the tip, and \( d \) is the instantaneous tip-sample distance. Capillary force arises from water that spontaneously condenses in hydrophilic surfaces. Basically, the water at the surface will form a water meniscus, when the tip is close enough. The size of the water meniscus can be described by the Kelvin radius [68]. Capillary forces are adhesive in nature, since the tip must break the water meniscus in order to leave the surface.

Short-range repulsive forces and adhesion emerge from the mechanical contact of the tip and sample, where the deformation depends on the applied force. There are models that describe the tip-sample repulsive interaction under different circumstances. The simplest model is Hertz, which ignores effects from adhesion. Slightly more sophisticated models have been presented by JKR [69] and DMT [70]. These models consider adhesion and provide analytical relationship between deformation and applied force. Also, the two share several assumptions, which are: the deformations are elastic and linear, the contact area is smaller than the tip and the contact area is symmetric with respect to the tip axis [68]. These assumptions do not hold for materials that undergo large deformations under the applied load, e.g. polymers. Polymers are viscoelastic, which is a non-conservative velocity-dependent behavior [71].

In the context of AFM, the most basic model that reproduces both stress relaxation and creep compliance of a viscoelastic material is the standard linear solid (SLS) model [72]. The SLS
is a linear model that does not consider the tip geometry. A non-linear SLS model [71] was introduced by utilizing a DMT spring as part of the SLS. Recently, a more advanced quasi-3D model has been introduced [73]. This model considers the tip geometry and the in-plane surface force of the outermost sample layer, which helps understand the complex interaction between the tip and a polymeric sample.

![Figure 8](from www.nanophys.kth.se/Force_distance_inAFM).

**Figure 8.** Schematic of the typical force versus distance between tip and sample in AFM considering van der Waals attractive forces and conservative contact interactions [from www.nanophys.kth.se/Force_distance_inAFM].

Considering van der Waals attractive force and conservative contact interactions, the force versus distance behavior of the tip and sample is shown schematically in Figure 8. Depending on the distance of the tip relative to the sample, the forces can be either attractive or repulsive. When the gradient of the force is positive, the force is attractive. When the gradient is negative, the force is considered as repulsive. As the tip approaches the samples, first it will feel an attractive force, then after mechanical contact it will feel a repulsive force. Contact, non-contact and intermittent contact regimes will be discussed below.
3.2 Contact or Static Mode AFM

![Schematic of contact mode AFM](https://usa.jpk.com)

Figure 9. Schematic of contact mode AFM [from /usa.jpk.com]. A tip attached to a cantilever is dragged across the sample surface, while deflection is kept constant. The cantilever deflection is measured using a laser beam and a position-sensitive photo diode.

The sensing unit in AFM is a tip attached to a cantilever, which acts as a spring of stiffness $k$ (Figure 9). In this mode, the tip is in constant contact with the sample, corresponding to the contact force [6] regime in Figure 8. The deflection of the cantilever is used as the feedback loop to scan the surface. The base of cantilever will move up or down while maintaining the deflection setpoint constant, thus measuring topography. The normal force applied by the cantilever to the surface is described by $F = ks$ (Figure 9). Strong lateral and normal forces are obtained and can cause damage to the surface. The surface damage is higher in very soft samples, such as cells. Another issue is that the full measurement of tip-sample force is not possible due to the snap-in or snap-out events. A force curve in contact mode AFM refers to the approach and retracts the base of the cantilever into the sample, while measuring the deflection of the cantilever. During the approach part of the force curve, the cantilever remains un-deflected until the gradient attractive
forces is larger than the stiffness of the cantilever. At that point, the cantilever tip gets pulled into the sample, thus named *snap-in*. As the approach continues, the cantilever deflection start to increase until the setpoint is achieved, then the cantilever retracts. The tip stays in contact with the sample until the restoring force of the cantilever exceeds the contact force (adhesion, increased van der Waals due to increased area of contact, mechanical contact, among other interactions) between the tip and the sample. When the tip leaves the surface, the event is named *snap-out*. A schematic representation of the whole process is shown in Figure 10. To improve the applicability of AFM to more sample systems, amplitude modulation AFM was introduced.

![Figure 10. Schematic representation of the snap-in and snap-out events observed in contact-AFM by the approach and retract of the cantilever to the sample.](image)

### 3.3 Amplitude Modulation AFM

Amplitude modulation AFM (AM-AFM) is a dynamic mode of AFM in which the cantilever is forced to oscillate *at or near* its resonance frequency [7]. Figure 11 shows schematically the basis for AM-AFM operation. Usually, the cantilever is excited by a piezoelectric element driven with a sinusoidal signal at a constant amplitude and frequency. The driving frequency is *at or near* the natural resonance frequency of the cantilever, which is given by \( \omega_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \) using the harmonic oscillator approximation. When excited and far from the sample surface, the cantilever exhibits an amplitude and phase response depicted in Figure 11a. This is
called the *free response* of the cantilever. A reduced amplitude is used as the setpoint for imaging. When the tip approaches the surface, the oscillation amplitude gets reduced to an established value (usually 60-80% of the free response), then the surface is scanned while maintaining the engaged amplitude constant. Two observables arise from this AFM scheme: amplitude and phase. The amplitude is an error signal obtained by comparing the instantaneous amplitude to the setpoint amplitude of the feedback loop. If the system is not moving the base of the cantilever fast enough, the instantaneous amplitude will be either 1 or smaller than the setpoint. In experiments, the amplitude signal should be kept as small as possible, thus minimizing error. The phase signal is discussed below.

**Figure 11. Schematic setup for AM-AFM.** The motion of the cantilever is detected with the laser beam deflection method and the typical response of the cantilever is shown in (a) [74]. A lock-in amplifier is used to measure the oscillation amplitude and phase shift between excitation and oscillation [75].

Theoretically, the cantilever-tip system can be approximated by a point-mass spring driven by an external force in the presence of the tip-surface forces [7]. The equation of motion for the damped harmonic oscillator is
\[ m \ddot{z} = -kz - \frac{m\omega_0}{Q} \dot{z} + F_0 \cos \omega t + F_{ts}(d) \]  

(2)

where \( F_0 \) and \( \omega \) are the amplitude and angular frequency of the driving force, respectively; \( m, Q, \omega_0 \) and \( k \) are the effective mass, quality factor, angular natural frequency, and force constant of the free cantilever, respectively, and \( F_{ts}(d) \) is the tip-sample interaction force. For AM-AFM, the excitation frequency is the natural frequency of the cantilever, \( \omega = \omega_0 \). The quality factor is defined as \( Q = \frac{\omega_0}{\Delta \omega} \), where \( \omega_0 \) is the resonant angular frequency and \( \Delta \omega \) is the resonance width at half maximum. In the absence of external forces (\( F_{ts} = 0 \)), the amplitude response of the cantilever is described by

\[
A(\omega) = \frac{F_0 / m}{\left( (\omega_0^2 - \omega^2)^2 + \left( \frac{\omega \omega_0}{Q} \right)^2 \right)^{1/2}}
\]  

(3)

and the phase shift can be calculated by

\[
\tan \phi = \frac{\omega \omega_0 / Q}{\omega_0^2 - \omega^2}
\]  

(4)

which describes the behavior shown in Figure 11a. Given the non-linear behavior of the force (Figure 8), analytical solutions for the engaged case are not trivial. Under the assumption of a weakly perturbed harmonic oscillator, the angular resonance frequency is related to the effective force gradient experienced by the oscillator through the equation [75],

\[
\omega_{eff} = \left( k - \langle \nabla F_{ts} \rangle \right)^{1/2}
\]  

(5)

The consequence of equation 5 is that the effective resonance frequency of the cantilever changes depending on the interaction force. When the gradient of the force is positive, the response curves shift to lower frequencies. On the other hand, when the gradient is negative, the response curves shift to higher frequencies. Since the cantilever is excited at its free resonance frequency,
the frequency shift associated to equation 5 gives origin to two regimes in AM-AFM, attractive and repulsive regimes [76]. Attractive regime has an associated phase lag larger than 90 degrees. Referring to the free response of the cantilever (Figure 11a), the phase response moves to lower frequency, thus higher phase value is measured. Imaging in attractive regime is called non-contact AM-AFM (see Figure 8) and the interaction is dominated by long-range van der Waals forces. Repulsive regime has an associated phase lag below 90 degrees. Again, referring to the free response of the cantilever (Figure 11a), the phase response moves to higher frequency, thus lower phase value is measured. Imaging in repulsive regime is also called intermittent contact AM-AFM or *tapping mode*, since the tip “taps” the surface. Since the gradient of the force greatly depends on the material under investigation, phase lag is loosely associated to material properties. For example, phase shift in heterogeneous samples is associated to local compositional variations [77].

### 3.4 Conductive-AFM

In conductive atomic force microscopy [78] (C-AFM), a conductive tip is brought into contact with a sample while applying a bias voltage, thus local current is mapped. Typically, the cantilever and tip are coated with a conductive material. C-AFM is a method based on contact mode AFM, so the tip is constantly in contact with the sample while the scan is performed. The bias voltage is applied while the scanning conductive tip serves as a movable nanoelectrode in continuous contact with the sample. The operation of C-AFM required a modification of our system. An externally connected low-noise current amplifier (FEMTO®, DLPCA-200) was used to measure the current flowing between the conductive tip and the sample. The FEMTO® is then interfaced with the AFM controller and software.
3.5 Contact Resonance Force Microscopy

In contact resonance force microscopy (CRFM), the resonance frequency and quality factor mechanically coupled tip and sample surface system are measured [79–81]. CRFM is a hybrid between static (measures topography) and dynamic AFM (measures resonance frequency and quality factor) (shown schematically in Figure 12a). Basically, the tip is in contact with the surface and a small sinusoidal oscillation is added, such that the tip oscillates while in constant contact with the sample. The two observables can be interpreted as conservative and dissipative interactions of the dynamic contact.

Figure 12. (a) Schematic diagram of the AFM probe vibrated while in contact with the sample surface. (b) Schematic representation of the tip–sample system with the representation of the contact coupling as an ideal elastic spring in parallel with an ideal viscous damper [79].

CRFM is implemented as the dual AC resonance tracking (DART) [82]. In CRFM-DART, the amplitude and phase of the cantilever response are monitored at two frequencies, one lower and one higher than the contact resonance frequency. Besides measuring the topography (by maintaining a constant deflection setpoint), the recorded amplitude and phase for each frequency are used to calculate the contact resonance frequency and quality factor at each pixel [82]. CRFM-DART will be referred to as “CRFM” throughout.
Using the Euler-Bernoulli beam model interacting with a Kelvin-Voigt spring-dashpot element at the tip-sample junction (Figure 12b), decoupling of the conservative and dissipative interactions of the tip-sample junction is possible [83]. Basically, the Euler-Bernoulli model

\[
EI \frac{d^4y}{dx^4} + \eta_\text{air} \rho A \frac{dy}{dt} + \rho A \frac{d^2y}{dx^2} = 0
\]  

is solved with the proper boundary conditions. At the base of the cantilever, x=0, the two boundary conditions are

\[
y = 0 \quad \frac{\partial y}{\partial x} = 0
\]

and at the tip where x = L are

\[
\frac{d^2y}{dx^2} = 0 \quad EI \frac{d^3y}{dx^3} = k^* y + \gamma^* \frac{dy}{dt}
\]

Above, E, I, \(\rho\), A and \(k_c\) are the Young’s modulus, cross-sectional moment of inertia, density, cross-sectional area and stiffness of the cantilever, respectively. The last boundary condition comes from the shear condition at the end of the cantilever, which depends on the force applied by the spring-dashpot system (Figure 12b). Using the model, relations between the observables and material properties are obtained.

The contact resonance frequency, which is higher than the free cantilever resonance frequency, is directly related to stiffness [84], while the quality factor maps the sample damping [85]. Based on equation 6, relations between contact stiffness, \(k^*\), and contact damping, \(\gamma^*\), and the observables can be derived [86]. The \(k^*\) is defined as

\[
k^* \frac{k}{k_c} = \frac{(k_n L)^3 (1 + \cos(k_n L) \cosh(k_n L))}{3 (\cos(k_n L) \sinh(k_n L) - \sin(k_n L) \cosh(k_n L))}
\]  

where \(k_n L\) is the \(n^{th}\) normalized wave number and is related to the contact frequency as
\[ k_n L_{\text{cont}} = k_n L_{\text{free}} \sqrt{\frac{f_{\text{cont}}}{f_{\text{free}}}} \] and \[ k_n L_{\text{free}} = 1.8751, 4.6941 \text{ and } 7.8548 \text{ for the first three eigenmodes.} \]

For the \( \gamma^* \), a first mode approximation yields

\[ \gamma^* = \left( f_{\text{cont}} Q_{\text{cont}} - f_{\text{free}} Q_{\text{free}} \right) \left( \frac{k_c}{2\pi f_{\text{free}}^2} \right) \]

(8)

Free refers to the free cantilever response and cont refers to the contact response of the cantilever.

An increase in the contact resonance frequency and quality factor is associated to a stiffer and less dissipative sample, respectively. On the other hand, a decrease leads to less stiff and more dissipative interaction. This can be inferred from equation 7 and 8, where \( k^* \) is proportional to \( \sqrt{f_{\text{cont}}} \) and \( \gamma^* \) is proportional to \( \frac{1}{Q_{\text{cont}}} \).

The contact resonance frequency and quality factor are referred to as mechanical parameters. Although, there are methods to calibrate for the Young’s modulus, they require a standard reference sample with similar properties to the unknown sample, including surface properties [73]. Also, polymer mechanical properties are very sensitive to the frequency of the measurement (viscoelasticity is a time-dependent behavior) [71]. In CRFM, an additional challenge is the inability to probe at frequencies lower than the kilohertz to megahertz range because of the resonance properties of cantilevers. Traditional testing of polymeric or biological materials is performed at a frequency range several orders of magnitude lower [87]. Moreover, not all frequencies can be investigated at will. The frequencies are limited to cantilever resonance modes. In practice, the instruments are able to track up to 4 modes [88], which means only 4 frequencies are investigated at the most. CRFM measurements are performed at a single oscillation frequency with a fixed amplitude, but generally provide qualitative contrast information [87]. Therefore, CRFM provides mapping of relative surface properties with high spatial resolution. Given the complexity of the interpretation of the measurements as mechanical properties, raw
signals are used to compare the mechanical parameters (contact resonance and quality factor) of fabricated samples using same cantilever and imaging conditions, which allow us to discuss their relative changes.

3.6 Bimodal AFM

Bimodal AFM is part of a family of techniques in AFM referred to as “multifrequency AFM” [89]. Multifrequency refers to the fact that several eigenmodes of the cantilever are excited simultaneously. Currently, three eigenmodes [17, 90] (excited simultaneously) have been used to visualize subsurface structures and four eigenmodes [91] have been investigated. The focus here will be amplitude modulation-open loop (AM-OL) bimodal AFM, which is an AFM scheme that excites two eigenmodes simultaneously. Different implementations of bimodal AFM have been introduced [75, 92, 93], but AM-OL is the simplest and most robust scheme. Also, the AM-OL scheme is implemented in most commercially available instruments. “Bimodal AFM” will refer to the case of AM-OL scheme throughout.

The main problem with AM-AFM was discussed by Cleveland et al. [64] by means of dissipated energy by the cantilever. An expression for energy dissipated by the cantilever was developed by performing an energy balance. It was discovered that in the absence of dissipation the relationship between phase lag \( \phi \) and amplitude \( A \) is not independent \( \phi = \sin^{-1} \left( \frac{A}{A_0} \right) \) (\( A_0 \) is the free amplitude). This means that for a surface that is not dissipative, there will be no contrast in the phase lag channel. To solve this issue, bimodal AFM was introduced in 2004 [16].

AM-OL bimodal AFM is the original introduced scheme [16]. This means that amplitude modulation (AM) is used to drive the fundamental eigenmode and open-loop (OL) is used to drive the higher eigenmode, whose phase and amplitude provided the compositional contrast. The OL eigenmode is driven with constant amplitude and frequency. The feedback loop is in the AM and
the OL eigenmode’s response is only observed. The existence of additional contrast channels in bimodal AFM generally guarantees that both topographical and compositional information can be obtained, since one can optimize the two relatively weakly coupled eigenmodes separately. Usually, the first eigenmode is used to obtain topography and the second eigenmode is used for material contrast.

Figure 13. Schematic of the implementation of AM-OL bimodal AFM [75]. AM-OL scheme is accomplished by adding the drive signals of two function generators for exciting the cantilever and using two lock-in amplifiers to track the amplitudes and phase shifts at the corresponding eigenmodes.

The implementation of bimodal AFM is shown in Figure 13. Two sinusoidal functions are added together and applied to the base of the cantilever by means of the piezoelectric element. The frequencies of the sinusoidal are at or near the eigenmodes of the cantilever. The first eigenmode engaged amplitude is used as feedback loop based on the setpoint and measures the topography. The higher eigenmode provides two extra observables, amplitude and phase. The free amplitude of the higher eigenmode is the key parameter governing the intensity of the tip-sample interactions for a given free amplitude and amplitude setpoint of the fundamental eigenmode (the drive
frequency is selected to be near the eigenfrequency). The work of Gigler et al. [66] explored the
effect of the higher to fundamental amplitude ratio ($A_i/A_1$) based on the contrast observed in the
phase channel of the higher eigenmode. They concluded that for repulsive bimodal imaging of
polymer surfaces, good contrast quality can be obtained for amplitude ratios ($A_i/A_1$) smaller than
10%, without affecting the topography feedback.

3.6.1 Mapping conservative and dissipative interactions in bimodal AFM

Energy-based quantities incorporate contributions from both observables, phase and
amplitude, and are more meaningful in terms of material property variation across the surface.
Specifically, the amplitude and phase signals can be converted into virial ($V_{ts}$) and dissipated power
($P_{ts}$), which are convolutions of the tip-sample interactions with position and velocity, respectively,
and are used to describe conservative and dissipative interactions [64, 92, 94]:

$$V_{ts,i} = \frac{k_i A_i}{2} \left[ A_i \left(1 - \frac{f_{exc,i}^2}{f_i^2}\right) - \frac{A_{0,i}}{Q_i} \cos \phi_i \right]$$  \hspace{1cm} (9)

$$P_{ts,i} = \pi f_{exc,i} \frac{k_i A_i^2}{Q_i} \left[ \frac{A_{0,i}}{A_i} \sin \phi_i - \frac{f_{exc,i}}{f_i} \right]$$  \hspace{1cm} (10)

where the index $i$ specifies the corresponding eigenmode under study, $k$ is the stiffness, $A$
the instantaneous amplitude, $A_0$ the free amplitude, $f_{exc}$ the excitation frequency, $f_0$ the free resonance
frequency, $\phi$ the phase, and $Q$ the quality factor. Note that $f_{exc}$ is approximately equal to $f_0$ in
bimodal AFM.
Figure 14. Comparison of mean phase (a), dissipated power (b) and virial (c) of the 1st and 2nd eigenmodes, including one standard deviation intervals to describe the contrast obtained in spin casted Nafion® thin film sample images [65]. Individual experiments are indicated by crosses in the lower tile and the corresponding standard deviations are shown on the top two tiles.

We introduced a more thorough approach [65] in which the effect of the free amplitude of the higher eigenmode is taken into account for the calculation of the energy quantities. With this method, dissipative and conservative interactions can be mapped with highest contrast by following few steps for repulsive tip-sample interactions. First, several images are obtained keeping all the parameters constant except for the free amplitude of the higher eigenmode which is increased. Second, energy quantities are calculated using equations 9 and 10. Finally, the contrast of the images is calculated by using frequency histograms of each image, fitting them to a Gaussian distribution to calculate the mean value and standard deviation and using the standard deviation as a metric for quantifying the contrast. Typical results are shown in Figure 14. Besides the systematic approach to image dissipative and conservative interactions, results are compared to numerical simulations. Comparing the dissipated power calculated from equation 8 with the one obtained from individual force curves, it is discovered that the higher eigenmode describes the dissipation better. Finally, it is observed that the free amplitude of the higher eigenmode affects
the different channels (phase, virial and dissipated power) differently, resulting in peak contrast at different amplitudes. This methodology presents a systematic approach to investigate material properties variations across surfaces with the highest possible contrast.

### 3.6.2 Effects of higher eigenmode free amplitude on the tip-sample interaction

![Graph](image)

**Figure 15.** Simulated peak forces, change in surface position and phase of the second eigenmode for a cantilever operating in bimodal AFM interacting with a quasi-3D standard linear solid surface for different free amplitudes. The parameters for the surface are: $k_1 = 7.5e^2 \text{ N/m/nm}^2$, $k_2 = 7.5 \times 10^{-2} \text{ N/m/nm}^2$, $c_{diss} = 1 \times 10^{-7} \text{ Ns/m/nm}^2$ and $k_{int}=0.24 \times 10^{11} \text{ N/m}^2$. The software and details of the method are described elsewhere [73]. The first eigenmode of the cantilever has a free amplitude of 100 nm and a setpoint of 75%. The cantilever parameters are taken to be similar to the commercially available AC160TS ($k_1 = 23 \text{ N/m, } f_1 = 380 \text{ kHz}$).

The effect of free amplitude of the second eigenmode interacting with a quasi-3D surface model is shown in Figure 15. The model treats the surface as a collection of standard linear solid viscoelastic elements with in-plane elastic surface elements. As the free amplitude of the higher mode increases, peak forces, change in surface position and the average phase value also increase. This outcome can be explained using the dimensionless equation of motion (EOM) of a damped harmonic oscillator [17].
\[
\frac{d^2 z}{dt^2} = -z + \frac{1}{Q} \left[ -\frac{dz}{dt} + \cos(t) \right] + \frac{F_{ts}(z_{ts})}{kA_o}
\]  
(11)

where \( A_0 \) is the free amplitude, \( z = z(t) / A_0 \) is the dimensionless tip position with respect to the cantilever base, \( z_{ts} = z_{ts} / A_0 \) is the dimensionless tip-sample distance (\( z_{ts} = z + z_{eq} \), where \( z_{eq} \) is the equilibrium position of the cantilever above the sample), \( t = \omega_o t \) is the dimensionless time, \( k \) is the cantilever force constant and \( F_{ts} \) is the tip-sample interaction force with the substitution \( A \approx A_o = F_o Q/k \) where \( F_o \) is the amplitude of the excitation force, and the damping and excitation terms have been combined, and have a common factor of \( 1/Q \). The free amplitude \( (A_o) \) and force constant \( (k) \) define how much the external forces (tip-sample interactions, \( F_{ts} \)) affect the dynamics of the excited eigenmode (last term in equation (11)). The force constant of the second eigenmode is approximately 40 times larger than the first eigenmode (308 for the third eigenmode), leading to increased penetration (change in surface position) and higher peak forces. These properties of multifrequency AFM have been exploited for subsurface compositional mapping [17], measuring phase contrast at different tip penetrations in trimodal AFM, but have not yet been used as a manipulator for functional material properties.

Also, if the free amplitude is big enough, the term containing the external forces becomes negligible and the equation of motion corresponds to the one of a freely vibrating cantilever. This means that the phase image for the higher eigenmode will have low contrast with a mean value near 90 degrees as the cantilever becomes more insensitive. The increase in phase 2 is shown in Figure 15 and also has been discussed experimentally [95]. Moreover, the phase shift scales as \( \Delta \phi_i = B \frac{Q_i}{k_i} \), where \( B \) depends on the type of interaction forces acting on the cantilever, \( Q_i \) is the quality factor and \( k_i \) is the force constant of eigenmode \( (i=2,3,\ldots) \) [90]. The force constant of higher eigenmodes scales with the square of the resonance frequency ratio \( (k_i = \left( \frac{\omega_i}{\omega_1} \right)^2 k_1) \), while
the quality factor is directly proportional ($Q_i = \left( \frac{\omega_i}{\omega_1} \right) Q_1$) [89]. This means that the phase shift becomes smaller (as the mode number increases), thus becoming insensitive. As a consequence, the phase contrast on the higher eigenmode, when operated in bimodal AFM, serves as evidence for enhanced cantilever penetration into the sample. This enhancement in penetration has been measured experimentally in [95].

3.6.3 Modification of polymer solar cells using bimodal AFM

To demonstrate the use of bimodal AFM as a tool for localized modification of functional materials’ properties, we study structures found in polymer solar cells active layers [96]. The aggregates found at the surface are characterized electrically with C-AFM using forward and reverse bias for electron and hole current maps. The analysis confirms defective charge transport, mainly for holes. The electrical defects are treated with the utilization of bimodal AFM to remove them (schematically shown in Figure 16a). Kelvin probe force microscopy is established as a quantitative technique that is sensitive to the electrostatic force and provides a measurement of the local potential difference between tip and sample material [97]. As shown in Figure 16b and c, the defects produce a potential difference and a phase shift relative to the surroundings. Bimodal AFM was then used as a nanomechanical manipulator in which greater compressive stresses were applied by the stiffer eigenmode (third eigenmode in this case). The enhancement in penetration is used to locally modify the structures. After the bimodal treatment, a recovery of the defective site is observed (Figure 16d and e), resulting in similar contrast to the untreated normal areas, which is also confirmed by the recovery of current for the treated area.
Figure 16. (a) Schematic of experimental setup for bimodal AFM showing the organic solar cell sample. The potential (b) measured with Kelvin probe force microscopy and the phase (c) from non-contact AM-AFM are shown for an untreated area. Corresponding signals (d-e) for the same area after the bimodal AFM treatment showing that the defects have been healed (central square) [96]. Scale bars are 500 nm.

3.7 Experimental rationale

A combination of AFM methods (schematically shown in Figure 17) will be used to characterize the electro-mechanical response of the nanocomposite to high-pressure induced by the tip. Specifically, the free amplitude of the higher eigenmode in bimodal AFM enhances the tip penetration into the sample and the applied force. In addition, having the increased number of observables in bimodal AFM helps keep track of the sensitivity of the cantilever. When the free amplitude of the higher eigenmode increases, the mode becomes more insensitive to the sample and starts to behave as a “free” cantilever; this can be inferred from equation (11). Basically, the phase signal will stay close to 90 degrees. These reasons support the utilization of bimodal AFM
as a tool for applying high-pressure. C-AFM and CRFM are established methods for the measurement of electrical and mechanical properties.

Figure 17. Schematic for consecutive operation of C-AFM, bimodal AFM and CRFM. The current will first be measured with a large scan size using conductive AFM (C-AFM). Then, reducing the scan size and operating the microscope in bimodal AFM, high-pressure is applied. Afterwards, the current is again measured and finally the mechanical properties are characterized by CRFM.

In the experiment, it is not possible to measure the applied force. It is possible to estimate the pressure using numerical simulations (for force estimation) and assuming the tip is spherical with a radius of 5 nm (typical value for commercially available tips). For the numerical results shown in Figure 15, the pressure can be calculated for the extreme values of free amplitude. Using the calculated peak force and the surface area of the spherical cap in contact with the sample, the pressure range varies from to 1.2 to 3.3 GPa. By using C-AFM and CRFM, the electro-mechanical response of the material to such high-pressure can be investigated. Besides all the advantages presented by bimodal AFM, AFM-based methods are the only available characterization techniques that are able to measure multiple responses in a localized (nanoscale resolution)
manner. The systematic interweaving of the AFM methods described above can be expanded to investigate other sample systems under localized high-pressure.

There are several requirements in terms of equipment and cantilevers that would make possible switching smoothly between imaging, application of high-pressure and functionality measurements using the Asylum Research MFP-3D microscope. For example, no physical connections or cantilevers should be changed in between measurements. Additionally, it is important to recognize that changing between schemes leads to lateral drift. To make sure the same area is being studied with subsequent methods, automatic cross-correlation needs to be used. Above all, the limiting factor is the availability of cantilevers with desired properties. There exist only a few commercially available cantilevers that can be used for both contact and bimodal AFM that are electrically conductive. The multi75E-G (Cr/Pt coated) cantilever, sold by Budget Sensors, has a fundamental stiffness around 2.5 N/m, which provides the capability of performing bimodal AFM, CRFM and C-AFM. Cantilevers with low fundamental stiffness benefit from the enhancement in penetration provided by bimodal AFM. It is possible to achieve greater penetration with AM-AFM by utilizing a stiffer cantilever or by exciting a single higher eigenmode instead of the fundamental mode. Stiff cantilevers are not recommended for contact mode methods, such as C-AFM and CRFM, because higher lateral forces results in sample damage.

3.8 Summary

Several basic AFM methods were discussed in detail. Also, the advantages of advanced schemes, such as C-AFM, CRFM and Bimodal AFM, were discussed in terms of the characterization capabilities of the methods. We developed a methodology based on bimodal AFM to map conservative and dissipative interactions between the tip and the sample originating from material properties with high contrast. Also, we demonstrated that the enhanced tip-induced stress
that bimodal AFM produces can modify surface structures, regarded as electrical defects, found on polymer solar cells. Finally, a combination of C-AFM, CRFM and bimodal AFM is discussed with the purpose of investigating the response of a multi-functional nanocomposite to high-pressure. C-AFM and CRFM measures electro-mechanical response of the nanocomposite.
Chapter 4: PEDOT:PSS/Nanoclay Composites: Synthesis, Morphology, Transparency and Electro-mechanical Properties

Electrically conductive polymers are a relatively new (discovered in 1977) class of materials with high intrinsic conductivity that possess the electrical properties of metals while retaining attractive mechanical properties and processing advantages of conventional organic polymers [98]. Poly(3,4-ethylenedioxythiophene): poly (styrenesulfonic acid) (PEDOT:PSS) was synthesized in 1988 [99]. PEDOT is built from ethylenedioxythiophene (EDOT) monomers and it is insoluble in many common solvents. Also, unstable in its neutral state, as it oxidizes rapidly in air [100]. The degree of polymerization of PEDOT is limited and it is assumed that PEDOT is a collection of oligomers with lengths up to 20 repeating units. To improve its processability, a polyelectrolyte solution (PSS) is usually added. The role of PSS is to act as the counter ion (it contains a sulfonate group) to keep the PEDOT chain segments dispersed in the aqueous medium. The morphology and chemical structure of the polymer blend is shown schematically in Figure 18.

Figure 18. (a) Schematic representation of the proposed top view morphology of a thin film PEDOT:PSS, where PEDOT particles are surrounded by a thin PSS-rich layer. PEDOT chains are displayed as short bar. (b) Chemical structure of the species present in the film [100].
A fundamental and still unresolved question is the nature of the charge transport in PEDOT:PSS [101]. It is believed that PEDOT/PSS films consist of conducting PEDOT-rich particles embedded in a quasi-insulating PSS matrix, as shown in Figure 18(a). Charge transport seems to occur via tunneling between these conductive islands. The electrical conduction mechanism is dominated by the conductive domains (PEDOT islands), which are randomly oriented. Large spatial variations in conductivity are expected to occur [102]. For example, upon spin-coating PEDOT:PSS from solution, the micelles are deposited as a film and can have conductivities on the order of $\sim 1$ S/cm [103]. Several methods have been reported to enhance the conductivity of PEDOT:PSS.

In general, increased conductivity is associated to a change in the morphology of the PEDOT:PSS film. Several investigations have shown that solvent processing of PEDOT:PSS significantly increases the conductivity [104–106]. PEDOT has a hydrophobic behavior and positively charged chains. PSS have hydrophilic properties and is negatively charged. Basically, the post-treatments take advantage of the polymers properties to modify their arrangement. When treated with sulfuric acid [106], $\text{H}_2\text{SO}_4$, the model describes a structure rearrangement into crystallized nanofibrils via a charge-separated transition mechanism. Concentrated sulfuric acid produces two ions, $2\text{H}_2\text{SO}_4 \leftrightarrow \text{H}_3\text{SO}_4^+ + \text{HSO}_4^-$, one positive and one negative that will interact with the polymer of opposite charge generating segregation, thus producing a morphology which favors electron conduction. Also, when treating the sample with methanol [105], which is hydrophilic, the mechanism of conductivity enhancement has been related to the interaction of the methanol with the hydrophilic PSS resulting in phase segregation. Charges and hydrophilicity/hydrophobicity have shown to have an effect in the final film morphology and electrical conductivity. Besides solvent treatment, annealing and mechanical treatments have
shown to also induce a change in morphology [103, 107]. The origin of this conductivity increase has been related to changes on interchain interactions due to conformational changes in PEDOT chains and the formation of larger PEDOT particles with increased tunneling between particles, but no consensus among the explanations has been found [108].

The most common method of preparation of PEDOT:PSS films is spin-casting [96, 100, 102, 103, 108–111], but other methods have been used. Solution shearing, which is a mechanical process, has been shown to produce highly conductive and transparent films [107]. In this method, the polymer solution is sheared by means of a blade at different speeds. Spray deposition has also been also used [104], but special equipment is required. The simplest method for PEDOT:PSS processing is drop-casting [98]. Basically, drops of the material’s solution are placed onto the surface of a substrate, and then the solvent is evaporated. The evaporation process is controlled by the solvent and the evaporation conditions. PEDOT:PSS has been investigated for use in a wide variety of applications including thin film transistors, light emitting diodes and memory applications [109]. Specifically, conductive films of high optical transparency are required in a myriad of applications, including electromagnetic shielding, antistatic layers, lighting displays, touch sensors, and as electrodes for photovoltaics [107].

In the case of the nanocomposite under study, PEDOT:PSS is mixed with nanoclay. PEDOT is conductive, hydrophobic and positively charged, PSS is hydrophilic and negatively charged, and the nanoclay is negatively charged as well. It is expected that the addition of the nanoclay will produce a morphology that does not significantly decrease the conductivity compared to bare polymer [5]. The nanoconfinement of the polymer may potentially lead to orientation of conducting domains or modulation of the PEDOT:PSS conduction band, which would be beneficial in generating highly conducting pathways. The resulting morphology of the
film and the distribution of the polymer chains have been directly related to changes in conductivity. The high-pressure study exploits the importance of the morphology to establish relations between strain, conductivity and mechanical property changes.

This chapter focuses on the synthesis and basic characterization of the PEDOT:PSS/nanoclay composites. The goal is to produce a highly transparent coating and characterize the electrical and mechanical properties. Two different types of nanoclay are used to prepare composites and then are compared to the bare polymer. Light spectroscopy helps elucidate the relation between thickness and light transmittance. AFM-based methods are used to measure local distributions of the electro-mechanical properties. Also, the electro-mechanical properties of the materials are compared for thick and thin coatings.

4.1 Nanocomposite Synthesis

The synthesis procedure of the nanocomposite is based on the self-assembly method reported in [25]. This method has proven to be relatively simple and produces highly organized nanocomposites. The first step in the synthesis process is to break apart the nanoclay into single sheets. Nanoclay dispersions containing 0.5 wt. % of Laponite RD (LAP) or Cloisite Na+ (MTM), both from Rockwood Industries, were prepared in deionized water (DI-H2O) and stirred for 24 hours at 1500 RPM to break the agglomerates. The dispersions are decanted for a few days to remove larger particles. It is important to verify the thickness of the dispersed nanoclay. Diluted dispersions are deposited onto cleaned Si substrate (used as reference) and then measured using AM-AFM. The measurements confirm that the resulting thickness of individual nanoclays after exfoliation is 1 nm, which is consistent with literature. The results are summarized in Figure 19 and Figure 20 for Laponite RD and Cloisite Na+, respectively. The figures include topography, cross-section and statistical analysis.
Figure 19. *Laponite RD* morphology. Topography image taken in AM-AFM (a). The cross section (b) shows the typical 1nm thick platelets and statistical analysis (c) shows a larger thickness since as shown in the cross section there are some double layers. The 0.5 wt. % solution was diluted to 1:20 volume and spin coated 30s @ 1000 RPM on a cleaned silicon substrate. The scale bar is 500 nm.

Figure 20. *Cloisite Na+* morphology. Same information as in Figure 19. The 0.5 wt. % solution was diluted to 1:20 volume and 3 μL drop were casted on a cleaned silicon substrate. The scale bar is 500 nm.
Figure 21. Comparison of drying parameters for as prepared samples using C-AFM. Left column shows the topography and current of a MTM sample dried overnight at 25 °C (the scale bar is 1μm). The right column is the same sample after re-drying it for 3 hours at 50 °C (The scale bar is 5μm). These images show the effect of trapped moisture in the nanocomposite.

The polymer Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Sigma Aldrich 768642), high-conductivity grade, in 1.0 wt. % solution in water is used as received. The core/shell nanoplatelets were prepared by slowly adding the nanoclay dispersion to a stirred polymer solution with a 33/67 (clay/polymer) weight ratio and stirred for one hour. The dispersions are degassed in a sonicator. All samples were drop casted in a 3/8 inch circular mask with 80 μL of the dispersion and dried at 25 °C for 12 hours. The dispersions with higher solids concentration
(as prepared) were treated at 50 °C to assure full solvent evaporation. Good control over the drying conditions of the nanocomposite is required to properly characterize the coating with AFM. The effect of trapped solvent is shown in Figure 21. As observed, if the coating is not properly dried the cantilever tip damages the surface, even under very low applied force. Since PSS is hydrophobic, it interacts with the water.

Different versions of the samples are prepared for the different kinds of experiments. Basically, three different substrates are used: silicon wafers (thickness measurements), ITO (electro-mechanical characterization) and glass slides (light spectroscopy). Silicon wafers (Ted Pella, Inc.) were sonicated in a sequence of isopropyl alcohol, ethanol, and DI-H2O; then heated with a butane torch (until bright orange glowing) for 30s for cleaning. Indium tin oxide coated PET (Sigma Aldrich 639281) with surface resistivity of 100 Ω/sq and the glass slides (micro cover glasses, 22 x 30mm x 0.13 - 0.16mm thick, Ted Pella, Inc.) were cleaned similarly (no torch). For convenience, “PPSS” refers to PEDOT:PSS (bare polymer), “LAP” refers to the Laponite-based nanocomposite and “MTM” refers to the Cloisite-based nanocomposite.

The samples produced with this methodology are called “as prepared”. The morphology of the as prepared samples is shown in Figure 22, using AM-AFM with a stiff cantilever. The PEDOT:PSS sample shows a fiber-like structure in the topography channel. The phase contrast in AM-AFM is loosely related to material properties contrast. For the nanocomposites, the phase channel could be associated to the distribution of the nanoclays, since stiffer cantilevers leads to more penetration, and the features resembles the morphology of the nanoclays. For LAP, there is a small domain size (tens of nanometers) and there is an increase in domain size for MTM (hundreds of nanometers) related to the nanoclay size. Also, it is observed that the morphology and surface texture of PEDOT:PSS and the LAP-nanocomposite are similar.
Figure 22. AM-AFM for as prepared samples. High resolution topography and phase channels are shown. The cantilever used was an AC160TS with $f_0 = 285.047$ kHz, $A_0 = 51$ nm, setpoint of 70 % and $k = 29.85$ N/m. The scale bar is 200 nm.

4.2 Characterization of Light Transmission

Most applications of PEDOT:PSS require optical transparency. In thick PEDOT:PSS films, the blue color of PEDOT dominates the transmittance spectra [104]. Thickness reduction is customary to achieve highly transparent films. In order to vary the thickness of the samples, reducing the amount of solids per volume is required. Solids reduction is achieved by diluting the original dispersion with water. Consequently, the amount of core/shell nanoplatelets per casting is reduced and results in thinner films. The core/shell nanoplatelets dispersions were mixed with DI-H2O in 1:2, 1:4, 1:8 and 1:16 dilutions and casted. For convenience, the samples casted from the undiluted dispersion are referred to as “thick” and the samples casted from 1:16 dilution are referred as “thin”. The LAP and MTM nanocomposites are compared to the bare PEDOT:PSS to
evaluate the change in transmittance caused by the addition of nanoclay.

A measurement method to characterize the thickness of the nanocomposite coating is needed, since the transmittance is related to thickness. The simplest method to measure thickness with AFM is the scratch method. Basically, the different dilutions from the materials (PPSS, LAP and MTM) are casted on a silicon wafer or glass substrate, and then the surface is scratched with a sharp knife. The interface, a scan area containing silicon and nanocomposite coating, is imaged using lightly repulsive AM-AFM. The thickness is calculated from the difference between the height histograms of the surface (coating) and the reference (silicon substrate). An example of the measurement is shown in Figure 23.

Figure 23. Example of the thickness measurements using the scratch method. The (a) topography, (b) cross-section and the (c) histogram are shown. The scale bar is 10 μm.

Transmittance spectra are used to investigate the transparency of the nanocomposite. The transmittance is defined as the ratio of intensity of the transmitted beam to that of the incident beam. Specific equipment is required for this measurement. The spectra are recorded using a 2 inch integrating sphere (IS200-4, ThorLabs) with a fiber-based compact spectrometer (CCS200, ThorLabs) spectrometer connected to a SLS201 light source. The transmittance at a wavelength of
550 nm (approximately center of visible light spectrum) is compared for different film thickness. Also, full spectrums for all the samples are compared.

**Figure 24.** Summary of the characterization of light transmission. The transmittance for the different samples is plotted versus the thickness for a wavelength $\lambda = 550$ nm. The thickness is varied by casting diluted dispersions. The colored areas correspond to the different dilution factors, which are specified at the top. Dashed grey line shows the transmittance of the substrate (glass slide).

Figure 24 demonstrates the tunability of the nanocomposites’ transparency by changing the thickness. The samples are casted onto glass substrates and the grey dashed line represents the transmission across the bare substrate. The trend shows that as the thickness decreases more light is transmitted, i.e. the transmittance approaches the value of the bare glass slide. The samples casted from the 1:16 dilution are referred to as the thin and transparent coatings, since that dilution ratio produced the most transparent and thinner sample. It is important to mention that the addition of the nanoclay does not significantly affects the transmittance. To compare the decay in transmittance the curves are fitted to an exponential function using the least square method. The exponential decay constants are: 0.00081 [1/nm] for PPSS, 0.00036 [1/nm] for LAP and 0.0006 [1/nm] for MTM, which means the transmittance decays faster in PEDOT:PSS compared to the
Laponite RD nanocomposite and the Cloisite Na+ nanocomposite is between the two. The addition of the nanoclay help reduce the decay of the transmittance. Also, it is known that Laponite RD-based nanocomposites produce films with higher transparency compared to Cloisite Na+ and that irregularities must be prevented to reduce detrimental light scattering within the film [2]. As has been shown before [45, 63], the addition of nanoclay helps in the formation of ordered phases of the polymer. The addition of nanoclay to the PEDOT:PSS possibly produce a morphology that benefits the transmittance of light at higher thicknesses.

![Optical transmittance spectroscopy](image)

**Figure 25.** Optical transmittance spectroscopy. The full spectrum is shown in these figures for (a) PPSS, (b) LAP and (c) MTM. Samples identify as 1 are thick and 5 are thin. Also, a visual comparison of the thick and thin samples is given. In (d), the top 2 samples are LAP and the bottom 2 samples are MTM.
Visual inspection of Figure 25d shows the transparency of the nanocomposites. The transmission for the thin MTM-nanocomposite is higher compared to the other samples. Since the dispersions of the nanoclays in water were decanted and MTM has a larger platelet size which facilitates precipitation, it is possible that a lower concentration of MTM was obtained for this dilution. Also, the transmittance of the nanocomposite is ruled mostly by the polymer, PEDOT:PSS. The transmittance for the nanocomposites has a magnitude comparable to the bare polymer. Analyzing the full spectrums (Figure 25a-c) for all the samples, the transmission is maximum in the blue end (around 475 nm) of the spectrum and then decreases when moving into the red, which is the typical behavior measured for bare PEDOT:PSS films [104].

**Figure 26.** AM-AFM for thin samples. The parameters used are same as in Figure 22. Similar features are observed. The scale bar is 200 nm.

It is demonstrated that the as prepared, thick samples are not transparent, but the thin
samples are highly transparent. Thick and thin samples are compared throughout. High resolution AM-AFM (Figure 26) with a stiff cantilever showed details on surface texture and material contrast, as previously shown for the thick samples. The phase contrast for the nanocomposites shows area segregation. In general, topography and phase for thick and thin samples look similar. To further investigate the multifunctionality of the nanocomposite, in next sections other properties of the nanocomposites are discussed for thick and thin samples.

4.3 Electrical Properties

The most important feature of PEDOT:PSS is its electrical conductivity. Electrical properties of the nanocomposites are investigated using C-AFM (refer to section 3.4) and compared to the bare polymer. In C-AFM, the applied voltage is defined by the user depending on the material. The mechanisms of current transport through organic media have been under investigation for many years [109]. There are three distinct regions in the current versus voltage curves for organic conductors [109, 112, 113]. Only at low voltages transport follows a linear, ohmic behavior [112]. From moderate to high voltages, non-linear behavior is expected and is controlled by distributed traps within the organic layer. In order to use Ohm’s Law to analyze the data, the measurements should be performed within the linear regime. To confirm linearity, C-AFM is performed and the voltage bias polarity is changed at the middle of the image. The ohmic behavior is better observed in Figure 27b. The conductive spots switch from -5 nA (top of the image, blue spots) to 5 nA (bottom of the image, yellow spots) when the polarity is changed from 100 to -100 mV in the middle of the image, while maintaining a background of zero current (green). Given the linearity, all samples are imaged with 100mV of bias voltage.

All the different samples needed to be compared. For a proper comparison, the electrical conductivity of the samples is calculated using $\sigma = \frac{IL}{VA}$, where $I$ is the total current (sum of all
pixels), $L$ is thickness of the film, $V$ is applied bias voltage and $A$ is the scanned area (image size). Results are summarized in Figure 28. Each point represents the average of 6 experiments and its standard deviation. Since many experiments were performed, a random order was used for either thick or thin samples. In summary, a random sample (either thick or thin) was placed in the microscope and one image was taken, then the sample was changed, repeating the process 18 times (6 per sample). All the areas used for the analysis are shown in Figure 29. The images show the distribution of the conductive sites.

![Figure 27](image1.png)

**Figure 27.** Voltage bias polarity dependence. The bias voltage is switched from 100mV to -100 mV in the middle of the scan. The scale bar is 1 μm.

![Figure 28](image2.png)

**Figure 28.** Electrical conductivity summary including average and one standard deviation, acquired using C-AFM. Each data point represents the average of six 5 μm x 5 μm current images,
including one standard deviation. The thick samples were imaged with 3.6 nN of normal force and the thin ones with 2.6 nN, both using ContE-G Cr/Pt coated cantilever. The current distribution per area are shown below.

Figure 29. Current distribution for the thick and thin samples for data shown in Figure 28, which also includes the imaging parameters. The scale bar is 1 μm.

From Figure 28 it is observed that the conductivity for the thick samples is inside of the range published for PEDOT:PSS [107]. Also, the average conductivity trend for the three samples (PPSS, LAP and MTM) is similar in both cases (thick and thin). Comparing the thick and thin samples, the calculated conductivity varies several orders of magnitude. The calculation of conductivity depends directly on the coating thickness, which goes from ~6 micrometers in the thick samples to ~100 nanometers in the thin samples (Figure 24). Also, there is a slightly smaller static force applied for the thin samples. It is known that the solvent casting parameters affect the morphology of polymers [114] and that the morphology highly influences the conductivity [115]. The thin samples are processed at a lower temperature to produce a homogenously thin and
transparent coating. An enhancement in conductivity is expected for highly oriented materials, which are usually obtained by thermal or mechanical treatments [116]. For thick PEDOT:PSS/nanoclay nanocomposites, thermal treatments showed that it is possible to increase the macroscopically measured conductivity of the nanocomposite to values near the bare PEDOT:PSS [5]. In this case, no thermal treatments were performed. The thin samples showed a decrease in conductivity possibly associated to non-favorable structural conformation. It has been reported that the percolation of current across a PEDOT:PSS film increases as the thickness increases, since is more probable to achieve larger PEDOT agglomerates [60]. When multiple PEDOT grains are stacked the number of interconnections and long-range connectivity increases, thus leading to improved conductivity.

There are several observations from the inspection of Figure 29. For all samples, the current is distributed in small conductive domains. For both thick and thin case, the distribution of the conductive spots is similar between the PPSS and LAP samples. Also, the thin MTM sample shows a segregation of the current into areas; i.e. the conductive spots are not randomly distributed across the whole area. These observations can be linked to the distribution and morphology of the nanoclay. Laponite Rd is small compared to Cloisite Na+. It is more probable for the PEDOT to form a conductive path around a 25 nm nanoclay (LAP) versus a nanoclay 10 times larger than that (MTM).

4.4 Mechanical Properties

After the electrical characterization, it is important to compare the mechanical properties of the samples. The comparison of mechanical properties is performed using CRFM. As described in section 3.5, CRFM measures the contact frequency and the quality factor, which are called mechanical parameters. The contact frequency is directly proportional to the stiffness and quality
factor is inversely proportional to damping. Figure 30 shows a summary of the mechanical parameters for thick and thin samples using the same cantilever and imaged in a random sequence. It is known, from macroscopic tensile testing, that the addition of nanoclays improves the stiffness of polymers [117]. As expected, for both cases (thick and thin) the average measured frequency for the nanocomposites is higher than the one for PPSS, which means that the addition of the nanoclay results in a stiffer coating.

Figure 30. Summary of mechanical parameters for all samples obtained using CRFM: (a) thick and (b) thin. Average frequency and quality factor values are obtained by fitting a Gaussian distribution to a histogram of the images; one standard deviation is also included. Images (5 μm x 5 μm) were taken with one cantilever (ContE-G Cr/Pt coated) using a normal force of 2.4 nN. The free resonant frequency of the cantilever was 15 kHz.

Comparing thick and thin samples, it is observed that the average frequency is lower for the thin samples, but the trends are similar. The reduction of stiffness for the thin samples comes with a reduction in the conductivity (refer to Figure 28), which implies that there is a different morphological arrangement in the thin samples. Since all the thin samples showed a reduction in the electro-mechanical response, the morphological outcome is ruled by the conductive polymeric matrix, PEDOT:PSS. It is known that the electrical conductivity of PEDOT:PSS film decreases as the thickness decreases because of the resulting structure [60]. Despite the extensive use of
PEDOT:PSS, only few mechanical properties’ investigations have been performed [60], which most have dealt with microscale film thicknesses [118, 119]. Films with nanoscale thickness have shown to have lower Young’s modulus, $E$, compared to thicker reported values [60]. The decrease in $E$ obtained for the thin films was associated to the intrinsic structure of the nanofilm, in which a loose packing of PEDOT-rich grains is obtained. In thicker films, the interconnections between neighbor grains is improved by the stacked, ‘‘pancake-like’’ structure, thus improving mechanical properties [120, 121]. They also discussed the role of humidity in the film, since PSS is hydrophilic. The AFM results from C-AFM and the contact frequency of CRFM confirm the change in packing of the thin coatings by measuring an inferior electro-mechanical performance compared to thick films. Most applications of PEDOT:PSS require thicknesses of tens of nanometers, for example polymer solar cells [122].

It is worth noting that in both cases, thick and thin, there was a decrease in the average frequency for MTM compared to LAP. In macroscale tension testing, MTM has shown to have higher stiffness than LAP [2]. CRFM measures the surface and the results are interpreted using one dimensional analysis that neglects in-plane surface elastic forces or three dimensional tip artifacts [73], but has proven to be a valuable technique for semi-quantitative comparisons [10, 82, 84, 85]. It is known that nanoclays with larger size produce a skin layer [2]. The skin layer is a heterogeneous surface layer which forms during the evaporation of the dispersion. Given the size difference of the nanoclays used, this layer has a more appreciable effect in MTM than in LAP. For stiffness, the MTM nanocomposite showed unexpected behavior given its size, i.e. lower stiffness compared to LAP. These incongruences may be attributed to the skin layer formation in MTM. The cantilever tip interacts with the outermost volume of the coating, which is the heterogeneous skin formation instead of an organized structure.
The average quality factor shows a different behavior compared to the average frequency. For the thick samples (Figure 30a), it follows the trend of the frequency for PPSS and LAP, but not for MTM. For the measured area, the quality factor for MTM is lower than the others, translating into more damping. The damping comes either from the confined viscoelastic material (the polymer) trapped between the MTM platelets (they have higher surface area resulting in more interaction with the surrounding polymer) or from the skin layer formation, resulting in more dissipation. In the next section, the relation of stiffness and damping in MTM nanocomposites is discussed. Cloisite Na+ agglomerates near the surface have shown an increase in damping for platelets placed near the surface, while showing higher frequency (Figure 33). The thin samples (Figure 30b) showed very similar quality factors. As previously discussed, the properties of the thin films are a result of the morphology obtained for PEDOT:PSS, when processed as a thin film. In the case of the nanocomposites, the damping mechanisms are dominated by the polymer, hence the quality factor is very similar for all the thin samples.

4.5 Electro-mechanical Relation

Previously electrical and mechanical properties of the nanocomposites have been discussed individually. Consecutive operation of C-AFM and CRFM is used to investigate spatial correlations between the electrical and mechanical response of the nanocomposites. This operation leads to lateral drift (lateral movement in between images). An automatic cross-correlation is performed to eliminate the drift effects. Figure 31 shows the electro-mechanical response of the as-prepared, thick samples. The out-of-plane current shows randomly distributed conductive spots across the measured area for the different samples. The distributions of the mechanical parameters show domains sharing similar properties. These domains are growing from the PPSS sample to the MTM sample, but they are uniformly distributed around the surface.
Figure 31. Typical correlated electro-mechanical properties of the thick samples: PEDOT:PSS (a-d), Laponite RD nanocomposite (e-h) and Cloisite Na+ nanocomposite (i-l). The columns represent topography, current, quality factor and frequency, respectively. Normal force applied to the surface is 3.6 nN (cantilever: ContE-G Cr/Pt coated). The free resonant frequency of the cantilever was 17.3 kHz. Scale bar is 1 μm.
Figure 32. Typical correlated electro-mechanical properties of the thin samples: PEDOT:PSS (a-d), Laponite RD nanocomposite (e-h) and Cloisite Na+ nanocomposite (i-l). The columns represent topography, current, quality factor and frequency, respectively. Normal force applied to the surface is 2.4 nN (cantilever: ContE-G Cr/Pt coated). The free resonant frequency of the cantilever was 14.1 kHz. The red circle shows an example of the relationship of observables for the enclosed area. Scale bar is 1 μm.

In Figure 32, the electro-mechanical response of the thin (transparent) samples is shown. The out-of-plane current shows different behavior in distribution for the three samples, especially for MTM. The LAP nanocomposite shows a reduced population of conductive spots compared to
the thick sample. Besides this, the electro-mechanical response for LAP and PPSS is very similar to the thick sample (Figure 31). The MTM nanocomposite shows segregation of current by areas with similar behavior shown by the mechanical parameters. The red outlined areas show the relation of areas with no current to the mechanical parameters in the MTM sample. In this case, the areas with no current are related to areas with higher quality factor and frequency.

**Figure 33.** Agglomerate of nanoclay found near the surface of a MTM thin sample. It shows a clear relationship in the electro-mechanical response. The scale bar is 500 nm.

The difference in electro-mechanical response of MTM for the thick and thin samples (Figure 31i-l and Figure 32i-l) arises from surface accumulation of nanoclays interrupting the percolation of current across the sample thickness. This can be better observed in Figure 33, where an agglomerate of nanoclay near the surface is measured. The defective area is stiffer but also more dissipative, while no current is measured across the surface. It is obvious that the thin MTM sample has segregation in the current and mechanical parameters, which is not observed for the thick sample where a homogeneous response was obtained. Such big defective areas are not observed in the LAP samples, which could be caused by the difference in size between the nanoclays (Cloisite Na+ platelets are larger). The segregation in MTM and the sparsity of conductive spots in LAP show that there is a difference in the self-assembly process or the morphology obtained for the thin samples. Both the current and mechanical parameters have changed for the thin samples.
The inhomogeneity is more noticeable for MTM because the platelets are larger compared to the tip diameter (tens of nanometers range).

4.6 Cross-Section Analysis

Composite materials based on nanoclay have a distinctive fracture surface morphology. One way of verifying the layered structure of the nanocomposites is to image the cross-section of the film after failure. The samples are broken in bending, while frozen in liquid nitrogen to minimize polymer deformation. Figure 34 shows the cross-sectional analysis with SEM for the LAP and MTM self-assembled nanocomposites. Typical features of fracture surface of a nacre-mimetic composite are observed [2, 48]. The Laponite nanoclay is smaller than the Cloisite (refer to Figure 19 and Figure 20 or reference [2]) resulting in a straighter and cleaner fracture surface. The thick samples serve as a comparison baseline for the thin and transparent coatings, since they burn under the electron beam.

![SEM images of cross-sections](image)

**Figure 34.** SEM characterization of the sample cross sections. The images were taken using a FEI Teneo LV. Samples were casted on a glass slide, then cooled down with liquid nitrogen and snapped in half. Samples were placed at a 45 degrees angle with respect to the electron gun, in order to observe the cross section. Scale bar is 5 μm.
Figure 35. AM-AFM characterization of the LAP cross section. Topography and phase for different scan areas are shown including the surface profile (f) for the smaller image. Schematic of sample failure is shown in (c). Scale bar is 5 μm for (a) and (d) and 200 nm for (b) and (e).

One major disadvantage of SEM is that the information about topography is lost; only 2-D images are produced. AFM provides a tool to investigate the actual morphology of the fracture surface, including variations in topography. The thick LAP sample is mounted in a glass holder (FFM1, Thorlabs) to have the fracture surface parallel to the x-y scan plane. Double sided tape and epoxy are used to avoid sample movement during scanning of the sample. Results are summarized in Figure 35. The 20 μm x 20 μm images for topography and phase (Figure 35a and d) confirm the previously measured thickness of around 5.5 μm. The phase image shows the difference in contrast between the glass substrate, the nanocomposite fracture surface, and the “air”. Then, the nanocomposite is imaged at a smaller length scale near the substrate. In Figure 35b and e, the
topography shows that there are elongated globules in the direction parallel to the substrate. These globules might be related to the “pancake-like” structure reported in [120, 121]. In the phase image, it is observed that these globules are composed of smaller units with different material contrast, possibly the nanoclay surrounded by the polymer. Since the images are taken in AM-AFM, material contrast is not guaranteed but the substructures exist inside the elongated globules resulting in a small phase shift. Given the roughness of the MTM sample, no clear image was obtained.

The samples are broken by holding both ends with tweezers and snapping them, schematically shown in Figure 35c. As the crack propagates into the nanocomposite, the stiff nanoclay will divert the growth direction. It is useful to analyze the height difference obtained from the cross-section of the topography measured with AM-AFM. The cross-sections for both images are shown in Figure 35f. The peak-to-peak distance is approximately 40 nm. Basically, this distance is approximately 2 Laponite plates (25 nm each). The plate size in Cloisite Na+ is about 260 nm with ±200 nm of standard deviation as reported in [2]. Extrapolating to the MTM case, the expected peak-to-peak distance could be up to approximately 1 μm, which relates to the observation in the SEM image. The Laponite RD nanocomposite showed a relatively flat fracture surface, related to nanoclay size, with typical features of nanoclay-based composites. The cross-section analysis confirms the achievement of the layered structure typical of polymer/nanoclay composites. Also, it provides information about the homogeneity of the structure by the information provided in the phase signal of the zoomed image.

### 4.7 Summary

Thick and thin nanocomposites were synthesized by self-assembly of core/shell
nanoplatelets via water evaporation. Several interesting properties of these films are investigated. Given the typical applications of PEDOT:PSS, optical transparency is required. The thin films prepared from Cloisite Na+ and Laponite RD showed high optical transmittance with the response at different wavelengths of light dominated by the polymer. The electro-mechanical characterization of the thin coatings demonstrated that the resulting morphology has lower conductivity and stiffness compared to thick samples, which is in accordance with previous research.

The electro-mechanical response of thin MTM nanocomposite obtained from correlated C-AFM and CRFM shows segregation by regions of the coating’s response. There are big areas with no current that are also stiffer, thus associated to nanoclay near the surface. When the tip hit the nanoclay, the effective tip radius increases to the size of the nanoclay thus reducing the applied pressure. Also, the mechanical response of MTM is not as expected since the mechanical properties measured at the surface show that it is softer than LAP, which is opposite of macroscale measurements. For this reasons the investigation will focus on thin and transparent Laponite RD nanocomposites. Adding Laponite RD to the PEDOT:PSS improves mechanical properties without considerably changing the electrical properties or the distribution of the conducting paths. The addition of nanoclay to the polymer improves applicability of the thin nanocomposite coating by having stiffer coatings with the added multifunctionalities related to the nacre-like structure (i.e. gas barrier, fire retardancy, etc).
Chapter 5: Structure and High-pressure Testing of PEDOT:PSS and Laponite RD Nanocomposites

The general characteristics of the nanocomposites have been presented in the previous chapter. The results from optical and electro-mechanical characterization help focus the investigation into the Laponite RD-based nanocomposite. The stiffness increased when the nanoclay was added to the bare polymer, while electrical conduction and distribution of conductive paths remained comparable. Before the high-pressure study is performed, the resulting internal structure of the nanocomposite needs to be investigated. It is expected from the synthesis procedure to obtain a layered structure, which is confirmed by the analysis of the fracture surface. The remaining unknown is the internal three-dimensional distribution of the filler in the matrix. The structural information facilitates the prediction and interpretation of the nanocomposite’s response to high-pressure. The first part of this chapter is dedicated to the elucidation of the three-dimensional internal distribution of the nanoclay. Specifically, the spatial distribution of nanoclay near the surface, the alignment of the nanoclay and the distance between nanoclays are measured by means of AFM methods. The second part of the chapter examines the effect of high-pressure in the nanocomposite coating.

5.1 Distribution of Nanoclay at the Surface

MTM nanocomposites displayed correlation between mechanical properties and position of the nanoclay near the surface, showed in section 4.5. Based on this finding, similar rationalization is used to investigate the distribution of Laponite RD near the surface. The strategy consists on mapping conservative and dissipative interactions between tip and sample using the bimodal AFM method developed (refer to section 3.6.1) for high contrast imaging. The distribution
of the virial and dissipated power is related to the position of the nanoclay, since it is expected to obtain different mechanical properties measured on top of the nanoclay versus the surrounding.

Bimodal AFM serves as a high sensitivity characterization tool, when properly operated. Bimodal AFM has shown the capability of enhancing material contrast when a proper free amplitude of the higher mode is selected [65, 66]. The material contrast given by the phase channel of the higher eigenmode has been related to changes in mechanical [123], electrical [124] and magnetic [125] properties. In this case, it is expected that the enhanced contrast of energy quantities provides information to infer local changes in mechanical properties of the surface, which correspond to the outermost layer of the nanoclay surrounded by polymer. In the case of the high-pressure treatment with bimodal AFM, the tip will interact with this layer of nanoclay first.

**Figure 36.** Measurement of virial and dissipated power for the second eigenmode of bimodal AFM in the nanocomposite surface for 33/67 ratio of Laponite-RD and PEDOT:PSS. The free amplitude of the first mode is 72 nm with a setpoint of 80% using a AC160TS cantilever with a stiffness of 23.7 N/m. The amplitude of the second eigenmode is increased in order to optimize contrast in the energy quantities (described in [65]) and summarized in (a) by plotting one standard deviation. Images b to d (topography, virial and dissipated power) correspond to the condition highlighted by the yellow area in (a). The scale bar (b) is 100 nm.
The investigation of the surface distribution of the nanoclay starts by obtaining images energy quantities (Figure 36 c-d) with the highest contrast possible (biggest standard deviation). Both channels, virial and dissipated power, show contrast corresponding to the circular nanoclays. The virial shows dark circular regions that can be interpreted as areas with more stored energy corresponding to the nanoclay. The dissipated power image shows dark and circular boundaries. These boundaries originate from the confined polymer around the nanoclays. It is worth mentioning that there are areas with higher concentration of polymer, thus providing with a path for current to flow. Then, the regions bounded or sharing similar contrast are compared in size to the average particle size reported for Laponite RD.

Analyzing the different regions measured in the energy channels with ImageJ, the measured average diameter is 24.1 nm in the virial image (210 particles found, Figure 37a) and 31.9 nm (169 particles found, Figure 37b) for the dissipated power image compared to a 25 nm reference diameter of the Laponite-RD nanoclay. The number of particles in the virial image is
higher. It is known that there might exist other cantilever conditions that result in enhanced contrast for the other channels [65], thus the contrast for one condition is different. In this case, the virial produced information that more closely resembles the geometry of the nanoclay. For a comparison, the energy quantities obtained with the nanocomposite are compared to the case in which nanoclay is purposely added onto the surface. In this case (Figure 38), the dissipated power shows similar features as the previously obtained for the nanocomposites. This confirms that the information obtained in Figure 36 originates from the embedded nanoclay in the polymer and the analysis of the regions in virial contrast are within 3.6% difference from the expected average size for Laponite RD nanoclay.

![Figure 38. Measurement of virial and dissipated power for the second eigenmode of bimodal AFM of Laponite-RD drop-casted on the surface of the nanocomposite. A volume of 10µL of a 1:40 dilution of 0.5 wt% dispersion of Laponite-RD in water was dried on the surface of a prepared nanocomposite coating. The free amplitude of the first mode is 72 nm with a setpoint of 75% using a AC160TS cantilever with a stiffness of 23.7 N/m. The amplitude of the second eigenmode is 1.5 nm. The scale bar is 100 nm.]

5.2 Nanocomposite Internal Structure: Alignment of Nanoclay

Once the distribution of nanoclay at the surface is determined, the analysis shifts towards the internal structure of the nanocomposite. To analyze the three-dimensional distribution of the
nanoclay a convoluted methodology is used. There are several mechanical models that describe the behavior of nanocomposites, especially with nanoclay filler. These models relate the mechanical response of the material to, usually, the concentration of nanoclay included in the system. Models have been developed for specific cases, for example unidirectionally aligned, random orientation, among others. Since the calculation of Young’s modulus with AFM methods is not reliable [73], strain is measured instead. The increased force obtained from bimodal AFM is used to compress the coating and calculate the strain for different nanoclay concentrations. The predicted strain from different mechanical models is compared to the experimental results. The combination of mechanical models that better fit the experiment provides information about the internal alignment of the nanoclay.

![Figure 39. Strain produced by bimodal AFM in the nanocomposite film for different Laponite-RD nanoclay concentrations by weight (red, black and blue markers). Calculated strain using a combination of the modified Pukánszky and Hui-Shia model (P-H-S, grey markers). All the results are fitted to exponential functions, shown in dashed lines (refer to Table 1 for details). For the experiments, the free amplitude of the first mode is 74 nm with a setpoint of 67% using a AC160TS cantilever with a stiffness of 23 N/m. Three different amplitudes (2, 10 and 20 nm) are used for the second mode. The samples were dried at 50 ºC in a 60% RH environment to produce a high quality](image-url)
and transparent coating for all nanoclay concentrations. All the AFM measurements were performed at a relative humidity of 25%.

Strain is calculated from bimodal AFM experiments. First, a reference measurement in repulsive mode AM-AFM is performed using the parameters given for the first eigenmode in Figure 39. Then, the free amplitude of the higher mode is gradually increased. The thickness is calculated by plotting frequency histograms of the height of the substrate and the nanocomposite, fitting a Gaussian distribution and taking the difference between the average of the two distributions. The thickness obtained from AM-AFM (only one eigenmode) is used as the original thickness \( l_0 \) for the strain calculation, \( \varepsilon = (l_0 - l)/l_0 \), where \( l \) is the reduced thickness obtained from an increased amplitude of the second eigenmode. The results in Figure 39 show a significant decrease in deformation as soon as the nanoclay is added to the polymer. The transparent coatings discussed in Chapter 4 contained 33% by weight Laponite-RD. The inset in Figure 39 shows that as the free amplitude of the higher mode increases, the strain approaches 2% for that concentration. It is worth noting that for samples characterized in a drier environment no measurable deformation in the coating was obtained. The behavior of the curves for different free amplitudes of the second eigenmode is best described by an exponential function, which results in R-squared values close to 1. Table 1 shows the parameters of the fit, including the R-squared value, which goes from 0.89 to 0.91.

Assuming that the nanocomposite has a linear-elastic behavior, strain can be estimated using models for composite materials’ Young’s modulus and stress behavior \( (\sigma = E\varepsilon) \). When the yield strength is considered as the limit of the linear response, the modified Pukánszky model [126] describes the stress. This model was optimized for describing the yield strength of polymer/nanoclay composites and is defined as \( \sigma_c = \sigma_m \left( \frac{1 - \phi_f^{0.5}}{1 + 2.5\phi_f^{0.5}} \right) e^{B_1\phi_f^{0.5}} \), where \( c \) is for
composite, m for matrix, f for filler (nanoclay), \( \phi \) is the volume fraction and \( B_1 \) is a parameter that depends on the interfacial interactions between the polymer and nanoclay. The Hui-Shia model [127] describes the Young’s modulus of a polymer matrix filled with unidirectionally aligned nanoclay and has been tailored to represent modulus in the direction perpendicular to the nanoclay surface. Also, this model considers the aspect ratio of the nanoclay, \( \alpha = t/D \) (t – thickness and D – diameter), which are \( t = 1 \) nm and \( D = 25 \) nm for Laponite-RD. Then, several equations comprise this model: 

\[
g = \left( \frac{\alpha}{1-\alpha^2} \right) \left[ -\alpha \sqrt{1 - \alpha} + \cos^{-1} \alpha \right] ,
\]

\[
\xi = \phi_f + \frac{E_m}{E_f - E_m} + 3(1 - \phi_f) \left[ \frac{(1-g)\alpha^2 - g}{\alpha^2 - 1} \right],
\]

and \( E_c = \frac{E_m}{1 - \frac{\phi_f}{\xi}} \), where \( E \) is the Young’s modulus. The volume fraction, \( \phi \), is related to the concentration by weight by 

\[
\phi_f = \frac{w_f/\rho_f}{w_f/\rho_f + (1-w_f)/\rho_m},
\]

where \( w \) is the weight percent and \( \rho \) is the density [128].

**Table 1.** Fitting parameters for an exponential function describing curves in Figure 39.

<table>
<thead>
<tr>
<th>( \varepsilon ) = ( Ae^{Bx} )</th>
<th>2 nm</th>
<th>10 nm</th>
<th>20 nm</th>
<th>P-H-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.94</td>
<td>2.87</td>
<td>4.28</td>
<td>3.46</td>
</tr>
<tr>
<td>B</td>
<td>-0.015</td>
<td>-0.021</td>
<td>-0.026</td>
<td>-0.046</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.89</td>
<td>0.9</td>
<td>0.91</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Combining the previously mentioned relations, the strain is calculated and plotted in Figure 39 (grey circles) using the parameters in Table 2. The trend (grey dashed line) shows an exponential decay \( (R^2 = 0.99, \text{Table 1}) \), which is similar to the experimental results. Also, the magnitude of the calculated strain lies in-between the experimental curves for 2 and 20 nm of free amplitude of the higher eigenmode (i.e. lowest and highest applied force). The models used were
specifically developed for composites of polymer/nanoclay with unidirectional alignment, thus the resemblance with the experimental results implicates that the coating contains ordered nanoclay. Other models have been used as a comparison for the experimental results and are discussed in the following subsection.

**Table 2.** Parameters used for the strain calculation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_m$ (Pa)</td>
<td>1.02E+09 (for 80nm thick film)</td>
</tr>
<tr>
<td>$E_f$ (Pa)</td>
<td>1.78E+11</td>
</tr>
<tr>
<td>$\alpha$ (t/D)</td>
<td>0.04</td>
</tr>
<tr>
<td>$\sigma_y$ (Pa)</td>
<td>4.28E+07 (casted film)</td>
</tr>
<tr>
<td>$\delta_m$ (g-cm$^{-3}$)</td>
<td>1.011 (dried film)</td>
</tr>
<tr>
<td>$\delta_f$ (g-cm$^{-3}$)</td>
<td>2.65</td>
</tr>
<tr>
<td>$a$</td>
<td>1.01</td>
</tr>
<tr>
<td>$k$</td>
<td>-9.52</td>
</tr>
<tr>
<td>$a_1$</td>
<td>0.99</td>
</tr>
<tr>
<td>$k_1$</td>
<td>-1.44</td>
</tr>
<tr>
<td>$B_1$</td>
<td>4.52</td>
</tr>
</tbody>
</table>

f - filler, m-matrix, E- Young’s modulus, $\sigma$- yield strength, $\delta$- density, t- thickness, D- diameter

5.2.1 *Effect of the selected mechanical model in strain prediction*

The modified Pukánszky model for yield strength and Hui-Shia model for Young’s modulus are selected as the best fit for the experimental results. The implication is that the
developed nanocomposites have an unidirectionally aligned nanoclay content. In order to verify this outcome, several combinations of different models are used to calculate the strain and compared it to the experimental results. Specifically, 3 models for yield strength and 3 models for Young’s modulus are used in combination resulting in 9 possibilities, which can be compared with experimental data. The used models [126] for yield strength are:

\[
\sigma_c = \sigma_m (a - k \phi_f) \tag{12}
\]

\[
\sigma_c = \sigma_m (a_1 - k_1 \phi_f^{0.5}) \tag{13}
\]

\[
\sigma_c = \sigma_m \left( \frac{1 - \phi_f^{0.5}}{1 + 2.5\phi_f^{0.5}} \right) e^{B_1 \phi_f^{0.5}} \tag{14}
\]

where \(c\) is for composite, \(m\) for matrix, \(f\) for filler (nanoclay), \(\phi\) is the volume fraction, \(a\) and \(a_1\) are fitting parameters close to 1, \(k\) and \(k_1\) are constants that depend on clay thickness, and \(B_1\) is a parameter that depends on the interfacial interactions. Equation (12) exhibits a linear relation between the yield strength of the nanocomposite and volume fraction, while equation (13) is a power law. From derivation, the \(k\)’s are parameters that only depend on the geometry of the nanoclay. The expressions are derived from Nicolais and Narkis [132], which only considers the decrease of the effective load bearing cross-section [133]. In cases where these equations fitted experimental results properly, \(k\)’s are considered a function of clay thickness, intercalation/exfoliation level and interfacial properties. On the other hand, equation (14), referred to as the modified Pukánszky model [129], combines: (i) a term that indicates the decrease of effective load-bearing cross section due to filler introduction similar to Nicolais and Narkis \(\left( \frac{1 - \phi_f^{0.5}}{1 + 2.5\phi_f^{0.5}} \right)\), (ii) \(B_1\) that is determined by the polymer/nanoclay interfacial properties and (iii) the non-linear relation observed in polymer/nanoclay composites between the yield strength and filler volume fraction. Then, the latter can be considered as the most comprehensive model.
For the Young’s modulus, the three models used are the Voigt [134], Halpin-Tsai [135] and Hui-Shia [127] models, set of equations 15 to 17 respectively.

\[ E_c = \phi_mE_m + \phi_fE_f \]  
\[ E_c = E_m \left( \frac{1 + 2\eta\phi_f}{1 - \eta\phi_f} \right) \; ; \; \eta = \frac{E_f}{E_m} - 1 \frac{E_f}{E_m} + 2 \]  
\[ E_c = \frac{E_m}{1 - \frac{\phi_f}{\xi}} \; ; \; \alpha = \frac{t}{D} = \frac{1}{25} \]  
\[ g = \left[ \frac{\alpha}{(1 - \alpha^2)^{1.5}} \right] \left[ -\alpha\sqrt{1 - \alpha} + \cos^{-1} \alpha \right] \]  
\[ \xi = \phi_f + \frac{E_m}{E_f - E_m} + 3(1 - \phi_f) \left[ \frac{(1 - g)\alpha^2 - g}{\alpha^2 - 1} \right] \]

These models have been widely applied to assess properties of polymer/nanoclay composites. The Voigt model is just a weighted mean of the properties of the individual components. Halpin-Tsai model is a semi-empirical relation that was originally developed for fiber-like inclusions in polymers. Hui-Shia derived equations for predicting the Young’s modulus of composites with aligned reinforcements (emphasis on plate-like reinforcements) and agreement of theoretical predictions with experimental results was found. The strain behavior for all the combinations is shown in Figure 40. From visual inspection, 2 curves (SQRT-Hui-Shia and Pukánszky-Hui-Shia) are similar in terms of shape and magnitude to the experimental results obtained. Experimental results are well fitted by an exponential function, which in the case of the calculation Pukánszky-Hui-Shia showed the most exponential behavior (R^2 = 0.99). From the comparison of several relevant models, it is confirmed that the coating is composed of unidirectionally aligned nanoclay filler.
Figure 40. Strain prediction, using several models, for a PEDOT:PSS and nanoclay composite. Linear corresponds to equation (12). SQRT corresponds to equation (13). The parameters used are shown in Table 2.
5.3 Nanocomposite Internal Structure: Core/Shell Nanoplatelet Geometry

It has been established that the filler is distributed in a unidirectional and aligned manner. The remaining unknown is the distance between the aligned nanoclays. It has been established in the process of synthesizing the nanocomposite that the as prepared dispersion consists of nanoclay platelets surrounded by the polymer. The thickness of the nanoclay is known and is 1 nm. By diluting the dispersion and depositing it onto a Si substrate, individual components, i.e. core/shell nanoplatelets, are measured with AM-AFM. The presence of polymer can be confirmed by increasing the applied force by the cantilever and measuring the compression of the polymer.

![Graph showing the measurement of an individual Laponite-RD nanoclay after polymer has been absorbed into the surface. Two separate experiments were performed in repulsive regime AM-AFM with a free amplitude of 60 and 120 nm, respectively, and a setpoint of 50%.](image)

**Figure 41.** Measurement of an individual Laponite-RD nanoclay after polymer has been absorbed into the surface. Two separate experiments were performed in repulsive regime AM-AFM with a free amplitude of 60 and 120 nm, respectively, and a setpoint of 50%.

In this case, the original dispersion ratio was 33/67 by weight of Laponite-RD and PEDOT:PSS and then it was diluted with deionized water. The as prepared dispersion contains a high concentration of core/shell nanoplatelets per volume. A highly diluted dispersion is drop-casted onto a silicon substrate (as reference) and measured with AM-AFM. The thickness of individual nanoplatelets surrounded by polymer is measured for two free amplitudes and shown in Figure 41. The measurement shows a thickness of approximately 3 nm (red curve in Figure 41) in lightly repulsive mode (free amplitude of 60 nm). Then, the free amplitude was increased to 120
Increasing the free amplitude results in an enhanced penetration of the tip into the sample, thus compressing the polymer-coated nanoclay. The reduction in thickness demonstrates the presence of polymer. The increased tip penetration results in the compression of the polymer, since it is softer compared to the nanoclay. This confirms that the nanoclay is in fact coated. The 1 nm thick nanoclay has a 1 nm coating of polymer in each face. When two nanoplatelets stack up, the interplatelet distance \((d^*)\) is 2 nm. For a similar nanocomposite, Mäkiniemi et al. [5] have reported a \(d^*\) of 2.08 nm obtained from x-ray diffraction analysis, which results in only a 3.9% of difference between the two measurements.

### 5.4 Idealized Geometry

Using the information obtained in previous sections, an idealized geometry for the coating is proposed. The measured thickness for the studied transparent LAP nanocomposite coating is approximately 100 nm (section 4.2). The individual nanoplatelet characterization showed that the basic unit of the nanocomposite has a thickness of 3 nm. It is assumed that the coating is 99 nm
thick (33 repeating units, stacked up) with an interplatelet distance of 2 nm and the bimodal treatment produces a deformation of 2%, as shown in the inset of Figure 39. The idealized structure is shown schematically in Figure 42. As revealed by mapping conservative and dissipative interactions the surface distribution of nanoclay is not perfect and some areas have more abundance of only polymer. Probably, many defects are present in the volume of the coating, but the idealized structure helps predict the effect of high-pressure at the surface and later analyze the results.

5.5 High-pressure Study

Once the internal structure of the nanocomposite is determined, the high-pressure study can be performed. Bimodal AFM is used to apply localized pressure to the nanocomposite. As discussed previously, the force applied by the tip to the surface increases with the use of higher eigenmodes and by increasing the free amplitude. The strategy is to measure the current before and after the treatment and the mechanical properties afterwards. This way the electro-mechanical response to the high-pressure is measured.

The specifics of the experimental approach are shown schematically in Figure 43. Three AFM-based methods, C-AFM, bimodal AFM and CRFM, are operated consecutively. The first step is to measure out-of-plane current with C-AFM before the bimodal AFM treatment as a baseline. Then, three consecutive bimodal AFM images were taken using the free amplitudes ratio of $A_2/A_1 = 0.3$ while zoomed into a smaller area. The microscope was switched back to C-AFM to obtain current and, lastly, CRFM to obtain mechanical parameters for the same area. A thermally stable microscope is required to reduce drift between images and automatic image cross-correlation removes the small lateral drift obtained. In summary, the order for the characterization and modification with high-pressure is: C-AFM, Bimodal AFM, C-AFM and CRFM. The topography from both C-AFM experiments and CRFM is compared to ensure that the cross-
correlation of the images was performed properly. The transparent Laponite RD coating is examined with this methodology and compared to the bare polymer and Cloisite Na+. The cantilever used is a Multi75E-G Cr/Pt coated. This cantilever provides the capability of switching between C-AFM, bimodal AFM and CRFM without replacing the cantilever and more importantly using the same imaging parameters for all samples. All the experimental parameters are kept constant throughout.

**Figure 43.** (a) Schematic illustration of the overall sample structure and the consecutive imaging of C-AFM and CRFM. (b) Illustration of the bimodal AFM setup and detailed nanocomposite description, including the expected sample response from the high-pressure treatment (red sinusoidal line).

The electro-mechanical response of the coating is tested after bimodal AFM is used as high-pressure stimulus for the brick-and-mortar functional nanocomposite. Prior experiments determined the electro-mechanical response of the LAP transparent coating as prepared. The distribution and trends of mechanical properties and conductivity were related to the morphology obtained for thin films, i.e. lower conductivity and stiffness are obtained for thin films. In previous sections, the internal distribution of the nanoclay filler was determined to have unidirectional alignment with a known inter-platelet distance. Taking these into consideration, the expected response to the bimodal AFM treatment is shown schematically in Figure 43(b). The increased
pressure and penetration obtained from bimodal AFM stimuli (red curve) forces the tip to interact with the buried nanoclays. The nanoclays move closer to each other reducing the inter-platelet spacing, \( d^* \). Basically, the local structure of the nanocomposite is modified by the high-pressure.

It is known that in PEDOT:PSS the conductivity depends on the polymer morphology [105, 106]. When the nanoclay moves from the initial configuration as a response to the bimodal AFM treatment, the morphology of the polymer surrounding the platelets gets reorganized locally. It is expected that the response to the bimodal AFM treatment is a change in out-of-plane current, which is characterized by C-AFM. Also, any reorganization of the internal structure will result in a change of mechanical properties, hence the use of CRFM for obtaining mechanical parameters.

Figure 44 shows a summary for the results of LAP, the current before and after bimodal AFM, and the mechanical parameters. The coating shows a local reduction of the out-of-plane current in the middle square (red square in Figure 44 (b)). This reduction in current comes with a change in the mechanical parameters. Specially, the quality factor clearly shows a central square with dimensions close to 1.5 μm x 1.5 μm, which is the image size for the bimodal AFM treatment. This result supports the expected structural change shown in Figure 43(b). The treated area showed less current and a change in mechanical parameters because of the platelets’ reorientation. When the spacing between nanoclay is reduced by the tip-induced pressure, the local electro-mechanical properties are affected. The mechanisms behind the change in current will be investigated in the following chapter. Although there is a reduction in current after the bimodal treatment, it does not completely halt the electron conduction. As investigated in section 5.1, the distribution of the nanoclay at the surface is not homogeneous. There are areas with higher concentration of polymer. Since no nanoclay will affect these areas, the current will remain unaffected after the bimodal treatment.
Figure 44. Electro-mechanical response of the transparent (thin) Laponite RD nanocomposite to the high-pressure treatment. Sequential imaging is used to acquire (a) current before the Bimodal AFM treatment, (b) current after the treatment and finally (c-d) mechanical parameters ((c) quality factor and (d) frequency) then the images are automatically correlated. A Multi75E-G Cr/Pt coated is used. The normal force applied is 12.5 nN, used for C-AFM and CRFM. The Bimodal AFM treatment was performed with the same cantilever with the following parameters: $f_1 = 68.6$ kHz, $A_{free1} = 155$ nm, $k_1 = 4.11$ N/m, setpoint = 50 %, $f_2 = 440$ kHz and $A_{free2} = 45$ nm (estimated using the theoretical optical sensitivity). Through the relationship $k_i = k_1(f_i/f_1)^2$, the higher (second) mode force constant can be approximated as $k_2 = 168.1$ N/m. Three consecutive bimodal AFM images (1.5 μm x 1.5 μm) were taken, approximately 2 minutes each. The bimodal treated area is enclosed by the red square. Scale bar is 1 μm.

In order to verify the reasoning behind the focus on the LAP coating, the MTM and PPSS thin samples are also investigated with the same procedure and under the same conditions as the thin LAP sample. In general, Laponite Rd produced a thin film morphology that resembled the bare polymer in terms of current distribution and have a small size, which is in the same order of magnitude as the tip diameter thus transferring the high-pressure. Figure 45 shows the same set of results for these two samples. The bimodal AFM treatment in PPSS and MTM did not produced any observable change in the electro-mechanical response of the material.
Figure 45. Subsurface modification for PPSS and MTM. Obtained by the same methodology and parameters used for Figure 44. There is no measurable response for the PPSS and MTM. The scale bar is 1 μm.

The local current reduction is a result of the addition of nanoclay; PPSS or MTM sample did not showed any variation in current under the parameters used. The electro-mechanical response to the bimodal AFM treatment is only measured for the LAP sample. Laponite RD has a diameter of 25 nm, which is in the order of the tip diameter and Cloisite Na+ an average of 260 nm [2]. One could assume that it is easier to move smaller things in confined spaces. When the tip interacts with nanoclay near the surface the effective tip radius is related to the size of the nanoclay, thus lowering the pressure for the case of MTM. Besides the platelet size, in MTM the current is segregated into hotspots and the formation of skin layer affects the surface structure. The size, skin formation and segregation are some of the reasons there was no measurable response in the MTM nanocomposite. For the PPSS case, there is no internal structure (nanoclay filler) to react to the
applied pressure, thus modifying the local morphology of the polymer. It is noteworthy to mention that the behavior of the surface of the nanocomposite is purely elastic. The topography (Figure 46) exhibited no surface deformation before and after the bimodal treatment. The bimodal treatment produces a subsurface modification without a measurable topography change at the surface.

![Figure 46. Topographies before and after the bimodal treatment. This images correspond to the topographies obtained from C-AFM. No plastic surface deformation is observed. Also, it shows the correlation of images for drift correction; the same area is shown in both images. The scale bar is 1 μm.](image)

To corroborate the current reduction in the LAP coating, another area is investigated and shown in Figure 47. All the relevant channels are shown, but in this case the raw data for C-AFM and CRFM, and topography for bimodal AFM is included. Again, the electro-mechanical response is visible after the bimodal treatment. The current shows a local reduction corresponding to the area treated with bimodal AFM. Also, the LAP coating showed a local change in the mechanical parameters. Comparing Figure 44 to Figure 47, the mechanical response varied differently for the
two areas shown. Specifically, in Figure 44 the frequency increased and in Figure 47 it decreased, and the opposite happened for the quality factor.

There are two reasons behind the change measured in mechanical parameters. First, the tip-nanoclay interaction defines the packing of the structure, which determines the measured mechanical parameters. Since the behavior of the surface is completely elastic, the tip reorients the buried nanoclay without damaging the organic phase. Depending on the tip-sample interaction the Laponite RD platelets reorient, resulting in different measurable mechanical properties. Second, a different eigenmode is used for the CRFM measurement. The measured contact frequency depends on the eigenmode of the cantilever used for imaging. In one case the first eigenmode is used and in the other case the second eigenmode is used. It is known that the mechanical properties of viscoelastic materials are dependent on the probing frequency [71]. Since the mechanical parameters are measured at different frequencies, the material behaves differently. In viscoelastic materials, high frequency probing leads to measurement of stiffer mechanical properties [73], which is the case in Figure 44 where the second eigenmode is used. Given that similar cantilever and parameters are used for the bimodal AFM treatment of the two areas, the second reason seems more reasonable.
Figure 47. Full raw signals for the high-pressure induced modification experiments in a LAP thin sample. Obtained by the same methodology previously described. The scale bar is 1 μm. These images have not been correlated.
5.6 Effect of Pixel Density

The main observations from the high-pressure study are: (i) the electro-mechanical response shows that only the addition of Laponite RD results in a conductivity decrease after the bimodal treatment and (ii) the topmost portion of the coating does not exhibit any noticeable permanent deformation after the bimodal treatment. The question remains as to how the embedded nanoclay reacts to the bimodal treatment. It is necessary to distinguish between two possibilities: (i) the nanoclays are rotated by the tip, or (ii) the tip squeezes nanoclays closer to each other. To answer this question, the most effective way to investigate this effect is by varying the distance between pixels during the bimodal AFM treatment.

Figure 48. (a) Schematic for the effect of pixel density on the change in conductivity produced by the bimodal treatment based on the interaction between the tip and the nanoclays (the polymer surrounding the nanoclays is not depicted in the schematic). The quantity of points and lines (forming a grid) was increased from 75 (low density) to 512 (high density) thus producing a grid of equally spaced pixels for a 2 µm x 2 µm bimodal image. Current images before (b, d) and after

(a)

Low pixel density:

26.6 nm

High pixel density:

3.9 nm

(b) Before

(c) After

(d) Before

(e) After

0 0 10 [nA]
(c, e) the bimodal treatment for low (b-c) and high (d-e) pixel density, respectively. The scale bar is 500 nm.

The measurements in AFM are performed by acquiring information about the sample at different locations of an x-y grid. When the distance between pixels is larger than the average diameter of the nanoclays, the tip will interact once at most with nanoclay (Figure 48, low density), making it prone to rotation in the cases where the impact is not centered in the middle of the particle. As the pixel density increases, the tip will impact the nanoclay in multiple points, leading to a more uniform compression (Figure 48, high density). Experimentally, the number of equally spaced grid points in a 2 μm x 2 μm image increase from 5,625 to 262,144 for the bimodal treatment. Using C-AFM, the current was measured before and after the bimodal treatment for low and high pixel density. For the experiments, a Multi75E-G Cr/Pt coated cantilever was used. The normal force applied for C-AFM is 4.6 nN. The Bimodal AFM treatment was performed with the same cantilever with the following parameters: f1 = 62.85 kHz, A_free1 = 127 nm, k1 = 3.03 N/m, setpoint = 50%, f2 = 405.9 kHz and A_free2 = 37 nm (estimated using the theoretical optical sensitivity [89]). Through the relationship k_i = k_1(f_i/f_1)^2, the higher (second) mode force constant can be approximated as k_2 = 124 N/m. Three consecutive bimodal AFM images (2 μm x 2 μm) were taken.

The current measured before and after the bimodal treatment is shown in Figure 48(b-e). Comparing the images visually, the low pixel density treatment shows similar features before and after the treatment. In order to properly compare the measurements before and after the treatment, the current in the measured area is added. The results are summarized in Table 3. The sample treated with low pixel density showed a decrease of 2.14% of the current, while the high pixel density bimodal treatment showed a reduction of 13.28%. The increased reduction in current is
directly related to the quantity of pixels, thus the tip squeezes nanoclays closer to each other. This feature is used to establish a theoretical framework to understand the nature of the current reduction. This discussion is developed in the next chapter.

**Table 3.** Values for the addition of the pixels shown in Figure 48(b-e) and the percentage difference percentage before and after the bimodal treatment.

<table>
<thead>
<tr>
<th>Pixel density</th>
<th>Addition of pixels [A]</th>
<th>Percentage Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>low before</td>
<td>6.26E-05</td>
<td>2.14</td>
</tr>
<tr>
<td>low after</td>
<td>6.12E-05</td>
<td></td>
</tr>
<tr>
<td>high before</td>
<td>6.23E-05</td>
<td>13.28</td>
</tr>
<tr>
<td>high after</td>
<td>5.45E-05</td>
<td></td>
</tr>
</tbody>
</table>

5.7 **Summary**

The structure and the response to high-pressure of the nanocomposite was investigated in this chapter. Several AFM methods are interweaved to modify and characterize the response of the material and to define the internal structure. The surface distribution of nanoclay was determined by using bimodal AFM to map conservative and dissipative interactions between the tip and sample. The analysis resulted in the observation of non-homogenous coverage of nanoclay at the surface. Using a combination of experiments and modelling of tip-induced strain, the internal structure is deduced to have unidirectionally aligned nanoclay with an interplatelet distance of 2 nm measured by AM-AFM. Given the structure, the high-pressure treatment is expected to reorganize the subsurface filler, thus modifying the electro-mechanical response of the coating. After the high-pressure treatment with bimodal AFM, a reduction in current and a change in
mechanical parameters is measured for the Laponite RD-based nanocomposite, but no response was measured for the bare polymer or the Cloisite Na+ nanocomposite. Since the Laponite RD platelet diameter is similar to the tip, the high-pressure gets transferred to the internal structure of the nanocomposite. It is noted that the high-pressure probably moves the embedded nanoclay closer to each other.
Chapter 6: Mechanism for the Change in Current

The conductivity of PEDOT:PSS has been shown to vary by several orders of magnitude depending on the processing conditions and the method used to produce thin films. The relation between the conductivity change and theoretical arguments have been studied in pioneering work by Nardes [100]. The anisotropic charge transport of PEDOT:PSS was correlated with the morphology, the shape, and the phase separation between PEDOT and PSS, using several models for conductivity in disordered media. Sir Nevill Francis Mott [136] developed the Mott variable-range hopping (VRH) theory that describes the low temperature behavior of the conductivity in strongly disordered systems. This model is well applicable to conducting polymers, hence Nardes et al. [100] used the VRH theory and its variations to correlate the morphology to the charge transport mechanism in PEDOT:PSS thin films.

As mentioned in Chapter 4, the morphology of spin-casted PEDOT:PSS films is believed to be a phase segregated material consisting of PEDOT-rich grains surrounded by a shell formed by excess PSS. The PEDOT-rich core of the grains has a much higher intrinsic conductivity than the PSS-rich grain boundary [121]. This morphology causes anisotropy in the measured conductivity when comparing the vertical and perpendicular directions relative to the surface. In previous research, to investigate the anisotropy in PEDOT:PSS, spin-casted thin films were designed with different electrode geometries to change the electric field to either parallel or perpendicular to the surface [121]. The conductivity is measured at different temperatures and fitted to the VRH model \( \sigma(T) = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{\alpha}\right] \). The exponent, \( \alpha \), changes from 0.25 to 1 from the parallel to perpendicular direction, which means that 3D-VRH rules the parallel direction and nearest-neighbor hopping rules the perpendicular direction. The mechanism of conduction is different depending on the value of the exponent \( \alpha \).
In the case of the C-AFM analysis of the transparent nanocomposite coating, the electric field is applied perpendicular to the sample by the tip. This means that the implications of nearest-neighbor hopping are of interest for the present investigation. Even though the experiments are performed on bare polymer [111], the results are of interest since we have discussed previously that the polymer rules the properties of the nanocomposite. One implication is that there exists a quasi-continuous 1-2 nm layer of insulative PSS separating PEDOT-rich particles in the perpendicular direction. As a result, there is a decrease in the out-of-plane conductivity up to 3 orders of magnitude lower compared to the in-plane case [111]. The electrons must tunnel across this insulative layer, thus limiting the current that can flow across the film. As discussed in section 4.3, the measured conductivity for thin films resulted in 3 orders of magnitude lower than the thick samples. The PSS layer serves as a barrier for the electrons. As mentioned in Chapter 4, several solvents or thermal treatments have shown to improve the conductivity of the PEDOT:PSS films. Further investigation showed that there is a change in the mechanism of conduction when the thin films are treated with different solvents [108]. It changes from 3D-VRH to almost 1D-VRH. This means that the electrons follow an almost 1D path in-between the electrodes.

The high-pressure investigation of the PEDOT:PSS-nanoclay composite produced a reduction in the out-of-plane current (measured with conductive AFM) and a change in the elastic and dissipative properties (measured with contact resonance force microscopy) of the treated area, which is a 2-dimensional region treated with bimodal AFM. Bimodal AFM leads to greater-than-typical tip indentation into the sample and peak forces. Given the structure of the nanocomposite, the bimodal treatment causes rearrangement of the embedded nanoclay platelets that produces a change in the local electro-mechanical properties. Measurable changes are observed for the Laponite RD nanocomposite, but not for the Cloiseite Na+ nanocomposite, nor the bare polymer
matrix. Consequently, the analysis of the change in out-of-plane current is based on the geometrical change in the internal nanoclay structure caused by the high-pressure, rather than changes in polymer morphology as previously described by fitting VRH-based models to data obtained from PEDOT:PSS thin films exposed to solvents [108].

In the following sections, the usage of a 1-D multibarrier tunneling model is described. The high-pressure treatment translates into a decrease in the distance between barriers. The nanoclay inclusions are treated as barriers for electrons, while the polymer is treated as having zero potential energy. The difference in the number of barriers used and their relative distance is discussed and related to experimental results.

6.1 Quantum Tunneling

![Diagram of quantum tunneling](image)

**Figure 49.** (a) The potential energy of a finite barrier [137] (b) Potential barrier $V(x)$ with $N$ equally spaced rectangular barrier [138].

In quantum tunneling, particles may be found on the opposite side of the potential barrier (Figure 49a) even if its energy, $E$, is lower than the barrier height, $V$. Classically, this is not a possibility. Solving Schrödinger for the three zones shown in Figure 49a using continuity of the amplitude and slope at the boundaries $x=0$ and $x=L$, the transmission probability can be calculated. The tunneling probability decreases exponentially with the thickness of the barrier and with $m^{0.5}$, which means that lighter particles are more effective at tunneling.
6.2 Multibarrier Tunneling

In the case of the nanocomposite, the nanoclay acts as a rectangular potential barrier. The idealized structure, discussed in section 5.4, contains several layers of nanoclay, thus the need for a multibarrier model. Taking a 1-D slice, Figure 49b shows the schematic for a multibarrier model. Esposito [138] derived an expression for the probability of transmission for the N-barrier system using Bloch wave approximation, which is a type of wavefunction that describes a particle in a periodically-repeating environment. The potential is defined as:

\[ V(x) = \begin{cases} V_0, & (i-1)L \leq x \leq (i-1)L + a \\ 0, & \text{otherwise} \end{cases} \]

The propagation of the particle through the barriers is described by the Schrödinger wave function.

\[ \psi(x) = \begin{cases} \psi_{2i}(x), & (i-1)L \leq x \leq (i-1)L + a \\ \psi_{2i+1}(x), & \text{otherwise} \end{cases} \quad (i = 1, 2, \ldots, N), \]

with:

\[ \psi_1(x) = e^{ikx} + Re^{-ikx}, \]

\[ \psi_{2i}(x) = A_{2i}e^{ik[x-(i-1)L]} + B_{2i}e^{-ik[x-(i-1)L]} \quad (i = 1, 2, \ldots, N), \]

\[ \psi_{2i+1}(x) = A_{2i+1}e^{ik[x-(i-1)L]} + B_{2i+1}e^{-ik[x-(i-1)L]} \times (i = 1, 2, \ldots, N-1), \]

\[ \psi_{2N+1}(x) = Te^{ik[x-(N-1)L]} \]

An alternative parametrization for the wave function (which is especially useful for large N) is using terms of the periodic and evanescent Bloch wave functions of the corresponding periodic barrier potential. This approach also allows to obtain closed expressions for the reflection and transmission coefficients for an arbitrary number of barriers. The presented methodology yields
an explicit expression for the calculation of transmission probability through a system containing $N$ number of barriers separated by a specific amount. The equation is

$$P_T(N) = \left[ \frac{4 \chi k}{k^2 + \chi^2} \right]^{2N} \left[ \frac{2 \chi k}{2 \chi k \cos k(L-a) - (k^2 - \chi^2) \sin k(L-a)} \right]^{2(N-1)}$$

where $a$, $N$ and $L$ are geometrical parameters, $k$ is the wave number and $\chi$ is a constant.

**Figure 50.** (a) Schematic of a 5 barrier system with reducing interbarrier distance (b) Transmission probability for the different cases shown in (a). Transmission probability for different number of barriers (c) and the effect of pressure for $N=3$ (d).

Using this equation, the transmission probability is calculated and shown in Figure 50 for three different cases. To include the effect of the high-pressure treatment, the distance between the barriers have been reduced from 2 nm to 1.8 nm to 1.6 nm (black, red and grey curves, respectively) to account for the compression of the material. The original state (black curves) is based on the
distances measured for the ideal structure of the nanocomposite. The 1 nm thick nanoclay serves as the barrier and is separated by 2 nm of highly conductive PEDOT. In Figure 50b the effect of the distance reduction is shown. As the distance between barriers decreases, the transmission probability curves get *stretched* along x-axis. This justifies having a different current before and after the application of high-pressure. Depending on where along the x-axis one is performing the measurement, the transmission probability could increase or decrease. All the experiments are performed under the same conditions, which means the same *window* is observed before and after the treatment. This will be discussed in details in subsequent sections. The position of the peaks in the transmission probability of electrons is the same for any number of barriers with the same spacing. This is shown in Figure 50c. When pressure is applied, the shape of the transmission curve changes. For example, for the case of 3 barriers (Figure 50d) when the inter-barrier distance is reduced the curve is a bit higher than the original structure.

6.2.1 Justification for the 1-D equally-spaced multibarrier model

As discussed previously, the analysis of the out-of-plane conductivity related a reduction of 3 orders of magnitude due to the presence of an isolative 1-2 nm layer of PSS separating the PEDOT-rich layers [111]. The thin nanocomposites showed a similar reduction of 3 orders of magnitude in conductivity compared to thicker samples and were similar to the bare polymer. Since the properties are dominated by the polymer behavior, the PSS probably has an effect as discussed by Nardes et al. [111]. Taking the PSS layer into account, a 1-D multibarrier model might include more rectangular potentials probably in between the ones corresponding to the nanoclay.

The out-of-plane conductivity is dominated by the barriers that exist in this direction. In our case, the barriers are the nanoclay aligned parallel to the substrate or PSS layers. Since the
PEDOT grains have high conductivity compared to the nanoclay or PSS layers, we assumed that there is no potential barrier corresponding to the PEDOT. This correspond to the lines with $V(x)=0$ in Figure 50a.

![Figure 50a and 50b](image)

**Figure 51. Effect of multiple asymmetric barrier on the transmission probability [139].**

The measured distance between nanoclay is 2 nm, which is the original distance between barriers used for Figure 50, and is assumed to correspond to PEDOT ($V(x)=0$). If the PSS layer is 1 nm it could add an extra barrier in-between the ones related to the nanoclay. Research on asymmetric barriers, Figure 51, showed that the resulting transmission probability curve is a superposition of individual curves with equally spaced rectangular barriers. First, the colored curves in Figure 51b resemble the ones calculated in Figure 50. Both approaches result in qualitatively similar transmission probability curves. The problem with the asymmetric barrier method is that there is no explicit solution for the transmission probability. Also, the resulting curve shows multiple peaks very close to each other that will make the analysis more complicated. The equally spaced multibarrier potential serves as a simple method to model the response of the nanocomposite coating to high-pressure. The high-pressure is assumed to compress the barriers, bringing them closer to each other.
6.3 Effect of the Number of Barriers

The bonding arrangement of the carbon atoms in the polymer molecule backbone is the reason for the characteristic electrical properties of PEDOT:PSS [140]. The presence of alternating double bonds and single bonds between carbons in the polymer chain are called conjugated bonds. There are four valence electrons in carbon. In conjugated polymers, one 2s orbital pairs with the two 2p orbitals to form 3 sp² hybrid orbitals, leaving one p orbital unhybridized [140]. Two of these orbitals form covalent bonds with neighboring carbons, the third generally forms a covalent bond with a hydrogen or side group. These are called σ-bonds. The unhybridized pₓ orbital overlaps with the unhybridized pₓ orbital from neighboring carbons, thus forming the so-called π-bond [140]. The electrons in the π-bonds are weakly bound, thus easily delocalized. These delocalized π electrons are the mechanism behind the conduction in these materials [100].

Going back to Figure 50b, the transmission probability curves shift from one another after the barriers move closer to each other. To properly compare the two cases, relevant x-values from the transmission probability curves should be taken. The wave number k is related to the kinetic energy of the electron through \( E = \frac{\hbar k^2}{2m} \). One way of comparing the different curves is to calculate the energy levels for the electrons in PEDOT, then calculate the transmission probability for those energy levels.

The Perimeter Free Electron Orbital Theory (PFEO) is a good tool for description of the energy levels for small conjugated molecules. In this model, the delocalized π electrons are treated as free electrons traveling in a loop around the conjugated molecular perimeter [141]. In the case of PEDOT, the perimeter is 0.774 nm [142]. Basically, the energy levels for the material are simplified to the case of an electron traveling on a ring. The energy levels for the PFEO are given by \( E = \frac{\hbar^2 k^2}{2mL^2} \), where L is the perimeter of the molecule.
Using the multibarrier tunneling model in conjunction with the PFEO, we can calculate the transmission probability for different conditions. Different number of barriers (N) is used to compare the curves. The strain calculated from the experiments (section 5.2) is 2%, which consist of 2 nm in the typical 100 nm thin coatings. For all cases, the 2 nm are equally distributed amongst the inter-barrier distance. The pixel-density analysis supports this interpretation. For example, if 3 barriers are taken into consideration the distance is decreased from 2 nm to 1 nm to account for the effect of the high-pressure in the structure. It is assumed that the nanoclay closer to the surface is moved by the tip. Increasing the number of barriers means that the tip is moving nanoclays deeper into the sample. Even though it is not possible to measure how much the nanoclays are reoriented, the implications from the theoretical model are discussed for the experiments.

![Graph](image)

**Figure 52.** Transmission probability for a multibarrier system combined with the PCEO model. Three different number of barriers are shown (N=3, 7 and 11) for the first 15 wave numbers. “Original” (black curves) refers to the untreated coating, basically the distance between barriers.
is 2 nm. “Pressure” (red curves) refers to the reduced inter-barrier distance corresponding to the high-pressure treatment.

The results for the transmission probability for the nanocomposite coating are summarized in Figure 52. There are two main observations from these results. First, if only the few first layers of the nanocomposites react to the pressure, the transmission probability should increase after the high-pressure treatment is performed (shown in Figure 52 for N=3). For the cases in which N increases, the transmission probability shows a mixed response. Depending on the energy of the electrons, either of the conditions (with or without pressure) will have an increase transmission probability. All the electrons in the material won’t have the exact same value of energy. They are rather distributed over some range of energies. However, the model predicts that there exists another energy condition at which the high-pressure application will increase the measured current. It is important to mention that the case for N=3 is not relevant since the experiment showed a decreased in the measured current, thus the transmission probability was reduced.

**Figure 53.** Electrical response of the transparent (thin) Laponite RD nanocomposite (same material used for the experiments and discussion in Chapter 5) to the high-pressure treatment. Sequential imaging is used to acquire (a) current before the bimodal AFM treatment and (b)
current after the treatment. A Multi75E-G Cr/Pt coated is used. The bimodal treated area is enclosed by the red square. In this case the bias voltage is 500 mV. All the previous characterization with C-AFM was performed at a bias voltage of 100 mV. Scale bar is 1 μm.

The experimental verification of the modeling results is shown in Figure 53. The applied bias voltage is increased to verify if the transmission probability increases after the bimodal AFM treatment. The region treated is bounded by a red square, and shows an increase in current after the high-pressure is applied. The increase in voltage increases the kinetic energy of the electrons. This results confirms that the model with the equally spaced barrier in conjunction with the perimeter free model reproduces the behavior of the material in response to high-pressure even with these simple 1-D approach.

6.4 Effects of Pressure in Conjugated Polymers

The model described in previous sections only considers the change in geometry of the internal structure of the material. We assumed that there are no changes in the 1-D multibarrier model arising from PEDOT. Several investigations have addressed the effect of high-pressure in conjugated polymers [143–148]. Pressure is a tool that enhances the intermolecular interactions in π-conjugated polymers and influence their molecular geometry [147]. Specific studies of conductivity found that for poly(alkyl-thiophene) the conductivity increases by increasing the pressure to 0.6 GPa and for poly(hexyl-thiophene) increases eightfold for 2 GPa [146]. Other investigations have found that the pressure decreases the electric bandgap in semiconducting polymers [143] and modify the optical bandgap in fluorescent polymers. Even though the results are not specifically for PEDOT, pressures in the range 0.6-2 GPa have proven to increase conductivity. In our case, the estimated pressure applied by the tip is in the range 1-3 GPa. The electro-mechanical characterization of bare PEDOT:PSS after the high-pressure treatment
demonstrated no change in the conductivity (refer to section 5.5). The assumption of no changes in the PEDOT configuration holds for the experimental conditions used, although it is known that the π-conjugated structure gets affected by pressure.

6.5 Summary

A simple 1-D multibarrier tunneling model is used to interpret the results from the experiments. By calculating the energy levels of PEDOT using the perimeter free model, the transmission probability is calculated for the original film and the treated film with high-pressure for different number of rectangular barriers. The effect of the high-pressure is considered by reducing the distance between the barriers. The outcomes from the model are that if only the first few layers react to the pressure the expected response is an increase in transmission and when more barriers are included a mixed response is expected, meaning that depending on the energy the transmission probability could either increase or decrease. For the experiments shown in Chapter 5, all the Laponite RD samples showed a decrease in the current. By increasing the voltage at which the C-AFM measurement was performed, the current after the bimodal AFM treatment showed an increase in the current, thus confirming the feasibility of the simple model presented.
Chapter 7: Conclusions

This dissertation features the development of a multifunctional nanocomposite based on PEDOT:PSS and nanoclay, the high-pressure study of the electro-mechanical response of the material and improvements in AFM methods for characterizing certain features of the nanocomposite. AFM provides a tool for characterization and modification of the material’s electro-mechanical properties by interweaving different methods. High-pressure studies help elucidate relations between morphology and electron transport across the nanocomposite thickness adding new potential applications for the PEDOT:PSS/nanoclay nanocomposite for new generation of advanced multifunctional materials.

PEDOT:PSS/nanoclay nanocomposite were synthesized by self-assembly of core/shell nanoplatelets via water evaporation. Optical, electrical and mechanical properties of the films were investigated. To produce transparent coatings, the thickness of the coating was reduced. The thin films prepared from Cloisite Na+ and Laponite RD showed high optical transmittance with the response dominated by the polymer. Thick and thin nanocomposites were prepared for comparison purposes. The electro-mechanical characterization of the thin coatings demonstrated that the thin coatings have lower conductivity and stiffness compared to thick samples. Previous research have attributed this behavior to the resulting morphology in thin PEDOT:PSS films. The thin Cloisite Na+ showed segregation in the electro-mechanical response obtained from correlated C-AFM and CRFM. The segregation produced big areas with no current and stiffer than the surroundings. Also, the effective tip radius increases to the size of the nanoclay thus reducing the applied pressure. Cloisite Na+ is 10 times larger than Laponite RD, which has a diameter of 25 nm. For these reasons, the investigation was focused on the thin and transparent Laponite RD nanocomposites. Besides the previously mentioned functionalities of the “brick-and-mortar” structure, the addition
of Laponite RD to the PEDOT:PSS improves mechanical properties without considerably changing the electrical properties or the distribution of the conducting paths.

Before the high-pressure study is performed, the spatial distribution of the nanoclay in the coating was studied. The surface distribution of nanoclay was determined by mapping conservative and dissipative interactions between the tip and sample. The observation was a non-homogenous coverage of nanoclay at the surface. Strain measurements with bimodal AFM in conjunction with modelling of mechanical properties were used to deduce the internal distribution of nanoclay. The coating showed the strain behavior of a matrix with filler unidirectionally aligned and separated by 2 nm (measured with AM-AFM). Given the structure, the high-pressure treatment reorganizes the subsurface modifying the electro-mechanical response of the coating. After the high-pressure treatment with bimodal AFM, the Laponite RD-based nanocomposite showed a reduction in current and a change in mechanical parameters. No response was measured for the bare polymer or the Cloisite Na+ nanocomposite.

Using a simple 1-D multibarrier model and an estimation of the energy levels for PEDOT, using the perimeter free model, the transmission probability was calculated for the original coating and the treated film with high-pressure. A different number of rectangular barriers was used. There are two important outcomes from the modelling. First, if only three barriers are used, the pressure is expected to increase the transmission of electrons through the coating. Second, when more barriers are included, the transmission could either increase or decrease depending on the energy. An experiment was added, where the bias voltage was increased. After the bimodal AFM treatment, the coating showed an increase in the current, thus confirming the feasibility of the simple model presented.
The electro-mechanical properties of PEDOT:PSS/nanoclay self-assembled nanocomposites are reported with the application as a transparent-conductive coating which reacts to high-pressure. C-AFM and CRFM measurements confirmed the subsurface modification by bimodal AFM with a reduction of local current and changes in the mechanical properties of the area. For the first time, bimodal AFM has been used as a tool to locally modify the subsurface of a functional material. The Laponite RD nanocomposite showed a better response to the stimuli given that its diameter is in the same order of magnitude as the tip. The mechanism for the reduction in electrical current was described by a 1-D model that shows the changes in transmission probability of electrons through the coating when the nanoclays are compressed closer to each other. This observation opens a new spectrum of applications for this type of brick-and-mortar multi-functional material. The experimental approach leverages from the intrinsic advantages of several scanning probe methods (C-AFM, CRFM and bimodal AFM) to modify, characterize and establish structure-functionality relations for advanced functional materials.

Sensing devices based on nanoclay or layered structures have mainly relied on the effect of external stimuli that affect the organic layer. Typically, these assemblies swell in the presence of temperature, pH change or salts. We have demonstrated that an invasive stimulus (pressure) for nacre-inspired functional nanocomposites has an effect in the local structure of the material. Bimodal AFM is a promising tool for inducing localized stress, which can be advantageous for studying other types of materials and the local relationship between structure and functionality. Moreover, the localized response of the conductive and transparent Laponite RD coating opens up new potential applications, as design of “smart” integrated systems for pressure sensing. In conjunction with the many other properties reported, e.g. gas barrier, excellent mechanical
properties and flexibility, the PEDOT:PSS/nanoclay brick-and-mortar structure has demonstrated to be a potential candidate for new generation of advanced multi-functional materials.
Chapter 8: Scientific Contributions

This chapter lists the main contributions of my work and publications.

8.1 Contributions

- Developed a methodology to map dissipative and conservative interactions between the tip and sample with high contrast by rational optimization of the free amplitude in bimodal AFM.

- Demonstrated that bimodal AFM serves as a tool to modify the surface and subsurface of functional materials by
  - the removal of surface agglomerates in polymer solar cells that hinder hole current.
  - the modification of the internal structure of bio-inspired nanocomposites.

- Successfully combined different AFM methods (C-AFM, CRFM and bimodal AFM) for electro-mechanical characterization and modification by high-pressure.

- Developed a conductive and transparent nanocomposite based on PEDOT:PSS and nanoclay that exhibited an ordered structure.

- Studied the effect of high-pressure applied with bimodal AFM to the local electro-mechanical properties.

- Demonstrated that high-pressure reorganizes the embedded nanoclay, thus modifying the transmission of electrons through the conductive nanocomposite.

8.2 Publications


Chapter 9: Outlook

In short term, optimization of the material can be performed as an attempt to maximize the response of the nanocomposite to high-pressure. The high-pressure treatment does not completely halt the electrical current, as demonstrated in section 5.5. By mapping dissipative and conservative interactions at the surface, it was discovered that the nanoclay was not homogeneously distributed at the surface. Two parameters that could be optimized are: (i) increase the concentration of nanoclay in the dispersion and (ii) optimize drying conditions to improve the self-assembly process. One of these might help with the distribution of the nanoclay, thus the tip will always interact with embedded nanoclays for treated areas.

Also, it is known that for conjugated polymers high-pressure treatments modify their intermolecular interactions and influence their molecular geometry, thus changing electrical properties. For the pressure range used in this study, PEDOT:PSS did not show any change of the electrical response. Increasing the pressure might be useful for investigating the bare polymer response to extremely high-pressure. If a change in electrical properties is obtained, it would be interesting to investigate how to couple the response of the bare polymer with the response obtained in the nanocomposites caused by the nanoclay compression. Using bimodal AFM, the pressure can be increased by utilizing higher eigenmodes for the treatment or optimizing the amplitude ratio. The pressure increases by increasing the free amplitude of the higher eigenmode, but in experiments it is possible to obtain cross-talk between the two eigenmodes in bimodal AFM. By optimizing the amplitude ratio, the higher eigenmode could operate with the biggest free amplitude possible without affecting the first eigenmode.

The analysis of the coating with the 1-D multibarrier model indicated that depending on the energy of the electrons the transmission probability could either increase or decrease.
Experimental evidence was obtained by increasing the bias voltage applied in C-AFM. The experiments should be performed at different bias voltages to investigate at which values the current increase or decrease. By sweeping the bias voltage the full response of the material to the high-pressure can be investigated. As shown in section 6.3, there is periodicity in the transition probability of electrons given by the model used. There are three parameters that could be investigated in short term, (i) concentration of nanoclay, (ii) applied pressure and (iii) applied voltage, in order to maximize the response of the material. In addition, thermal or solvent treatments could help increase the conductivity of the nanocomposite, since adding the nanoclay resulted in a decrease of conductivity compared to the bare polymer.

The typical architecture of inverted polymer solar cells consist of a Ag-layer on top of PEDOT:PSS [149]. In application, any crack in the Ag leads to diffusion of moisture and oxygen into the active layer. Since the addition of nanoclay increase the barrier properties of polymers, using the conductive nanocomposite serves as a secondary encapsulation mechanism, thus reducing degradation of the active layer.

The integration of hard particles into a soft matrix has gained interest for the design of advanced functional materials. Recent studies have investigated the relationship between applied stress and rotation of the embedded hard particles [52]. In terms of mechanical properties, particle rotation is accounted as the primary mechanism for increased toughness and energy dissipation [51]. When periodicity of the inclusions is obtained, tunability of the photonic [150] or phononic [151] band gap has been achieved by applying mechanical stress. The PEDOT:PSS nanocomposites reacts to stress in the structure by changing the amount of current that flows across the coating. It shows a modification of the electron tunneling barrier that depends on the stress, and how much the nanoclays move closer to each other. These findings open the possibility for
mechanically-tunable electrical properties in similar materials and the use of AFM as a convenient tool for investigating responses of the materials in-situ.

The synthesized nanocomposite highlights that synergistic properties can be achieved using nacre-mimetic design. With proper tailoring, this approach can be used in the future to design materials with tailored anisotropic conductivities, in addition to sensing capabilities. The most evident application is as pressure sensors. Also, by adding a third material to the coating, other sensing devices could be designed. For example, adding a material that swells in the presence of chemical vapors or humidity causes internal stresses that modifies the position of the nanoclay locally, thus changing the conductivity. Ternary nanocomposites could also be designed to react to magnetic fields. Adding a magnetic nanosheets or nanoparticles, the internal structure of the nacre-inspired nanocomposite can be modified by external magnetic fields. The working principle is the effect of the change in interplatelet distance on the conductivity of the film.
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