

**SELF-ASSEMBLY AND REACTIVE MOLDING TECHNIQUES FOR
CONTROLLING THE INTERFACE AND DISPERSION OF THE
PARTICULATE PHASE IN NANOCOMPOSITES**

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**SELF-ASSEMBLY AND REACTIVE MOLDING TECHNIQUES FOR
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LIST OF ABBREVIATIONS

PNC	Polymer Matrix Nanocomposite
CW	Cellulose Whiskers
MMT	Montmorillonite Clay
FA	Furfuryl Alcohol
PFA	Polyfurfuryl Alcohol
30BMMT	Organomodified MMT Cloisite 30B®
NaMMT	Sodium MMT Cloisite Na ⁺ ®
OOTF	Organized Organic Thin Film
SAM	Self-Assembled Monolayer
SMS	Smart Molecular Solder
MCC	Microcrystalline Cellulose
-CN	Nitrile functional group
-NC	Isonitrile functional group
-SH	Thiol functional group
-COOH	Carboxylic acid functional group
-NCS	Isothiocyanate functional group
PM-IRRAS	Polarization Modulation - Infrared Reflection Absorption Spectroscopy

SUMMARY

Self-assembly and reactive molding techniques have been explored as two complementary approaches aimed at overcoming the agglomeration tendency of nanoparticles so that they can be adequately dispersed in polymer matrix nanocomposites (PNCs). Self-assembly was exploited as means of controlling the interface of metallic substrates by functionalizing the surface with difunctional molecules. Reactive molding was exploited as a means of producing PNCs by using a polymerizable solvent medium to disperse nanoparticles of cellulose whiskers (CW) and montmorillonite clay (MMT).

The motivation driving the self-assembly approach is that by modifying for example metal nanoclusters with difunctional linker molecules, their interaction with a polymer matrix can be increased, resulting in better nanoparticle dispersion. However for this approach to work, the linker molecules must have a strong affinity for the substrate, and they must bond to the substrate through only one terminal functional group, with the other terminal group pointing away from the substrate. Therefore, in the first part of this thesis, competitive self-assembly between difunctional molecules bearing thiol, isocyanide, carboxylic acid, nitrile and isothiocyanide functions was studied on Cu, Ni, and Pt substrates. The organized organic thin films (OOTFs) produced in this manner were characterized by x-ray photoelectron spectroscopy (XPS) to determine which functional group exhibits the highest affinity for each substrate. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) was used to determine which linker molecules exhibit the desired vertical-bonded configuration. It was found that the isocyanide and thiol functions have the strongest affinity for copper, followed by

carboxylic acid. However, dithiols adsorb in a flat configuration on the substrate, while 1,4- phenylene diisocyanide (PDI) and 1,4- terephthalic acid (TPA) both adopt the vertical-bonded configuration. Taken together, of the difunctional molecules studies in this work, PDI and TPA are the most suitable linker molecules for functionalization of copper. Similarly, PDI preferentially adsorbs over TPA on Ni, and self-assembles with one terminal group pointing away from the surface. The functionalization of Cu and Ni nanoclusters (proposed for future work) should therefore focus on the use of PDI or its oligomeric analogs. On Pt, it was also observed that PDI preferentially adsorbs over TPA, however none of the difunctional molecules studies in this work self-assembled in the vertical-bonded configuration, but only in flat, surface-parallel configuration. Self-assembly of difunctional molecules does not appear to be effective for controlling the interface of Pt substrate.

The motivation driving the reactive molding approach is that nanoparticles refined from biomass or minerals typically already have an array of functional groups (often hydroxyl groups) present at the nanoparticle surface. The natural surface functionality of these types of nanoparticles can be exploited to disperse them in a polymerizable solvent medium, followed by in-situ polymerization, thus preserving their dispersion in a PNC. Therefore, in the second part of this thesis, furfuryl alcohol (FA) was used to disperse nanoparticles of cellulose whiskers (CW) and montmorillonite nanoclays (MMT). It was found that in the temperature range 50°C – 150°C, acid sites which are present at the surface of both CW and MMT nanoparticles trigger the in-situ polymerization of FA to polyfurfuryl alcohol (PFA). X-ray diffraction (XRD) of the MMT-PFA nanocomposites confirmed that in-situ polymerization leads to complete exfoliation of the MMT into individual platelets. This shows that reactive molding of FA with CW or MMT offers an attractive processing route for producing PFA matrix PNCs. For both CW-PFA and

MMT-PFA nanocomposites, the fine dispersion of nanoparticles in the matrix is evidenced by significant increases in thermal stability compared to pure polymer. At a nanoparticle loading of only 0.75 phr, CW - PFA nanocomposites show an increase in the temperature at onset of degradation of nearly 80°C compared to pure polymer. This is attributed to effective immobilization of PFA at the CW surface, and promises increased mechanical properties (proposed for future work). MMT-PFA nanocomposites show an increase in the temperature at onset of degradation by 49°C – 56°C, at a clay loading of 10 phr. At 800°C, the residual mass of PFA filled with organomodified MMT is 7 - 12% higher compared to PFA without MMT. The increased thermal resistance of the MMT-PFA nanocomposites compared to CW-PFA nanocomposites can be attributed to the retarded out-diffusion of decomposition products thanks to the ‘labyrinth’ morphology of exfoliated MMT in the matrix. Since FA is produced in commercial quantities from agricultural residues, the PNCs thus produced represent advanced materials which can be constituted completely from natural materials outside the petrochemical supply chain.

Finally, an important difference between oxidative and non-oxidative degradation of MMT - PFA nanocomposites was discovered. Under oxidative degradation, sodium MMT appears to accelerate the decomposition of the PFA matrix above 450°C, while in contrast the behavior of PFA filled with organomodified MMT is similar to that under non-oxidative degradation. Tentatively, it is proposed that acidic sites of sodium MMT are responsible for the accelerated degradation under oxidative conditions. In organomodified MMT, these sites are blocked by residues of the organic modifier. This result highlights the importance of studying degradation of MMT modified PNCs both under oxidative and non-oxidative conditions.

CHAPTER 1

INTRODUCTION

Composites are an important class of materials defined as having a matrix, which can be a metal, a ceramic or a polymer that has been modified with a particulate phase of fibers, whiskers, flakes, or conductive filler like carbon black. Composites are designed to take advantage of the most desirable characteristics of each constituent material while negating their negative properties. For example, polymer matrix composites offer a higher strength-to-weight ratio compared to pure polymer.^[1] Polymer matrix nanocomposites (PNCs) are an attractive new class of polymer matrix composites under intense development. A PNC consists of a polymer matrix, in which nanoparticles defined as having at least one characteristic dimension, i.e. length, width or thickness in the range of 1- 100 nm have been dispersed. Ideally, the nanoparticle phase is evenly dispersed in the matrix. A few examples of nanoparticles used in PNCs are metal nanoclusters, carbon nanotubes, nanoclays, and nanofibers of cellulose, often called “whiskers”.^[2, 3] Depending on the type of nanoparticles used, the physical properties of the resulting PNC may be superior to those achieved in corresponding conventional polymer composites or pure polymer. Remarkable increases in tensile modulus and strength, glass transition temperature, flame retardancy and barrier properties (permeability) have been observed in PNCs with nanoparticle loadings of less than 5.0% wt.^[4, 5] In some cases the small size of the nanoparticles also affords improved optical properties, e.g. transparency, or antibacterial properties.^[6, 7] This makes PNCs attractive for a wide range of applications including automotive parts, barrier films for food packaging, and materials where transparency or flame retardancy is required.^[8] In many cases, the enhanced properties of PNCs can be attributed to the high surface area of the nanoparticle phase. For example, nanoparticles of cellulose (cellulose “whiskers”), have a

surface area in the range of 150 - 170 m²/g, while nanoclays (layered silicates) may have surface areas as high as 750 m²/g.^[2, 9-11] When well dispersed in the composite matrix, the high surface area of the nanoparticle phase leads to high interfacial area between matrix and filler, and this in turn leads to the immobilization of the matrix polymer at the nanoparticle surface.^[12] This largely explains the increase in thermo-mechanical properties compared to unfilled polymer.^[13] Unfortunately, the high surface area of the nanoparticles also poses a significant processing challenge during PNC fabrication. High particle surface area translates to high surface energy and low thermodynamic stability, and therefore there is a strong tendency for the nanoparticles to agglomerate so the surface energy of that phase can be reduced. This, in conjunction with the high viscosity of the matrix polymer makes it difficult to produce stable, uniform dispersions of the nanoparticles throughout the matrix.^[12] A uniform dispersion of the particulate phase is especially important for those PNCs in which the formation of a percolating network of nanoparticles is necessary for achieving desired mechanical, electrical or thermal properties.^[5] Inhomogeneities in particle size and particle dispersion reduce the mechanical properties of the composite and negate the unique advantages of PNCs. A second challenge is that the small size of the nanoparticles makes the characterization of these particles and their dispersion in the matrix, much more difficult compared to conventional fillers. Hence, the high surface area of the nanoparticle phase can be regarded as the most desirable structural feature in PNCs, but at the same time also the least desirable processing parameter.

This thesis explores two different types of techniques aimed at overcoming the agglomeration tendency of nanoparticles so that they can be adequately dispersed in polymer matrix nanocomposites (PNCs). In the first part of this thesis, discussed mainly in chapters four and five, the self assembly of difunctional linker molecules is explored as a means of functionalizing the surface of copper, nickel and platinum. Controlling the interface functionality of metallic substrates in this manner has broad potential to increase

dispersion in PNCs where the use of metal nanoparticles is desired, for example to impart electrical conductivity.^[14] The second part of this thesis, discussed mainly with in chapters six and seven, explores the use of furfuryl alcohol both as the initial medium for dispersing nanoparticles of cellulose whiskers (CW) or montmorillonite nanoclays (MMT) and as the monomer precursor for the in-situ polymerization of the PNC matrix. Reactive molding in this manner has broad potential to increase dispersion in PNCs when using nanoparticles refined from biomass or minerals, e.g. wood and clay, which in contrast to synthetic metal nanoclusters, already possess an abundance of surface functional groups.

The premise underlying the self-assembly approach is simple: by selectively functionalizing the surface of a metal substrate, its interaction with a polymer can be increased, provided that the polymer in turn contains suitable sites for interaction with the surface. Applying this technique to metal nanoclusters should therefore afford better particle-matrix interaction, counteracting nanoparticle agglomeration and improving the dispersion of nanoparticles in a PNC matrix. Increasing the strength of the particle-matrix interaction would also lead to better shear transfer from the matrix to the nanoparticle, which is essential for high mechanical strength in composites.^[15] This kind of surface functionalization involves the self-assembly of α,ω -difunctional “linker” molecules, e.g. dithiols and diisocyanides, into “chemically sticky” organized organic thin films (OOTFs).^[16] An α,ω -difunctional linker molecule is a monomer (or oligomer) which presents a reactive chemical group (or “functional” group) at each end of the molecule. To form a chemically sticky OOTF, as shown schematically in Figure 1, the linker molecules must self-assemble in a “standing up phase”, where each molecule adsorbs in a vertical, or near-vertical configuration, bonding to the substrate through one terminal

group, with the other terminal group pointing away from the surface, providing free sites for bonding to another molecule or top substrate.^[17-19] Hence, each terminal group acts like a nanosized alligator clip for chemically bonding specific substrates to each other.^[20]

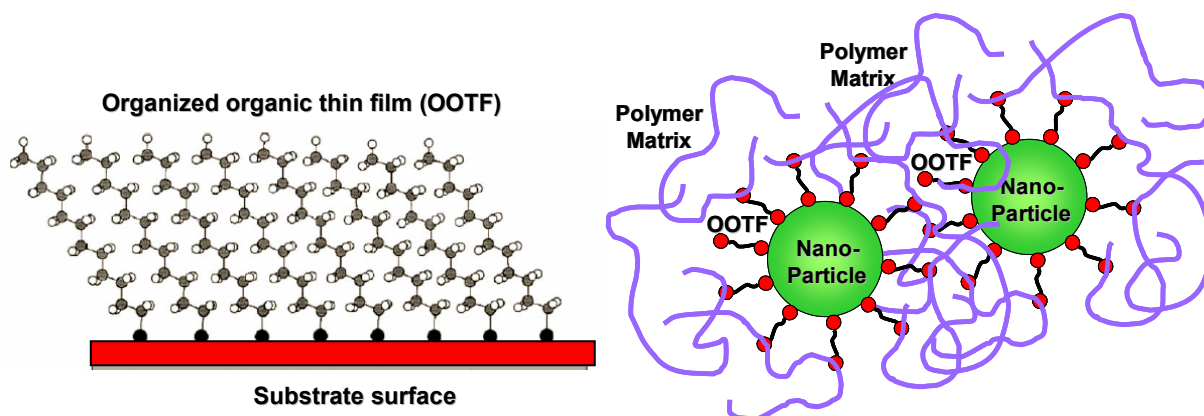


Figure 1. Schematic representation of chemically sticky OOTFs on (a) a flat substrate and (b) as a coupling agent in a conductive PNC.

Linker molecules with a range of different functional groups, e.g. thiol, hydroxyl, carboxyl, isocyanide, and nitrile, have been used to prepare OOTFs on a variety of metal and semiconductor substrates.^[16, 21-27] Much of the work to date has been with different thiol-terminated molecules on Au.^[24] This is because the thiol function has a strong affinity for Au, but also because Au is highly stable to oxidation, lending it to experimentation under “ideal” conditions. Because of the historical emphasis on the thiol-Au system, a great deal of experimental work still remains to characterize self-assembly of difunctional linker molecules on substrates other than Au. Little is known about the relative affinity of different functional groups for Cu, Ni and Pt, and even less is known about the ability of different linker molecules to undergo self-assembly on these substrates, or the resulting adsorption geometry. Therefore, in the first part of this thesis work, a range of difunctional molecules were systematically allowed to undergo

competitive self-assembly on substrates of Cu, Ni and Pt. Afterwards, the substrates were characterized by a combination of XPS (X-ray photoelectron spectroscopy) and PM-IRRAS (polarization modulation infrared reflection absorption spectroscopy) to determine which functional groups preferentially adsorbed at the surface, and which linker molecules formed sticky OOTFs on each substrate. As a result, the functional group which exhibits the highest affinity for each substrate was identified, while simultaneously establishing which linker molecules are able to form sticky OOTFs on Cu, Ni and Pt. Conversely, linker molecules or processing conditions which lead to weak physisorption, flat surface adsorption, or “hairpin” bonding in which both terminal groups of a linker molecule with a flexible “backbone” chain bond to the same substrate, were identified and rejected as unsuitable for surface functionalization.^[24, 28]

The premise underlying the reactive molding approach is that nanoparticles refined from wood and clay naturally contain an abundance of surface functional groups. For example, the surfaces of nanoparticles of CW and MMT are richly hydroxylated.^[29, 30] The natural surface functionality of these types of nanoparticles can be exploited to produce a stable dispersion of the nanoparticles in a polymerizable solvent medium, followed by in-situ polymerization, thus preserving their uniform dispersion in the PNC after matrix consolidation. A significant advantage of this approach is that it avoids the use of surfactants. This is important because while the introduction of a surfactant may help to initially stabilize the nanoparticles against agglomeration, surfactant molecules may weaken the interface between particulate phase and PNC matrix, and hence lower composite strength in the consolidated PNC. Another major benefit of the reactive molding approach is that it avoids the use of inert solvents, since the matrix precursor itself provides a suitable medium for the dispersion of the nanoparticles. This is important because by eliminating the need for solvent removal, closed molding processed can be

used, and the molding process made more economical and environmentally sound. For this approach to work, monomers must be identified which offer the right combination of i) low viscosity, ii) strong chemical affinity for functional groups at the nanoparticle surface and iii) reactivity toward in-situ polymerization. A fourth criterion of increasing importance is the preference for bio-based monomer – nanoparticle systems which can be sourced completely from natural materials outside the petrochemical supply chain.^[31]

Therefore, the second part of this thesis work explores the use of furfuryl alcohol (FA) as a polymerizable solvent for nanoparticles of CW and MMT. FA, the hydrophilic monomer precursor of polyfurfuryl alcohol (PFA), is bio-based and available on an industrial scale.^[32] CW nanoparticles were produced by acid hydrolysis of microcrystalline cellulose (MCC) and the whisker morphology was characterized by AFM. PNCs were then successfully produced by reactive molding of the CW – FA and MMT-FA systems. A combination of DSC and IR was employed to characterize the reaction chemistry of the MMT – FA and CW – FA systems, as well as their curing behavior. The thermal stability of cured CW – PFA and MMT – PFA nanocomposites was characterized by DSC and TGA. The reactive molding of montmorillonite clay (MMT) nanocomposites was achieved by the in-situ intercalative polymerization of FA inside the interlayer galleries of the MMT. The process of intercalation and exfoliation was studied using XRD. Finally, the oxidative and non-oxidation degradation behavior of CW – PFA and MMT – PFA nanocomposites was compared using TGA.

CHAPTER 2

BACKGROUND

2.1 Polymer matrix nanocomposites

Composites are an important class of materials defined as having a matrix, which can be a metal, a ceramic or a polymeric material, that has been modified with a particulate phase of fibers, whiskers, flakes or a filler such as talc, wood flour or carbon black.^[33] Composites are designed to take advantage of the most desirable characteristics of each constituent material while negating their negative properties. For example, fiber glass reinforced plastics offer higher strength-to-weight ratio compared to pure polymer, by combining the relatively low density of the polymer matrix with the relatively high modulus and thermal stability of the glass fiber reinforcement. Conductive plastics can be produced by embedding a conductive filler material such as carbon black or particles of a conductive polymer in an otherwise insulating polymer matrix.^[34] In some cases, the main purpose of the filler is to simply increase bulk at low cost.

With the advent of polymer matrix nanocomposites (PNCs), further increases in composite properties have been made possible. PNCs represent a new class of polymer matrix composites, which consist of a conventional polymer matrix in which nanoparticles have been dispersed to provide the desired increase in performance. Nanoparticles are defined as particles having at least one characteristic dimension, i.e. length, width or thickness in the range of 1- 100 nm.^[3, 10] A few examples of nanoparticles used in PNCs are metal nanoclusters, carbon nanotubes, nanoclays, e.g. montmorillonite, and nanofibers of cellulose, often called “whiskers”.^[7, 35-37] The physical properties of PNCs are often found to be much superior to those achieved in pure polymer or in the corresponding conventional polymer composites at equal filler concentration. For example, PNCs reinforced with various nanoclays, nanotubes or

nanofibers show remarkable increases in tensile modulus and strength (strength-to-weight ratio), heat deflection temperature, onset of degradation, glass transition temperature, flame retardancy and barrier properties (permeability).^[38] In some PNCs, the small size of the nanoparticles affords increased transparency or antibacterial properties. These enhanced features of PNCs are in addition to the corrosion resistance, noise dampening, and parts consolidation advantages offered by polymer matrix composites in general. This makes PNCs very attractive for a wide range of general applications, such as car parts, sporting goods, and films for packaging. PNCs filled with conductive nanoparticles target a number of specialty applications, including anti-static coatings and packaging, EM-shielding, and self-regulating heaters.^[39, 40]

In some PNCs, the nanoparticles are characterized by a high aspect (length-to-diameter) ratio. For example, the aspect ratio of cellulose whiskers (CW) is in the range of 50 – 100.^[2, 5] Such nanoparticles are able to form of a percolating network of rigid particles above the percolation threshold concentration, which can be achieved at 1 wt% of filler.^[5] Large increases in thermo-mechanical or conductive properties observed in PNCs filled with high aspect ratio nanoparticles have been attributed to this percolation mechanism. In all PNCs, the nanoparticles are characterized by higher specific surface area as compared to conventional fillers. Nanoparticles of cellulose (cellulose “whiskers”), have a surface area in the range of 150 - 170 m²/g, while nanoclays (layered silicates) may have surface areas as high as 750 m²/g when exfoliated into individual platelets.^[9, 10, 41, 42] This affords increased interaction with the polymer matrix, while also minimizing the weight fraction of filler which typically has a higher density than the matrix polymer. When well dispersed in the composite matrix, the high surface area of the nanoparticle phase leads to high interfacial area between matrix and filler, and this in turn leads to the immobilization of the matrix polymer at the nanoparticle surface. The enhancement in thermo-mechanical properties observed in PNCs is generally attributed to this phenomenon. In this case, the thermo-mechanical performance of a PNC is governed

by the strength and the nature of the interaction between matrix and the surface of the particulate phase. As with conventional polymer matrix composites, efficient shear transfer from the matrix to the particulate phase depends on strong chemical and/or physical adhesion between the polymer matrix and the particulate surface. At the particulate surface, a layer of immobilized polymer is produced as a function of the work of adhesion.^[1, 13] The thickness of this layer in turn influences the thickness of the interphase region. The interphase is defined as the region that develops between the particle surface and those regions of the polymer matrix exhibiting bulk properties. The morphology of the interphase in PNCs depends on the flexibility of the matrix polymer chain and on the functional groups along the chain backbone. The interphase may occupy a high volume fraction of the PNC and dominate the thermo-mechanical properties of a PNC; for a well dispersed particulate phase, the average inter-particle distance may approach the radius of gyration of a single polymer chain.^[12] While the intricate interplay between interface and interphase is still not well understood and will likely be the topic of intense research for years to come, it is clear that the high surface area of the nanoparticles in a PNC highly accentuates the need to control the interface of the particulate phase in PNCs. This in turn calls for processing techniques capable of tailoring the surface chemistry and the physical structure at the interface between the particulate phase and the polymer matrix.

The high surface area of the nanoparticles poses a significant processing challenge during PNC fabrication. High particle surface area translates to high surface energy and low thermodynamic stability, and therefore there is a strong tendency for the nanoparticles to agglomerate so the surface energy of that phase can be reduced.^[12] This, in conjunction with the high viscosity of the matrix polymer makes it difficult to produce a uniform dispersion of the nanoparticles in the polymer phase, and to maintain this dispersion during consolidation of the PNC matrix. Inadequate particle dispersion has the potential to reduce the high mechanical properties of the composite thereby negating

one of the most sought-after advantages of PNCs. A uniform dispersion of the particulate phase is especially important for those PNCs in which the formation of a percolating network of nanoparticles is necessary for achieving desired mechanical, electrical or thermal properties.^[2] An additional challenge presented by PNCs at the processing stage is that the small size of the nanoparticles makes the characterization of these particles, and their dispersion in the matrix, much more difficult compared to conventional fillers.

The need to neutralize the agglomeration tendency of nanoparticles in order to better solubilize, disperse and stabilize the particulate phase in the polymer matrix during PNC fabrication can be addressed in several different ways. For example, the surface chemistry of the nanoparticle can be modified to aid dispersion. This can be achieved by adding surfactants to break up aggregates of nanoparticles.^[43] This approach has a major drawback: while the use of surfactants may help to initially stabilize the nanoparticles against agglomeration, the surfactant molecules may weaken the interface between particulate phase and PNC matrix, and hence lower composite strength in the consolidated PNC. An alternate surface chemistry approach involves grafting polymers onto the particle surface filler to increase compatibility with a matrix. A different approach that has been used to achieve the desired dispersion in cellulose whisker PNCs is the suspensions mixing technique.^[44, 45] This technique is based on diluting the whiskers in an aqueous suspension, which is then combined with a polymer suspension, followed by film casting. An intimate nanoparticle – polymer mixture can be achieved in this manner, which is preserved as the water is evaporated during matrix consolidation. A major drawback with this approach is that it is only suitable for forming films, and moreover, this technique requires solvent (water) removal, which may leave defects (voids) in the final composite. A third approach, which has been used to produce polymer layered silicate clay PNC is the in-situ intercalative polymerization technique.^[4, 38] This approach uses the in-situ polymerization of a monomer or oligomer inside the interlayer galleries of a 2:1 layered silicate to achieve exfoliation of the clay aggregates.

One of the attractive features of this approach is that it does not require the use of any surfactants or inert solvents that have to be evaporated during the matrix consolidation process. Rather the matrix precursor itself provides a suitable medium for the dispersion of the clay nanoparticles. The suspensions mixing and in-situ intercalative polymerization techniques are discussed in more detail in the following sections, in the context of cellulose whisker and layered silicate nanocomposites, respectively.

2.1.1 Cellulose whisker nanocomposites

Polymer nanocomposites can be made using cellulose in the form of cellulose nanocrystals or cellulose whiskers. Pure cellulose is a biopolymer, specifically the polysaccharide of D-anhydroglucose units connected through β -1,4-glycosidic ether bond.^[46] See Figure 2.

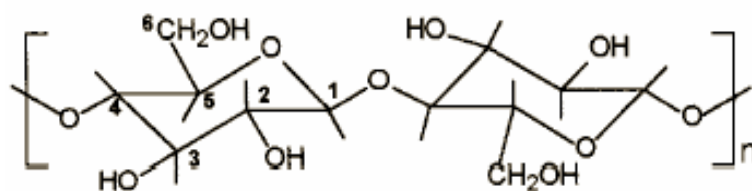


Figure 2. Molecular structure of cellulose.

Wood is by far the main source of cellulose, though it also occurs in plant fibers and in the shells of tunicates (a sea animal), and is also produced by certain bacteria. Wood fibers exhibit a complex, hierarchical composite structure, consisting of a matrix of amorphous lignin and hemicellulose, reinforced with semicrystalline fibers of cellulose, as shown in Figure 3.^[30, 47] In the pulping process, most of the lignin and hemicellulose content is dissolved and removed, to allow extraction of the cellulose fibers from the wood fibers. Cellulose fibers extracted from wood by means of traditional pulping processes are suitable for papermaking, but they exhibit relatively poor mechanical

properties compared to man-made fibers, due to a high concentration of defects, and variability depending on the fiber source.

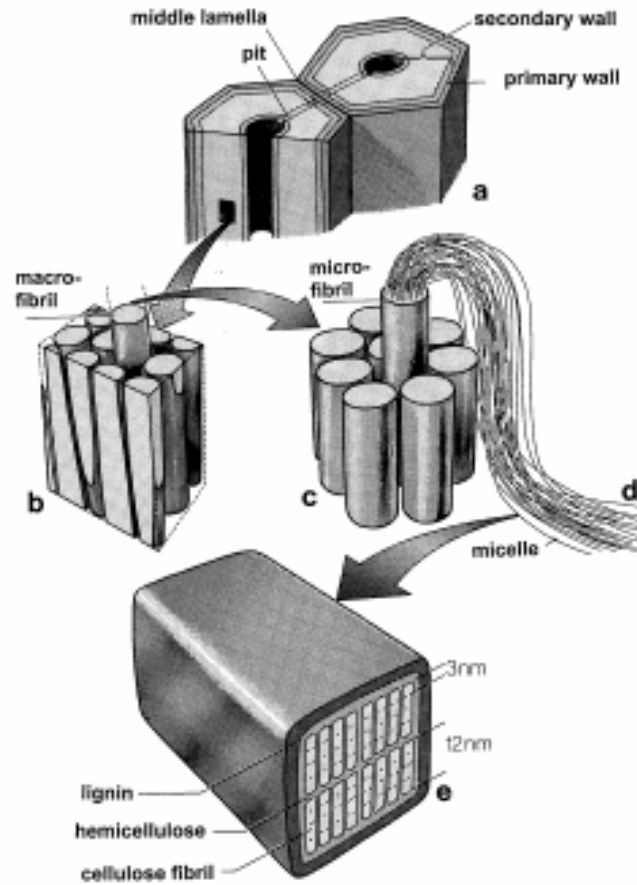


Figure 3. Hierarchical supermolecular structure of cellulose. ^[48]

The wall of a cellulose fiber in turn exhibits a complex, laminar structure, wherein each layer consists of smaller, unidirectional fibers, or microfibrils, in the range of 5 to 50 nm wide, and anywhere from 100 nm to several microns long, depending on the source.^[48] Each layer of microfibrils varies with respect to fibril orientation (microfibril angle). Microfibrils in turn have a composite structure, consisting of slender cellulose crystallites, or “whiskers”, with diameters on the order of 5 nm, which are threaded together and embedded in the microfibrils between amorphous regions of cellulose and hemicellulose.^[49] Hence, cellulose can be viewed as a composite material from the

nanoscale perspective (whiskers in microfibrils), the microscopic perspective (microfibrils in fibers) and the macroscopic perspective (fibers in wood).

Historically, the use of cellulose fibers in polymer matrix composites has been mainly as a cheap filler in the form of wood flour.^[2] Although wood flour does increase the dimensional stability of a polymer composite, it does not significantly increase the strength of the composite due to its relatively low degree of cellulose fiber refinement. In addition, cellulose is hydrophilic, because of its many hydroxyl groups and ether links, and this leads to high moisture uptake. Moisture adsorption tends to lower the mechanical strength of cellulose composites over time, because water has a plasticizing effect at the fiber-matrix interface.^[50, 51] By chemically modifying the cellulose surface, moisture uptake can be decreased. For example, the hydroxyl groups at the cellulose surface can be reacted with acetyl groups, thereby rendering the cellulose surface hydrophobic. The hydroxylated surface of cellulose also makes it incompatible with many low cost thermoplastic matrices such as polyethylene (PE), and polypropylene (PP), which are hydrophobic. However, the compatibility of cellulose with these polyolefines can be increased by reacting the hydroxyl groups with coupling agents, e.g. diamines, diisocyanates or silanes.^[51-54] Grafting of matrix-compatible side chains, for example maleic anhydride-modified polypropylene, is also effective for compatibilizing the cellulose fiber surface with polyolefinic matrices.^[53, 55, 56]

The extraction of microfibrils or whiskers from cellulose fibers enables their use as a highly effective reinforcement in polymer matrix composites. Depending on the source, and on the chemical treatment during extraction, the elastic modulus of microfibrils varies in the range of 70 to 140 GPa.^[2, 57, 58] This compares favorably with other fibers commonly used as reinforcement in high performance composites, e.g. glass and aramid fibers, and represents a dramatic improvement compared to regular wood and cellulose fibers, the modulus of which typically does not exceed 40 GPa.^[47] However, defects are still present in microfibrils in the form of regions of amorphous cellulose.

Cellulose whiskers constitute the reinforcing element in the cellulose microfibrils. By carefully refining the microfibrils, for example by acid hydrolysis, the amorphous cellulose can be removed and the remaining high aspect ratio, crystalline cellulose nanofibers extracted. A suspension of tunicin whiskers is shown in Figure 4.

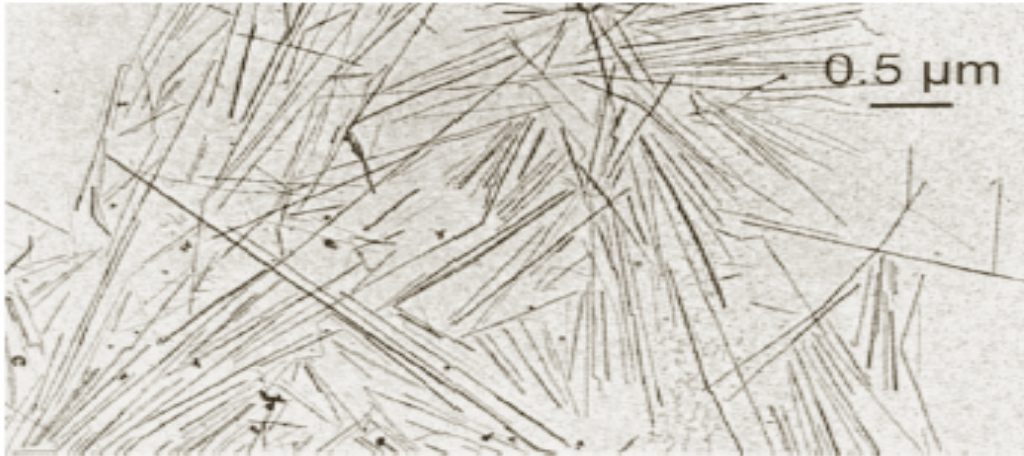


Figure 4. Suspension of whiskers from tunicin.^[30]

Strong intermolecular hydrogen-bonding in cellulose whiskers gives them a high degree of crystallinity and a high elastic modulus, making them highly suitable for use as a PNC reinforcement. The elastic modulus of a defect-free monocrystal of cellulose has been calculated to be at least 100 GPa with some estimates as high as 250 GPa.^[30, 57] Cellulose whiskers are also characterized by a high aspect ratio, estimated in the range of 50 - 200.^[2, 9, 59, 60] This enables them to attain a percolation threshold of as low as 1 wt%.^[2] Above the critical percolation threshold concentration, cellulose whiskers form a rigid, interpenetrating network throughout a polymer matrix. This mode of reinforcement is complementary to the effect of large surface area, which leads to a large interface area in the composite, typically 150 - 170 m²/g.^[2, 9] As discussed above, a general characteristic of PNCs is that immobilization of the matrix polymer at the nanoparticle surface leads to significant increases in the thermo-mechanical performance of the PNC. A third mode of composite reinforcement which has been observed in PNCs both with polar matrices, e.g.

polyhydroxybutyrate (PHB) and starch, and non-polar matrices, e.g. PP and high density polyethylene (HDPE), is the ability of cellulose whiskers to induce transcrystallinity. Transcrystallinity involves creating a crystalline interphase between the fiber surface and matrix.^[2, 9] The cellulose fiber acts as a nucleation site for crystallization of the matrix polymer. Transcrystallinity enables significant improvements in fiber – matrix bonding and hence interfacial shear strength and toughness. Several studies have focused on achieving a better understanding these different reinforcement mechanisms in cellulose whisker PNCs.^[9, 30, 53] The modulus and strength of PNCs reinforced with whiskers compares favorably with composites reinforced with glass and aramid fibers, aluminum, and magnesium alloy.^[47, 57] At a cellulose whisker concentration of 6 wt %, high increases in modulus and elongation at break have been obtained for polystyrene-butylacrylate copolymer matrix composites.^[5]

PNCs have been produced using cellulose whiskers both with thermoplastic matrices, e.g. polyethylene oxide (PEO), plasticized polyvinyl chloride (PVC) and polycaprolactone (PCL), and with thermosetting phenolic and epoxy matrices.^[61, 62] Significantly, whiskers can be incorporated into biodegradable and biocompatible matrix materials, e.g. starch, silk-fibroin and bacterial polyester, e.g. PHB.^[42, 57, 63, 64] However, strong hydrogen bonding interactions between cellulose molecules tends to make homogeneous dispersion of cellulose fibers difficult, especially in a non-polar matrix. Dispersion of cellulose fibers through melt processing is not an option because decomposition of the polymer occurs prior to melting.^[65, 66] To date, good dispersion of cellulose microfibrils has been achieved only by the “dispersions mixing” method (also called “suspensions mixing”).^[30, 45] This involves mixing a dispersion of whiskers in a dilute aqueous suspension with a second suspension of matrix polymer, followed by film casting. This technique produces an intimate mixture of cellulose and matrix polymer, which is preserved as the water is evaporated during matrix consolidation. High strength composite films have been produced. A major drawback with this approach is that is only

suitable for forming composite films, and that the consolidation of the polymer matrix requires volatilization and removal of the solvent phase, which may create defects (voids) in the final product and poses economic and environmental concerns.

2.1.2 Layered silicate nanocomposites

Another area within the field of polymer matrix nanocomposites is the synthesis of polymer layered nanocomposites using layered silicates, e.g. montmorillonite clay, as the nanoparticle phase. For MMT, the aspect ratio is in the range of 20 – 100, and the elastic modulus of a platelet has been estimated as approx. 270 GPa.^[67] MMT is a layered silicate, belonging to the 2:1 phyllosilicate (phyllo = leaf) family, and consists of stacks of thin platelets.^[10] Each individual platelet consists of an octahedral alumina sheet, sandwiched between two tetrahedral silica sheets (hence the 2:1 ratio). This is shown in Figure 5. The platelets have a net negative charge due to substitution of some of the Al^{3+} cations with Mg^{2+} ions. This charge is counterbalanced by inorganic cations, e.g. Na^+ confined to interlayer galleries between platelets. This causes platelets to form stacks (“tactoids”) held together by electrostatic forces. In PNCs, the goal is to produce a structure in which the tactoids are intercalated and expanded like an accordion, or exfoliated to individualize the platelets. The lamellar morphology of montmorillonite (MMT) clay makes it an ideal additive for bulk composites and films where high barrier properties are required. The morphology of exfoliated MMT PNCs is often modeled as a labyrinth, providing an excellent barrier for mass transport, retarding diffusion through the matrix.

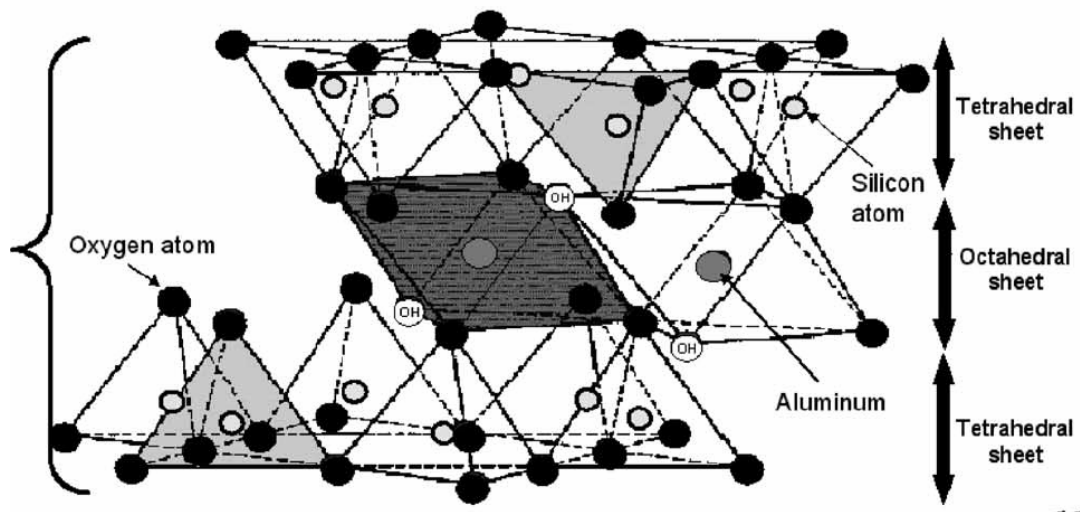


Figure 5. Structure of montmorillonite clay.^[68]

To date, the in-situ intercalative polymerization technique is one of the most successful techniques for producing MMT nanocomposites on an industrial scale. The first step of this process, as shown in Figure 6, involves the intercalation of a monomer or low molecular weight precursor into the galleries of the silicates.

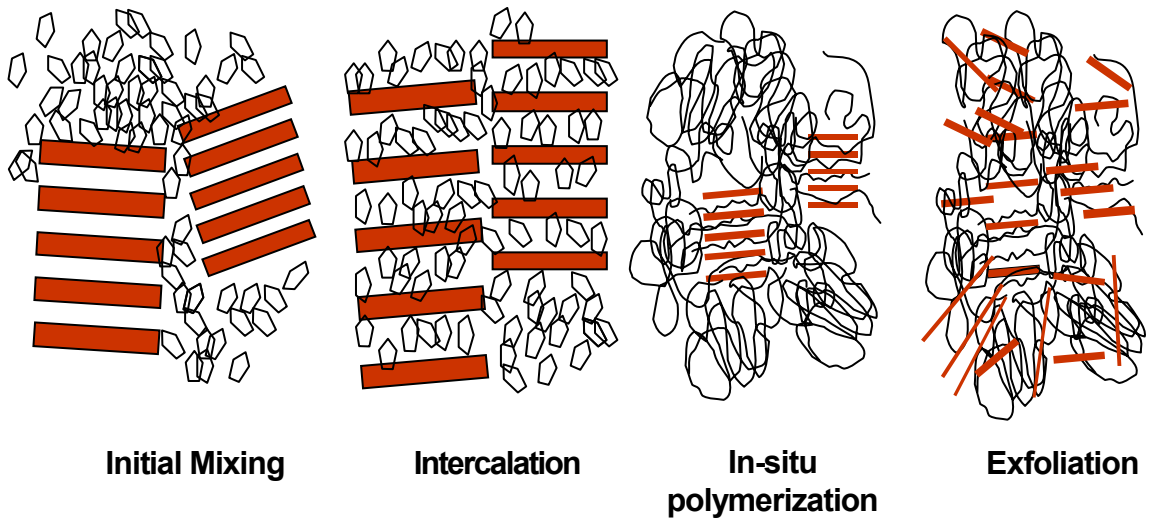


Figure 6. Steps in the in-situ intercalative polymerization technique.

Subsequent to intercalation, in-situ polymerization of the intercalated species inside the galleries gradually forces apart the individual silicate platelets. The final result of in-situ intercalative polymerization is an exfoliated structure in which the silicate layers are individualized and surrounded by the matrix polymer, or an intercalated structure in which the polymer chains are partially immobilized within the galleries of the silicate. Often, mixed structures are obtained.^[4] In in-situ intercalative polymerization, the surface chemistry of the clay surface is selected for compatibility with the intercalating monomer. Naturally occurring montmorillonite is hydrophilic. However the silicate surface can be rendered organophilic by ion exchange with e.g. onium ions with aliphatic or aromatic functions for compatibility with an organophilic intercalate. A range of organomodified MMT is commercially available.

PNCs modified with nanoclays show remarkable increases in thermo-mechanical properties. The clay – nylon PNC Toyota Research produced for under-hood applications in the Toyota Camry is a good example. By incorporating a small amount of montmorillonite clay into a nylon matrix, the heat distortion temperature of the composite increased by 87°C, allowing its use in under-the-hood automobile components.^[69]

2.1.3 Metal nanoparticle filled nanocomposites

In addition to nanofibers and nanoclays, polymer matrix nanocomposites can also be filled with colloidal particles. For example, one of the earliest types of nanocomposites designed by man is colored glass embedded with metal nanoparticles.^[14] Today, metal nanocluster filled PNCs are synthesized to exploit the size-dependent properties of metal nanoparticles, for example lower melting point compared to bulk metal and superconductivity.^[70] Applications for metal nanoparticle filled PNCs include coatings, electronics, catalysis, and antibacterial materials.^[70, 71]

A polymer matrix can be filled with nanoparticles either by producing the nanoparticles in-situ through vapor deposition or growth from an appropriate metal salt

precursor.^[7, 72] Alternate methods involve mixing nanoclusters together with the polymer in melt or resin form.^[14] Prior to dispersion in a polymer matrix, metal nanoparticles can be coated, or “capped” to stabilize them against agglomeration and thereby increase their dispersibility.^[71] One of the methods by which this is achieved is the use of monofunctional ligands such as alkane thiols, to form monolayer protected clusters (MPCs). Once an MPC has initially been capped with an monofunctional ligand, exchange reactions with difunctional ligands can be conducted to functionalize the MPC.^[73] Displacing the capping ligand with for example a hydroxyl-terminated or amine-terminated thiol, opens the MPC up to amide or ester coupling reactions with carboxylic acid groups.

2.2 Self-assembly as a means of modifying surface properties

Organized organic thin films (OOTFs) have been successfully prepared on a variety of substrates to study and to optimize surface properties such as wetting, chemical resistance, and biocompatibility.^[24] Such films are spontaneously formed when amphiphilic surfactant molecules, e.g. short-chain alkane thiols or fatty acids, are allowed to self-assemble into a monolayer or multilayer structure on a specific substrate, as shown in Figure 7.^[27, 74] Much of the pioneering work on OOTFs was carried out in the 1980's by Nuzzo, Allara, Whitesides, et. al.^[22, 75, 76] The main driving force for self-assembly is strong chemisorption between the headgroup and the substrate. However, other energetic factors are also important, such as intermolecular interactions, including solvent – solute interactions, and tailgroup – tailgroup interactions. The adsorption configuration of a given molecule also depends on headgroup – substrate bond, but also on different intermolecular interactions. In the case of aromatic molecules, aromatic bonding may be important. Aromatic bonding may occur between the adsorbed molecule and the substrate, leading to flat adsorption, or alternately, it may lead to intermolecular “ π -stacking”.

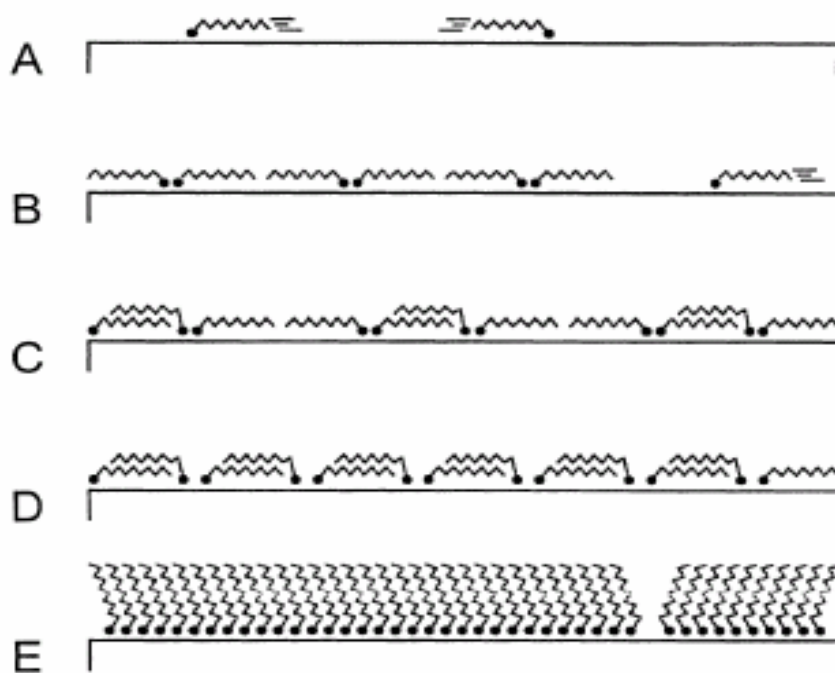


Figure 7. Self assembly of simple amphiphiles into a monolayer, the simplest kind of organized organic thin film.^[24]

Because the molecular orientation is determined by the interplay between the various inter- and intramolecular forces, it is not always predictable. For example, dicyanobenzene adsorbs flat on Ag, enabling interaction between the metal and the π -conjugated ring system as well as the π -conjugated cyano group. However, when the isocyanide group ($-\text{NC}$) is substituted for the cyano group ($-\text{CN}$), the preferred bonding configuration is a surface-perpendicular orientation, in which a single isocyanide group is terminal bonded to the metal surface. In such a configuration, the metal surface can no longer have direct interaction with the phenyl ring or the pendent isocyanide group. Considering that the isocyanide group typically exhibits stronger adsorption on metal surfaces than the cyano group, this change in bonding configuration seems counterintuitive.^[23, 25, 77-79]

2.2.1 Self-assembly of difunctional molecules

To date, the vast majority of the work with OOTFs has dealt with the self-assembly of monofunctional molecules, in particular the thiol-on-gold system. Monofunctional molecules have the ability to form SAMs (self-assembled monolayers). In SAMs, the single functional group is bonded to the substrate, while the backbone chain and a non-reactive tail group point away from the substrate. Hence, the surface of the SAM is chemically inert, because no functional group is available at the surface of the SAM for further reaction.

However, OOTFs can also be produced by difunctional “linker” molecules bearing reactive functional groups at each end. Linker molecules have the potential to bond to the substrate through one functional group, while the other functional group points away from the substrate. The functional group pointing away from the substrate is still reactive and capable of bonding to other substrates or molecules. The preparation of this type of “chemically sticky” OOTF greatly increases the range of possibilities for tailoring a surface, because it provides a means of bonding adlayers to a target substrate. For example, an OOTF can be used to attach a polymer to a metal, provided that the polymer contains suitable sites for interaction with the free functional groups of the linker molecules in the OOTF.^[17, 19, 26, 62] By extension, OOTFs can also be used to create multilayer “sandwich” structures at the nanoscale.

The self-assembly of difunctional linker molecules is even more complex than the self-assembly of simpler monofunctional molecules. Since both terminal functional groups are reactive, they may both bond to the bottom substrate. As noted above, the requirement for forming a chemically sticky OOTF is that the constituent difunctional molecules bond to the substrate through only one terminal, and collectively form a chemically reactive surface with the terminal group disposed away from the substrate. If kinetic trapping in a surface-parallel “lying-down” phase occurs in the early stages of

self-assembly, this prevents the molecules from achieving the required surface – normal, i.e. “standing up”, bonding configuration.^[16, 24, 28, 75]

2.2.2 Functional groups available for self-assembly

As noted above, of the various functional groups available for self-assembly experiments, the thiol group has received most attention, due to its strong affinity for Au substrate.^[75] Comparatively less work has been done to characterize the behavior of carboxylic acid, isocyanide, hydroxyl, carboxyl, isocyanide, and nitrile groups. Little is known about the ability of difunctional molecules bearing these functional groups to undergo self-assembly into sticky OOTFs.

The functional groups investigated in this work were thiol (–SH), carboxylic acid (–COOH), nitrile (–CN), isocyanide (–NC), and isothiocyanate (–NCS). Difunctional molecules with all the above functional groups are known to chemisorb onto various metallic substrates.^[16, 18, 21, 23-26, 80] Phenyl isothiocyanate is known to adsorb on Cu, where it has sufficient adsorption strength to act as a corrosion inhibitor.^[81] However, the mode of adsorption (chemisorption versus physisorption) is not clear. The carboxylic acid group is generally considered a weak adsorbent on metals such as Au, Ni and Pt. However, carboxylic acid -terminated mercaptoundecanoic acid has sufficient affinity for Au and Cu to occasionally cause “hairpin bonding”, i.e. adsorption through both thiol and carboxylic acid groups, as evidenced by loosely ordered self-assembled monolayers.^[82] Fatty acids (i.e. carboxylic acid - terminated alkane chains) have long been known to self-assemble into OOTFs on Pt substrates. However, the adsorption of dicarboxylic acids into a standing up phase OOTF on Pt has not been described. The isocyanide group has received some attention, since it has been shown to have an affinity for Au comparable to that of thiol. The self-assembly of monofunctional isocyanides on Pt has been described in the literature and it appears that isocyanide has a high affinity for Pt.^[16, 28, 83, 84] In one study, the adsorption of 1,6 diisocyanohexane on Pt was shown to produce OOTFs with

good barrier properties, although unfortunately no IR spectra were provided to demonstrate a standing up phase.^[85]

2.2.3 Substrates available for self-assembly

Self-assembly studies have been carried out on a variety of substrates including metals and semiconductors.^[24] Of the various metallic substrates selected for self-assembly studies, Au has been by far the most popular choice. This is because the thiol function has a strong affinity for Au, but also because the noble metal nature of Au renders it highly stable to oxidation, and hence it provides a model surface for self-assembly experiments under “ideal” conditions.^[74] Because of the historical emphasis on the thiol-Au system, a great deal of experimental work still remains to characterize self-assembly of difunctional linker molecules on substrates other than Au. Comparatively few studies have described the self-assembly of difunctional molecules on Ag, Cu, Ni or Pt, or their adsorption geometry on these substrates. The tendency of Cu to rapidly form a layer of native oxide was early implicated as an impediment to forming high quality, reproducible OOTFs on Cu.^[86] However, by minimizing exposure of freshly evaporated Cu surfaces to air, or by following reasonable pretreatment procedures, such as polishing and acid cleaning, OOTFs can be produced on Cu surfaces of sufficient quality to retard further oxidation.^[87-90]

The high conductivity of metals like Au, Ag and Cu makes them suitable for applications in conductive PNCs. In addition, nanoparticles of Ag also have anti-bacterial properties.^[91] As discussed in the introduction, the presence of a “chemically sticky” OOTF at the surface of a metal nanoparticle has the potential to increase the interaction between the nanoparticle surface and a surrounding matrix polymer (see above, Figure 1). Sticky OOTFs can only be formed by linker molecules with a high affinity for the substrate and which are not prone to undergo flat surface adsorption, or “hairpin” bonding in which both terminal groups of a linker molecule with a flexible backbone

bond to the same substrate. OOTFs possessing a π -conjugated backbone structure, i.e. “molecular wires”, are capable of providing electrical connectivity in addition to mechanical bonding to the nanoparticle.^[19, 20, 92] Finally, OOTFs have the ability to stabilize the nanoparticles against further growth by providing a protective molecular coating. This is critical in applications where the nanoparticles are in the size regime where important size-dependent properties must be retained.^[93]

2.3 Reactive molding techniques for composite manufacture

The main distinctive of reactive molding is that complete polymerization of the entire polymer matrix is effected in the mold, starting from a system of monomers or other low molecular weight precursors. Reactive molding differs from conventional molding of thermoplastics where a polymer is introduced to a mold, after a process of melt-blending at high viscosity, and simply allowed to solidify in the mold. It also differs from molding of thermosetting materials where a resin is mixed with a monomer like styrene, which acts at first as a solvent to reduce viscosity, and later as a crosslinking agent during curing in the mold.

The most common reactive molding process today is reaction injection molding – RIM. The RIM process is typically a two-component system based on the polymerization of diisocyanate with diol, plus a small amount of polyol for crosslinking, and catalyst.^[94] The components are mixed together by impingement in a mixhead, followed by injection into a mold. In the mold, polymerization occurs very rapidly as the hydroxyl groups of the polyol component react with isocyanide groups to form urethane linkages. To extend the use of RIM to composite applications, structural reaction injection molding (SRIM) and reinforced reaction injection molding (RRIM) processes have been developed.^[95, 96] RIM chemistry is suitable for incorporation of cellulosic fillers, and to an extent, cellulose fibers are used in RRIM composites.^[97] The low abrasion of cellulose fibers compared to inorganic fillers, e.g. chopped glass fiber makes

it especially suitable for RRIM processing.^[53] In addition cellulose is light-weight, affordable, renewable, environmentally benign, and biodegradable. One of the main limitations for the use of cellulose in polymer matrix composites in general, is the strongly hydrophilic nature of cellulose, which causes problems with moisture absorption, as discussed above.^[2, 50, 51] However, when using cellulose as a filler for RRIM composites, the hydroxyl groups at the cellulose surface can be exploited to increase the fiber – matrix interaction and enhance composite strength. Cellulose fiber reinforcement has been shown to double the modulus of SRIM composites at only 4 wt %, due to its ability to provide hydroxyl groups for crosslinking reactions with isocyanate groups in the matrix.^[98]

2.3.1 Materials and methods for reactive molding of nanocomposites

For processing of PNCs, reactive molding offers several important advantages over competing processes. For example, in conventional melt blending of thermoplastics, it is difficult to disperse the particulate phase in the polymer, and to completely wet the surface of the particulate phase due to the high viscosity of the polymer melt. In contrast, the low initial viscosity of a reactive molding system is conducive to achieving a dispersion of nanoparticles in the monomer phase, without having to add any solvents to lower system viscosity. Moreover, reactive molding processes are closed-mold processes, which avoids the environmental concerns associated with open mold processes.

The in-situ intercalative polymerization of layered silicates is perhaps the best example of reactive molding of nanocomposites today. In-situ interactive polymerization of layered silicates, which was discussed above, can be achieved either with thermosetting matrices, such as polyurethane and epoxy, or with thermoplastic systems, such as nylon-6.^[4, 38] A general requirement for reactive molding of nanocomposites is that the particulate phase of a PNC is compatible with the monomer phase of the reactive molding system, which acts as a polymerizable solvent. This makes it possible to achieve

and maintain a fine dispersion of the particulate phase in the monomer during matrix consolidation, resulting in excellent particle distribution in the final PNC. Above, it was noted that the hydroxylated surface of cellulose makes it reactive to isocyanate. Cellulose whiskers may therefore represent the ideal particulate phase for a “nano-RIM” process. For this to be achieved, the whisker - polyurethane system needs to be better characterized, so that the RIM process can be adapted to fabrication of cellulose whisker PNCs. Stereolithography, which has also been referred to as “UV-RIM” (i.e. ultra violet light induced reaction injection molding), is a second reactive molding process, which has found application in rapid prototyping.^[99, 100] The low viscosity of a UV-RIM resin should also be conducive to achieving a dispersion of nanoparticles in the PNC matrix.

Although a range of reactive monomers could be selected for reactive molding of polymer nanocomposites, bio-based monomers with the potential to replace materials traditionally derived from the petrochemical supply chain are of particular interest today. On one hand, the Technology Roadmap for Plant/Crop-Based Renewable Resources 2020 (sponsored by the U.S. Dept. Of Energy), calls for 10% of basic chemical building blocks to be plant-derived by 2020.^[31] On the other hand, the Forest Products Industry’s Agenda 2020 identifies the critical importance of nanotechnology in the development of new generations of high-value, high-performance materials from forest-based products. One polymerizable solvent – monomer, which satisfies these various requirements for a reactive molding system is furfuryl alcohol.

2.3.2 Furfuryl alcohol as a precursor for polymer matrix composites

Furfural alcohol (FA) is a bio-based material, produced by hydrogenation of furfural on an industrial scale. Furfural (furfur = bran) has been prepared in commercial quantities for many decades from pentose-rich agricultural residues, including rice hulls, bagasse, oat hulls, and corn cobs. Furfural can also be derived from wood and wood products, which represent a second natural storehouse for furfural.^[101]

The resinification of FA was reported on as early as 1873.^[102] The resonance structures of the furan ring make it susceptible to substitution at the C2 and C5 “alpha” positions, and hence FA behaves like a difunctional monomer. In the early stages of resinification, FA polymerizes predominantly through “head-to-tail” reactions, in which the hydroxymethylene function of one molecule reacts with the hydrogen at the C5 position of the furan ring of a second molecule, yielding a methylene bridge. This is shown in Figure 8.

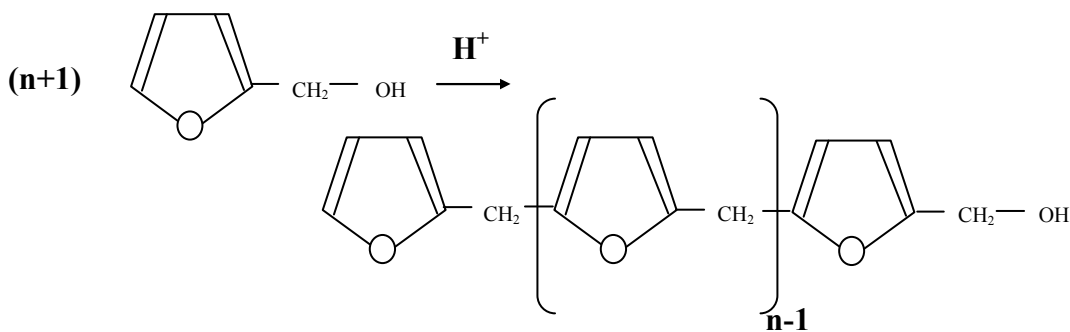


Figure 8. Initial condensation step in the homopolymerization of furfuryl alcohol.

“Head-to-head” condensation between hydroxymethylene groups, yielding dimethylene ether bridges, also occurs at this stage. In addition, levulinic acid and lactone byproducts may be produced as a result of hydrolytic ring cleavage of furan rings.^[102] Crosslinking occurs in the later stages of resinification. Though still not well understood, the crosslinking mechanism most likely involves condensation between the methylol group at the end of one chain and the methylene bridge of second chain. Reactive hydrogens in unsaturated sequences along the chain backbone may play a mediating role. A second crosslinking mechanism involves formaldehyde, which is split off when dimethyl ether bridges decompose to methylene bridges.^[103-105] The polymerization of FA to PFA is typically catalyzed using a Brönstedt acid e.g. sulfuric, hydrochloric and para-toluene sulfonic acid (PTSA).^[105] When using strong mineral acids such as these, overcatalysis

may lead to an explosive reaction. To avoid this hazard, polymerization can alternately be effected in the presence of γ -alumina, owing to its Lewis acidity. Common applications of PFA include adhesives, corrosion resistant coatings and composites, as a binder material in foundry cores. Many applications of PFA owe to the thermal stability of the aromatic furan ring, which gives it high inherent flame retardancy, low smoke release and high char yield.

While PFA is hydrophobic, its precursor, furfuryl alcohol (FA), is hydrophilic and completely soluble in water, due to the hydroxyl group of the side chain and the oxygen heteroatom of the furan ring. When FA is polymerized in the presence of wood pulp, the result is that FA mostly phase separates from the cellulose phase, producing a mixture of free cellulose and crosslinked PFA.^[106] However, grafting of PFA to pulp and flax fibers has been achieved through a process involving free radical polymerization.^[105, 106] When polymerized by acid catalysis in the presence of fine silica particles, FA forms a crosslinked polymer that is attached covalently to the silica surface. The PFA coverage is dense enough to rendering the silica hydrophobic.^[107]

Finally, it is also worth noting that the polymerization of FA to PFA can be achieved using UV radiation. The UV-photopolymerization of FA has been investigated for its potential application as a resin for stereolithography.^[108, 109] As with conventional RIM, UV-RIM requires low viscosity precursors, and hence FA, which is a clear liquid of low viscosity at room temperature, lends itself to this application.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Self-assembly experiments

3.1.1 Conceptual approach

The overall objective of the self-assembly experiments was to produce OOTFs in which the molecules adopt a standing up phase configuration as required for a sticky surface, on substrates of Cu, Pt and Ni. To achieve this, linker molecules bearing thiol (–SH), carboxylic acid (–COOH), nitrile (–CN), isocyanide (–NC), and isothiocyanate (–NCS) were used.

Due to the sensitivity of the self-assembly process to surface contamination, metal substrates were never reused, rather for each self-assembly experiment, fresh metal substrates were prepared by vapor deposition on polished silicon wafers. Silicon wafer were never reused, rather fresh wafer were used for each experiment. Fresh metal substrates were always dipped immediately into adsorption solution in a cleanroom environment. Exposure of the substrates to ambient was limited to 5 minutes to avoid surface contamination, and in the case of Cu and Ni, to minimize surface oxidation.

To compare and rank the adsorption affinities of different functional groups for the different substrates, competitive self-assembly was performed from adsorption solutions containing pairs of linker molecules at equimolar concentration. For each two-component adsorption system, linker molecules with identical backbone structures were used, to minimize differences in intermolecular interactions and solvent-solute interactions, and highlight chemisorption of the terminal group on the metal substrate as the dominant factor determining the outcome of preferential adsorption. Whenever possible, molecules with π -conjugated phenylene backbones were used, to avoid hairpin bonding of both terminal groups to the substrate. π -conjugated phenylene molecules were

also of interest as they represent model molecular wires for the preparation of conductive OOTFs.

Long adsorption time (at least overnight) was allowed, to ensure complete OOTF formation. Given sufficient time, the molecules with the functional groups exhibiting strongest chemisorption to the substrate should form the OOTF. Even if adsorption kinetics initially should favor physisorption or chemisorption by the species which adsorbs more weakly, displacement reactions in favor of the species exhibiting the strongest chemisorption will occur over time.

To determine which of the linker molecules in each adsorption pair preferentially adsorbed, qualitative chemical analysis was performed using a combination of electron spectroscopy (XPS) and vibrational spectroscopy (PM-IRRAS). The peaks and chemical shifts in the XPS spectra enable the identification of the molecules at the surface, regardless of adsorption orientation. In contrast, the information obtained from PM-IRRAS analysis is useful for identifying which difunctional molecules adopted a standing up phase configuration at the surface. In PM-IRRAS infrared light is reflected off a surface to be analyzed, at a grazing angle. Before impinging on the surface, the light is passed through a polarizer which splits it into two beams, one of which is perpendicular to the surface plane. The surface-perpendicular light undergoes a phase change when reflecting off the surface, which increases its local intensity. This allows the light to interact very strongly with the vibrations of any molecules on the surface possessing a dipole moment perpendicular to the surface.^[27] When the light frequency matches one of the vibrational modes of a molecule on the surface, this is seen as a peak the spectrum of reflected light. The frequency of light is scanned in the region of 800 cm^{-1} to 4000 cm^{-1} . The absorption peaks for the functional groups of interest are in this range.

3.1.2 Materials used for competitive self-assembly

Metal coatings were made by e-beam evaporation of >99.99% pure metal targets of Cu, Ni and Pt (Kurt J Lesker) onto fresh double sided polished 2" (100) silicon wafers from Virginia Semiconductor or Montco Silicon. All linker molecules and solvents were purchased from Sigma Aldrich or Alfa Aesar and used as received. Chemical purity was $\geq 98\%$, with the exception of 1,6-hexanedithiol ($\geq 97\%$), and 1,4-benzenedithiol ($\geq 95\%$).

3.1.3 Technique used for competitive self-assembly

All adsorption solutions were prepared in new glassware, which was first cleaned by rinsing in deionized water, acetone, and pure adsorption solvent. Each solution contained two different difunctional molecules, which were usually symmetric, at equimolar concentrations in the range of 1.0 to 5.0 mM. Tetrahydrofuran (THF) was used, without degassing, as the solvent in all adsorption experiments, unless otherwise specified.

Cu films of 150 to 250 nm thickness were produced by e-beam evaporation (CVC Products) at 3×10^{-6} torr or less. Cu films were deposited onto adhesion layers of 10 to 50 nm Ti or Cr. Deposition rates were $\leq 6 \text{ \AA/s}$, to minimize heating of the substrates during deposition, which may otherwise cause high residual stress on the film, and diffusion of Si or adhesion layer metals to the film surface.^[110, 111] After each metal deposition, the deposition chamber was back-filled with nitrogen. Films produced under similar conditions have been shown to have a predominantly (111) crystalline orientation.^[88] Freshly prepared metal substrates were carefully removed from the tray holder of the e-beam evaporator and transferred directly in a class 10 cleanroom environment to their adsorption solutions. Exposure to ambient was limited to approximately five minutes prior to immersion.

After the specified immersion time, which was always at least 18 hours to ensure formation of a complete OOTF, substrates were removed from adsorption solution, and

rinsed with disposable pipettes in pure solvent to remove all loosely bound molecules. Samples emerged autophobic from all solutions.

3.1.4 Characterization techniques

XPS (x-ray photoelectron spectroscopy) spectra were collected mostly on a Surface Science Instruments SSX-100 at Georgia Tech, though some analysis was performed using a Kratos Axis Ultra, located at the Center for Microanalysis of Materials at University of Illinois. Both instruments used a monochromatized Al x-ray source, a base pressure $\leq 3 \times 10^{-8}$ torr, and charge neutralization. Each sample was focused individually. No differential charging was observed on any of the samples analyzed. For peak fitting, software from a commercial vendor (XPS International, Inc.) was used. The maximum allowed FWHM for any peak was normally constrained to 1.6 eV. Peak fitting solutions were sought for $\chi^2 < 2$, Shirley background subtraction, and allowing up to 5% peak asymmetry, and 20% Lorentzian contribution (80% Gaussian) as required to optimize the peak fit on the low binding energy side. All peaks were internally referenced to carbon as aromatic hydrocarbon at 284.8 eV.

PM-IRRAS (polarization modulation infrared reflection absorption spectroscopy) spectra were collected on a Nexus 870 (Thermo Electron) with a PM-IRRAS attachment including a photoelectric modulator (Hinds) and a nitrogen cooled MCT detector, at near grazing angle. An average of 1000 scans per analysis was collected, with a resolution of 2 to 4 cm^{-1} . Spectra were collected from a minimum of three spots at various points on each semi-wafer substrate, and compared for consistency, to confirm reproducibility.

Reflectance spectra are expressed $\Delta I/I = 100 \times (I_s - I_p)/(I_s + I_p)$, converted to arbitrary units.

I_p and I_s designate the spectra collected parallel and perpendicular to the plane of incidence, as usual.^[112]

3.2 Reactive molding of cellulose whisker nanocomposites

3.2.1 Conceptual approach

The overall objectives of the reactive molding of cellulose whisker nanocomposites were to 1) disperse cellulose whiskers in FA monomer, and 2) to achieve in-situ polymerization of the CW – FA dispersion using FA as a polymerizable solvent medium.

Due to the richly hydroxylated surface of CW whiskers, FA was chosen for its ability to compete with hydrogen bonding between whiskers, and because it is bio-based. Cellulose whiskers were prepared by hydrolysis with sulfuric acid, because the surface of such whiskers contains sulfonic acid groups – HSO_3 .^[9, 11, 113] These residual acids present catalyst sites for polymerization of FA in close contact with the whiskers surface. The sulfonic acid groups on the whiskers surface also help to electrostatically stabilize the CW against agglomeration while in suspension during synthesis.

To characterize the curing behavior and to investigate how the presence of CW influences the polymerization of FA, FTIR and DSC spectra were collected before and during the resinification process.

As a qualitative measure of CW dispersion in the cured PNC, coded CW-PFA, TGA was performed to compare the thermal stability of the PNC compared to pure polymer. It was also desired to perform DMA to compare the mechanical strength of the PNC compared to pure polymer, providing that adequate specimens without too many defects could be produced.

3.2.2 Synthesis of cellulose whiskers

Cellulose whiskers were prepared, starting from MCC precursor (Avicel, Aldrich) to streamline the procedure. The main steps in the whiskers synthesis were 1) acid hydrolysis (62% H_2SO_4 , 12.5 ml/g cellulose, 55°C, 2h) which dissolves most of the

amorphous cellulose, leaving only the crystalline whiskers intact 2) refining and purification of the solid residue remaining after the hydrolysis by repeated cycles of ultracentrifuging followed by resuspension and washing of the solids in distilled water until turbid supernatant was obtained, 3) dialysis against distilled water to pH 5 - 6, and iv) freeze drying. The freeze-dried whiskers can then be transferred to the FA monomer phase. To confirm this procedure yields CW with the desired nanoscale morphology, samples of the aqueous suspensions were slowly concentrated by open evaporation to the range 2.7 – 3.5% and viewed through crossed polars. The concentrated suspension initially showed flow birefringence, and with continued concentration, also birefringence at rest.^[113]

3.2.3 Resinification of furfuryl alcohol with cellulose whiskers

To determine whether CW has a catalytic effect of the resinification of FA, in a typical experiment, 0.75 – 1.0 phr freeze-dried CW was redispersed in FA by means of a brief ultrasonication treatment (Fisher 500W, 25 – 50% amplitude, 15 minute bursts) followed by heating to 50°C for additional dispersion. At 50°C, the sulfonic acid residues are stable, and deesterification is not expected. After 1h at 50°C, the mixture was heated to the target reaction temperature until resinification of FA to PFA occurred.

To characterize the curing behavior and to investigate how the presence of CW influences the polymerization of FA, FTIR and DSC spectra were collected before and during the resinification process.

3.2.4 Curing of cellulose whisker – polyfurfuryl alcohol composites

Oven-curing of the CW – PFA resins was done in two stages, first at 130°C for 75 min, and then at 210°C for 105 min. Oven-cured samples showed no residual cure exotherm when scanned by DSC, but only a broad decomposition peak above 250°C with a peak max at 360°C.

3.2.5 Characterization techniques

To estimate the aspect ratio of the whiskers, AFM (close contact mode) was performed on dried films of dilute CW suspensions. Imaging was done in close contact mode using silicon tips, on a Pacific Nanotechnology scanner, varying the scanning frequency between 0.5 – 1 Hz, and z-setpoint as required for each scan. Conventional TEM analysis was not successful due to low contrast. However the dispersion of CW in its initial aqueous suspension after neutralization and dialysis against distilled water was successfully imaged by cryo-TEM. Cryo-TEM samples were prepared by ultrafast cooling with liquid N₂ to vitreous state, and maintained in that state during the TEM imaging process with the use of a cooling-holder system.^[114] The samples were imaged in bright field mode using low electron- dose in a Technai (formerly Philips) G2 TEM, at 120 kV accelerating voltage.

To characterize the curing behavior and to investigate how the presence of CW influences the polymerization of FA, FTIR spectra were collected on a Nexus 870 (Thermo Electron) in transmission mode. An average of 50 scans per analysis was collected, with a resolution of 2 cm⁻¹. In FTIR, the polymerization of FA is normally accompanied by significant increases in the intensity of the peak at 1562 cm⁻¹, assigned to the skeletal vibration of 2,5 disubstituted furan rings.^[102, 104] At the same time there is a decrease in peak intensity for the broad peak in the hydroxyl stretching region (3200 – 3600 cm⁻¹) and for the peak at 3120 cm⁻¹, assigned to the in plane stretch of the hydrogen at the C5 position of the furan ring.^[115] The intensity of the sharp peak at 1504 cm⁻¹ is assigned to the ring stretching of the furan ring, and is prominent both in FA and PFA spectra.

To characterize the thermal stability of PNCs, TGA data was collected on a TA Instruments Q50, at a heating rate of 10°C/min. Samples were heated up to 800°C under a flow of 25 ml/min nitrogen to study non-oxidative degradation, and under a flow of 25 ml/min air to study oxidative degradation.

3.3 Reactive molding of montmorillonite nanocomposites

3.3.1 Conceptual approach

The overall objectives of the reactive molding of montmorillonite nanocomposites were 1) disperse montmorillonite clay in FA monomer, and 2) to achieve the in-situ intercalative polymerization of FA inside the interlayer galleries of the MMT clay to effect complete exfoliation of the MMT platelets.

Due to the richly hydroxylated surface of MMT, FA was chosen for its ability to compete with hydrogen bonding between platelets, and because it is bio-based. In addition, FA has water-like viscosity at room temperature, which facilitates penetration of FA into the interlayer galleries of MMT.

The MMT surface contains Lewis acid sites, and this was exploited to catalyze the in-situ interactive polymerization of FA in close proximity to the MMT surface facilitating exfoliation and platelet dispersion.^[29] At the same time, the MMT-catalyzed polymerization of FA is mild, compared to when Brönstedt acids like sulfuric, hydrochloric and para-toluene sulfonic acid (PTSA) are used. When using strong mineral acids such as these, overcatalysis may lead to an explosive reaction. To avoid this hazard, polymerization can also be effected in the presence of γ -alumina, which has Lewis acid sites in the form of highly acidic hydroxyl groups.^[116]

3.3.2 Types of montmorillonite clays used

Two types of MMT – sodium montmorillonite (Cloisite® Na, Southern Clay) and an organomodified montmorillonite (Cloisite® 30B) - were used to prepare MMT – PFA nanocomposites, denoted NaMMT–PFA and 30BMMT-PFA, respectively. The organic modifier in Cloisite® 30B is methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium, where tallow is 65% C18, 30% C16 and 5% C14.

3.3.3 Resinification of furfuryl alcohol with montmorillonite clay

MMT-PFA resins were produced by charging FA (99% pure, Sigma-Aldrich), and 10 phr MMT (parts per hundred resin, actually FA) to a round bottom flask, homogenizing the mixture by vigorous agitation with a magnetic stir bar, and slowly heating to the target reaction temperature of 150°C. Preliminary DSC (differential scanning calorimetry) surveys indicated that MMT possesses sufficient catalytic activity (attributed to Lewis acidity) to effect the polymerization of FA to PFA above approx. 140°C. Therefore, the reaction mixture was maintained at a reaction temperature of 150°C until resinification of FA to PFA occurred.

To provide a basis for comparison with PFA modified with CW and MMT, PFA resin without CW or MMT was prepared using 5phr γ -alumina (nanopowder, Aldrich) as a catalyst. The resin obtained after reaction at 100°C for 12 hrs (denoted GAl-PFA) was stable during storage (at room temperature) for several months.

To characterize the curing behavior and to investigate how the presence of MMT influences the polymerization of FA, FTIR and DSC spectra were collected before and during the resinification process.

To monitor the exfoliation and polymerization process, X-ray diffraction data was collected before and during the resinification process.

3.3.4 Curing of montmorillonite – polyfurfuryl alcohol composites

Oven-curing of the MMT – PFA resins was done in two stages, first at 130°C for 75 min, and then at 210°C for 105 min. Oven-cured samples showed no residual cure exotherm when scanned by DSC, but only a broad decomposition peak above 250°C with a peak max at 360°C.

3.3.5 Characterization techniques

The morphology of the MMT used in the preparation of MMT – PFA nanocomposites was examined by AFM, by drying dilute aqueous suspensions on a smooth silicon wafer. Imaging was done in close contact mode using silicon tips, on a Pacific Nanotechnology scanner, varying the scanning frequency between 0.5 – 1 Hz, and z-setpoint as required for each scan.

To monitor the degree of intercalation and exfoliation of the MMT at various stages of resinification, x-ray diffraction (XRD) was used. X-ray diffraction data was collected on a Rigaku Miniflex diffractometer, at a scanning rate of $0.5 \text{ degrees s}^{-1}$, using Cu K α radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The change in the d_{001} spacing (i.e. the basal spacing) of the MMT tactoids was calculated from the position of the diffraction peak using Bragg's law, $2d\sin\theta = \lambda$. The interlayer gallery spacing was then estimated by subtracting $10 \text{ \AA}$ (the thickness of a single platelet) from the calculated basal spacing.^[10]

FTIR data was collected on a Thermo Nicolet Nexus 870 unit, using ZnSe windows. A minimum of 50 scans were collected at a resolution of 2 cm^{-1} . In FTIR, the polymerization of FA is normally accompanied by significant increases in the intensity of the peak at 1562 cm^{-1} , assigned to the skeletal vibration of 2,5 disubstituted furan rings. At the same time there is a decrease in peak intensity for the broad peak in the hydroxyl stretching region ($3200 - 3600 \text{ cm}^{-1}$) and for the peak at 3120 cm^{-1} , assigned to the in plane stretch of the hydrogen at the C5 position of the furan ring. The intensity of the sharp peak at 1504 cm^{-1} is assigned to the ring stretching of the furan ring, and is prominent both in FA and PFA spectra. The Al-O stretching vibration from MMT can also be observed in the FTIR spectrum at approximately 520 cm^{-1} .

TGA data was collected on a TA Instruments Q50, at a heating rate of $10^\circ\text{C}/\text{min}$. Samples were heated up to 800°C under a flow of $25 \text{ ml}/\text{min}$ nitrogen to study

degradation under non-oxidative conditions. A second series of samples were heated under a flow of 25 ml/min air to study degradation under oxidative conditions.

CHAPTER 4

COMPETITIVE SELF-ASSEMBLY ON COPPER

4.1 Chapter overview

This chapter describes the results of competitive self-assembly of symmetric difunctional molecules on Cu. Previous studies have been performed under UHV conditions, to completely avoid surface oxidation. However in this work, freshly prepared Cu surfaces were allowed to undergo brief exposure (≤ 5 min) to air prior to immersion in adsorption solution. For this reason, the Cu surfaces are termed “ambient Cu” to distinguish them from Cu kept under UHV conditions. Linker molecules bearing thiol (–SH), carboxylic acid (–COOH), nitrile (–CN), isocyanide (–NC), and isothiocyanate (–NCS) were systematically allowed to undergo competitive self-assembly to determine which of these functional group provides the strongest adhesion on ambient Cu, and secondly, to investigate the feasibility of producing chemically sticky OOTFs on ambient Cu.

4.2 Results of competitive self-assembly on copper

4.2.1 Nitrile versus isothiocyanate

Figure 9 shows the XPS survey spectrum after competitive adsorption between terephthalonitrile (NC- ϕ -CN) and 4-cyanophenyl isothiocyanate (NC- ϕ -NCS) at a concentration of 1 mM, for 24 hours. The presence of carbon and nitrogen peaks at approx. 285 eV and 400 eV, respectively, are consistent with adsorption of terephthalonitrile. No sulfur peaks were detected in the XPS spectrum, which demonstrates that terephthalonitrile preferentially adsorbs over 4-cyanophenylisothiocyanate. This indicates that the nitrile group has a higher affinity for

ambient Cu than the isothiocyanate group. Hence, the order of preferential adsorption is – CN > –NCS. As expected, a small oxygen peak was observed at 531 eV, consistent with a minor degree of oxidation of Cu to Cu₂O.^[26, 117]

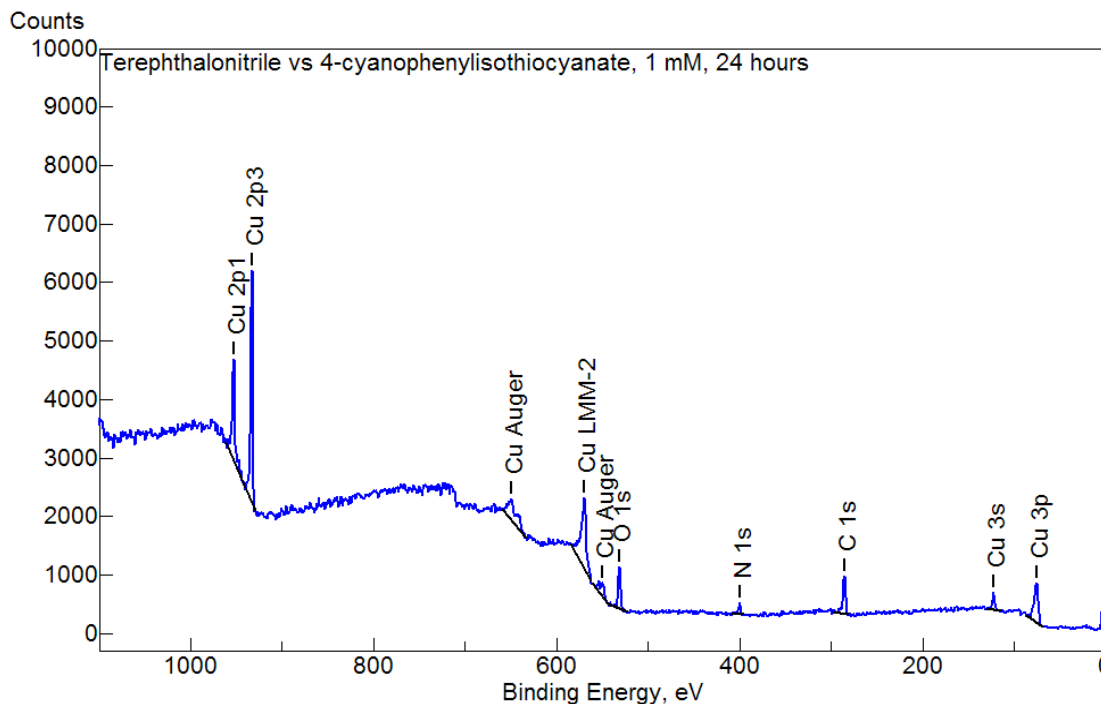


Figure 9. XPS analysis after competitive adsorption between terephthalonitrile and 4-cyanophenylisothiocyanate.

The adsorption characteristics of nitrile-substituted benzenes varies depending on the metal substrate. For example, benzonitrile adsorbs on Cu(111) and Au(111), with both nitrile and ring plane axes parallel to the surface, while on Ni(111) and Rh(111), the conjugation between the nitrile group and phenyl ring is broken to accommodate η^2 (N,C) bonding through the nitrile group alone.^[25, 79, 118] In the present case, the PM-IRRAS spectrum (not shown), revealed no peaks which could be assigned to the nitrile group or to the phenyl backbone. Adsorption in either η^1 (N) configuration, as expected for metal-nitrile compounds in bulk form, or in η^2 (N,C) configuration, as proposed for

some alkane dinitriles on Cu, would result in the molecule having a free nitrile group protruding away from the surface, with an IR-visible vibration somewhere in the vicinity of the gas phase frequency of 2270 cm^{-1} .^[23, 25, 26] The lack of peak intensity in this region demonstrates that both nitrile groups, and hence the phenyl ring, are adsorbed flat and parallel to the surface.

4.2.2 Carboxylic acid versus nitrile

Figure 10 shows the XPS spectrum after competitive adsorption between terephthalic acid ($\text{HOOC}-\phi-\text{COOH}$) and terephthalonitrile at a concentration of 1 mM each, for 18 hours. Carbon and oxygen peaks were detected at approx. 284.8 eV and 531.8 eV, respectively, while no nitrogen peak was detected in the XPS spectrum. This is consistent with preferential adsorption of terephthalic acid over terephthalonitrile. The high resolution carbon spectrum confirms the assignment of the carbon peak to carboxylic acid. In the peak fit for C 1s, shown in Figure 11, there are three peaks at 284.8 eV, 286.0 eV, and 288.6 eV, corresponding to aromatic carbon, carbon adjacent to either carboxylic acid group, and carbon in carboxylic acids groups, respectively.^[119] This indicates that the carboxylic acid group has a higher affinity for ambient Cu than the nitrile group. Since the nitrile group has a stronger affinity for ambient Cu than isothiocyanate, terephthalic acid should also preferentially adsorb over isothiocyanate, and this was confirmed with XPS. Hence, the order of preferential adsorption is $-\text{COOH} > -\text{CN} > -\text{NCS}$. A similar preference for carboxylic acid over nitrile has been observed for cyanobenzoic acid on Ag, which adsorbs through the COOH group.^[23]

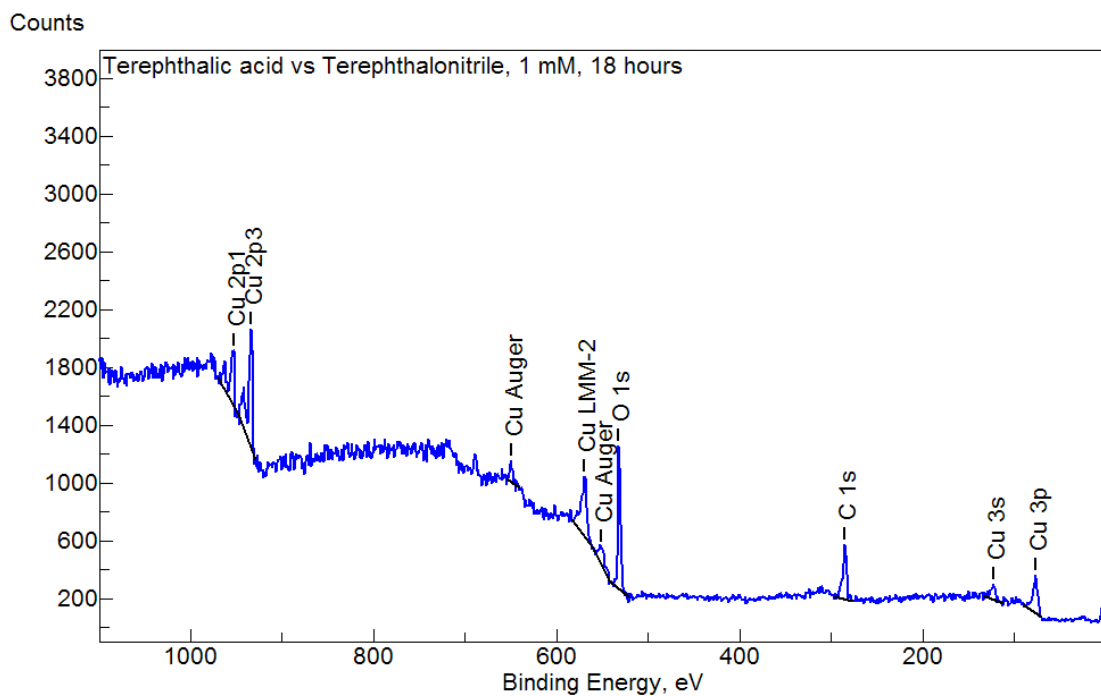


Figure 10. XPS analysis after competitive adsorption between terephthalic acid and terephthalonitrile. The absence of nitrogen shows that no terephthalonitrile has adsorbed.

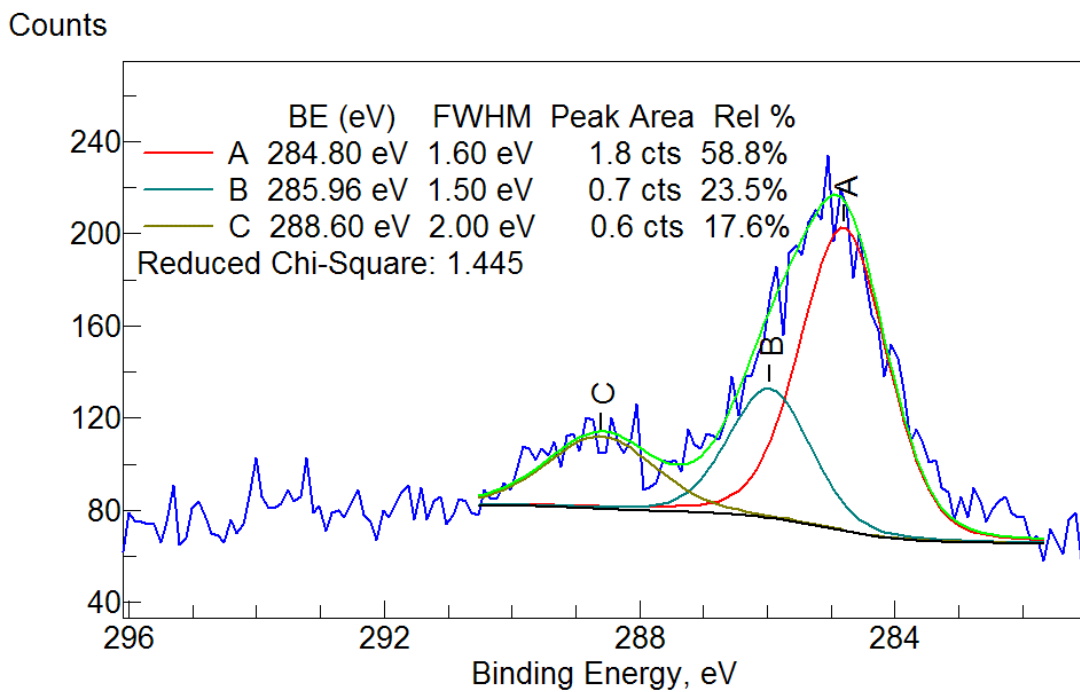


Figure 11. Carbon peak after competitive adsorption between terephthalic acid and terephthalonitrile.

Figure 12 shows the PM-IRRAS spectra in the 1200 to 1800 cm^{-1} region after competitive adsorption between terephthalic acid and terephthalonitrile (bottom) and between terephthalic acid and p-phenylene diisothiocyanate (top), at a concentration of 1 mM for 18 hours. Both spectra exhibit similar features, consisting of absorption peaks at 1407 cm^{-1} , 1433 cm^{-1} , and 1585 cm^{-1} , corresponding to the symmetric stretch of free COO^- , the symmetric stretch of COO^- bonded to the surface, and the asymmetric stretch of bonded COO^- , respectively.^[120-122] The asymmetric stretch of free carboxylate groups is presumed hidden in the low frequency shoulder of the peak at 1585 cm^{-1} . The peak at 1600 cm^{-1} is assigned to the in-plane vibration mode of the phenyl ring, and the peak at 1507 cm^{-1} is identified as the vibration along the long (4,4') axis of the phenyl ring.^[121, 122] Based on the presence of vs absorption peaks and the in-plane stretching vibrations of the phenyl ring, terephthalic acid must be adsorbed in a upright, but tilted configuration, through one COO^- group, with the other oriented away from the surface. This configuration, in which the carbons of the carboxylic acid groups bonded to the surface experience slightly different chemical environments compared to the carbons of the pendant groups, is consistent with the broad (2 eV) XPS carbon peak at 288.6 eV.^[123]

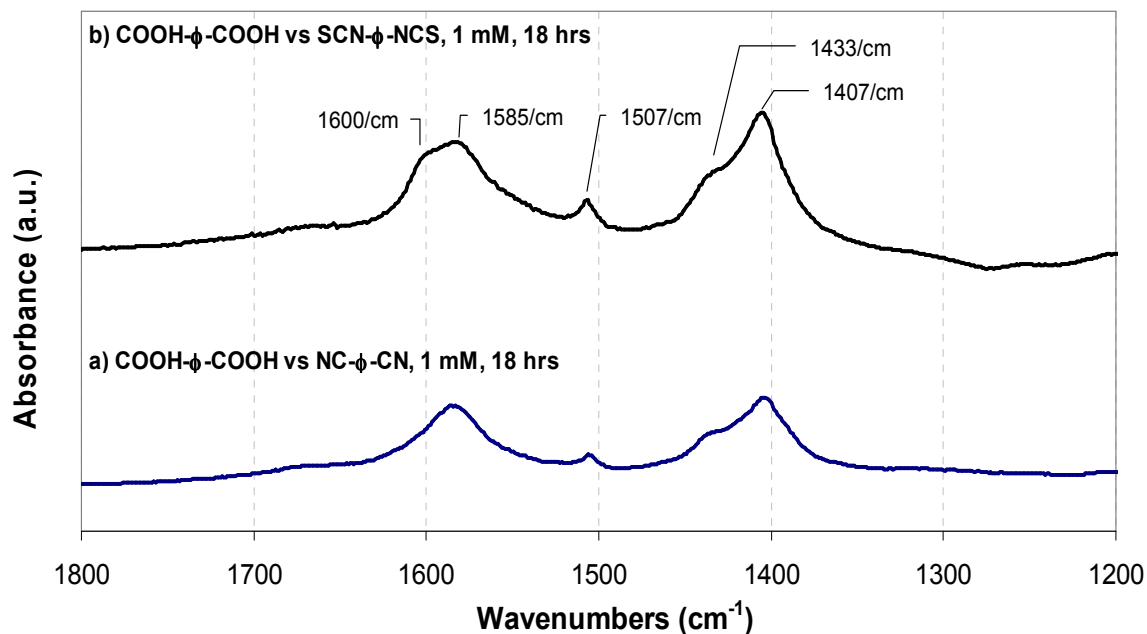


Figure 12. PM-IRRAS analysis after competitive adsorption between terephthalic acid and terephthalonitrile (bottom) and p-phenylene diisothiocyanate (top) for 18 hours.

Some of the PM-IRRAS scans revealed an additional peak around 1700 cm^{-1} , which is in the range expected for the C=O stretch of side-by-side, or “polymeric” hydrogen-bonded carboxylic acid groups.^[124, 125] Several vibration peaks associated with ring stretching along the 4,4' axis of the phenyl ring were also observed. As shown in Figure 13, samples immersed for an extended adsorption time of 3 weeks prior to analysis exhibited higher intensity of the peaks for the COO^- stretching and the phenyl ring stretching vibrations, while the peak intensity in the range of 1700 to 1740 cm^{-1} completely vanished. Taken together, these observations are consistent with formation of a single layer OOTF adopting an increasingly surface-perpendicular molecular orientation over time.

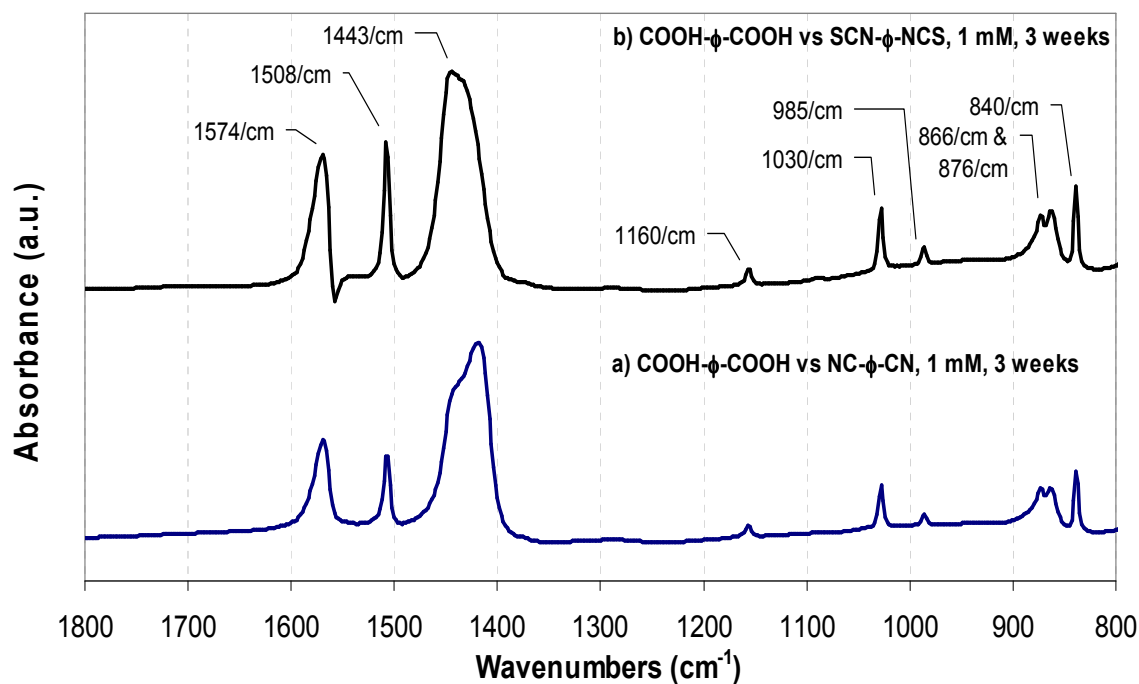


Figure 13. PM-IRRAS analysis after competitive adsorption between terephthalic acid and terephthalonitrile (bottom) and p-phenylene diisothiocyanate (top) for 3 weeks. Note vibration peaks associated with phenyl ring stretching at 1160, 1030, 985 cm^{-1} , and 840 cm^{-1} .

4.2.3 Thiol versus carboxylic acid

Figure 14 shows the XPS analysis after competitive adsorption between 1,4-benzenedithiol ($\text{HS-}\phi\text{-SH}$) and terephthalic acid at a concentration of 5 mM, for 24 hours. The presence of carbon and sulfur peaks at approx. 285 eV, 164 eV and 228 eV is consistent with adsorption of thiol on the surface.

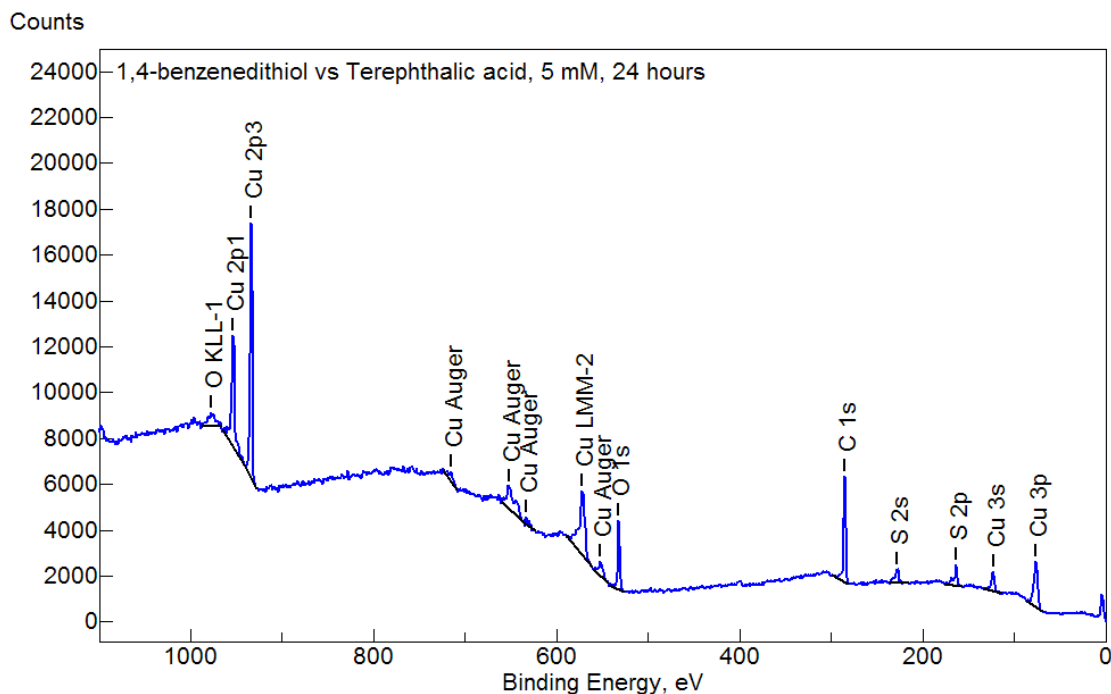


Figure 14. XPS analysis after competitive adsorption between 1,4-benzenedithiol and terephthalic acid.

The peak fit for the C1s peak, shown in Figure 15a, exhibits two peaks, at 284.8 eV and 286.2 eV, corresponding to aromatic carbon and carbon adjacent to thiol, respectively.^[126] Significantly, there is no intensity in the region of 288 to 289 eV, which indicates that no adsorption of carboxylic acid has occurred. This demonstrates that 1,4-benzenedithiol preferentially adsorbs over terephthalic acid. Hence, the order of preferential adsorption is $-\text{SH} > -\text{COOH} > -\text{CN} > -\text{NCS}$. This is consistent with previous work showing that COOH-terminated alkanethiols chemisorb on Cu through the thiol group rather than through the carboxylic acid group and that alkanethiols end-functionalized with the nitrile group adsorb through the thiol group.^[22, 125, 127, 128]

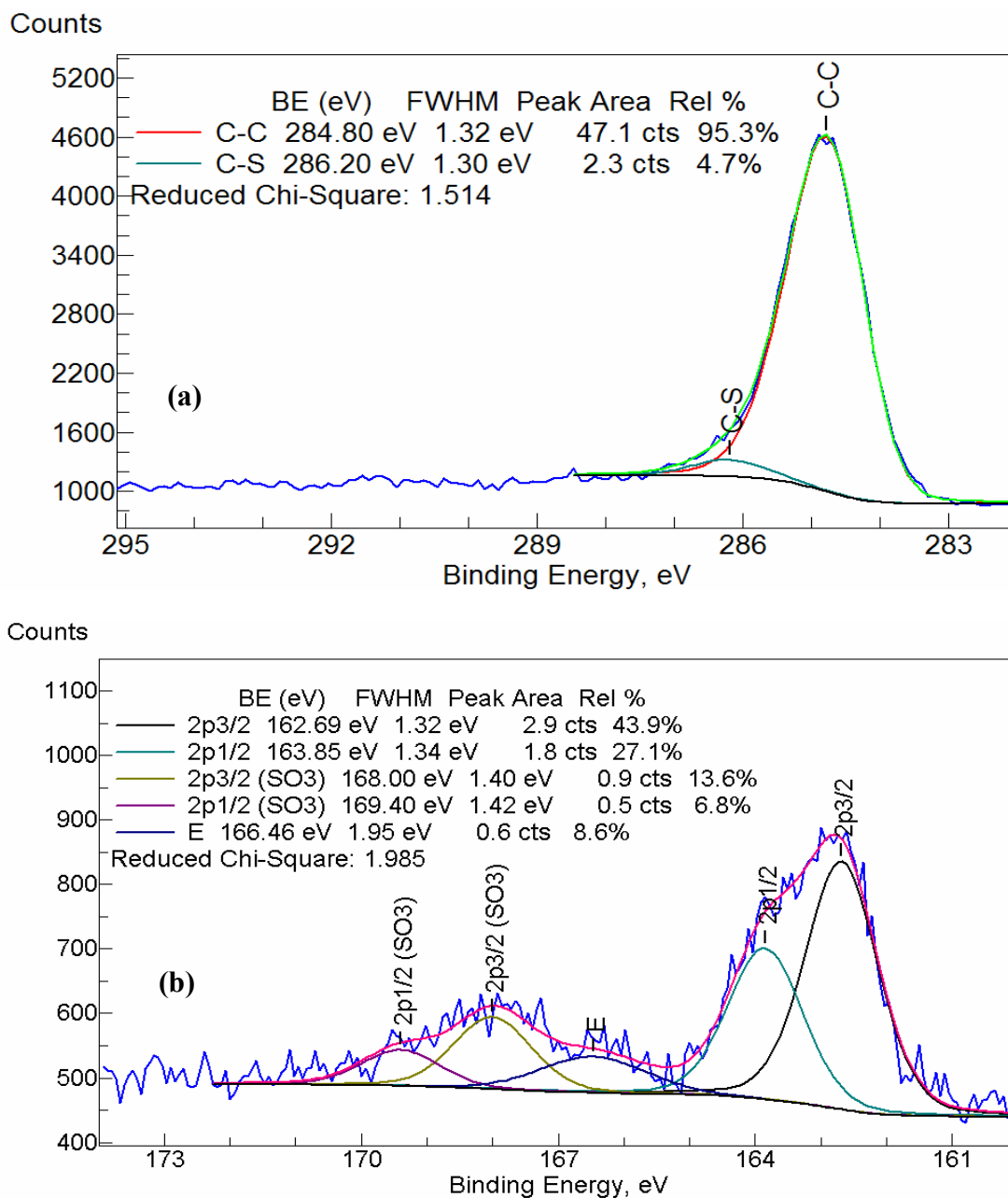


Figure 15 (a) Peak fitting of carbon peak of Figure 14. Note that no peak intensity is observed in the range of 288 eV to 289 eV. This shows that no carbon is present as C=O, hence, no terephthalic acid has adsorbed. (b) Sulfur peak of Figure 14, showing that significant oxidation of free thiol groups to sulfonate occurred after 24 hours adsorption time.

Figure 15b shows the sulfur peak after 24 hours adsorption. In addition to the main 2p_{3/2} / 2p_{1/2} doublet with 2p_{3/2} centered at 162.9 eV, corresponding to thiolate, there is also a second doublet with 2p_{3/2} centered at 168.0 eV. Since aromatic thiols are known to oxidize, even under conditions where the oxygen content of the adsorption system is minimized (i.e., by N₂ flushing and deoxygenation of solvent prior to sample immersion), the peak in the high binding energy region is assigned to sulfur in sulfonate groups.^[86, 88, 129, 130] The oxidation of thiol to sulfonate increased dramatically when the concentration was increased to 5 mM and the adsorption time extended to 1 week. In parallel, the ambient Cu surface was observed to undergo further oxidation to Cu(II), as evidenced by the appearance of a broad satellite (shake-up) peak between the Cu 2p_{3/2} and 2p_{1/2} peaks, shown in Figure 16. It has been suggested based on previous findings that the oxidation of thiol to sulfonate and the oxidation of Cu (I) to Cu (II) may be related processes.^[88]

OOTFs formed from COOH-terminated alkanethiols chemisorb on Cu have been noted for surface pitting.^[86] This was also observed in the present study for an OOTF of mercaptoundecanoic acid on ambient Cu. Defects are thought to be introduced by inversion, whereby an occasional COOH group bonds to the Cu in lieu of thiol, and by the formation of hairpin bonds, or “loops”, where both terminal functionalities group have bonded to the surface.^[82]

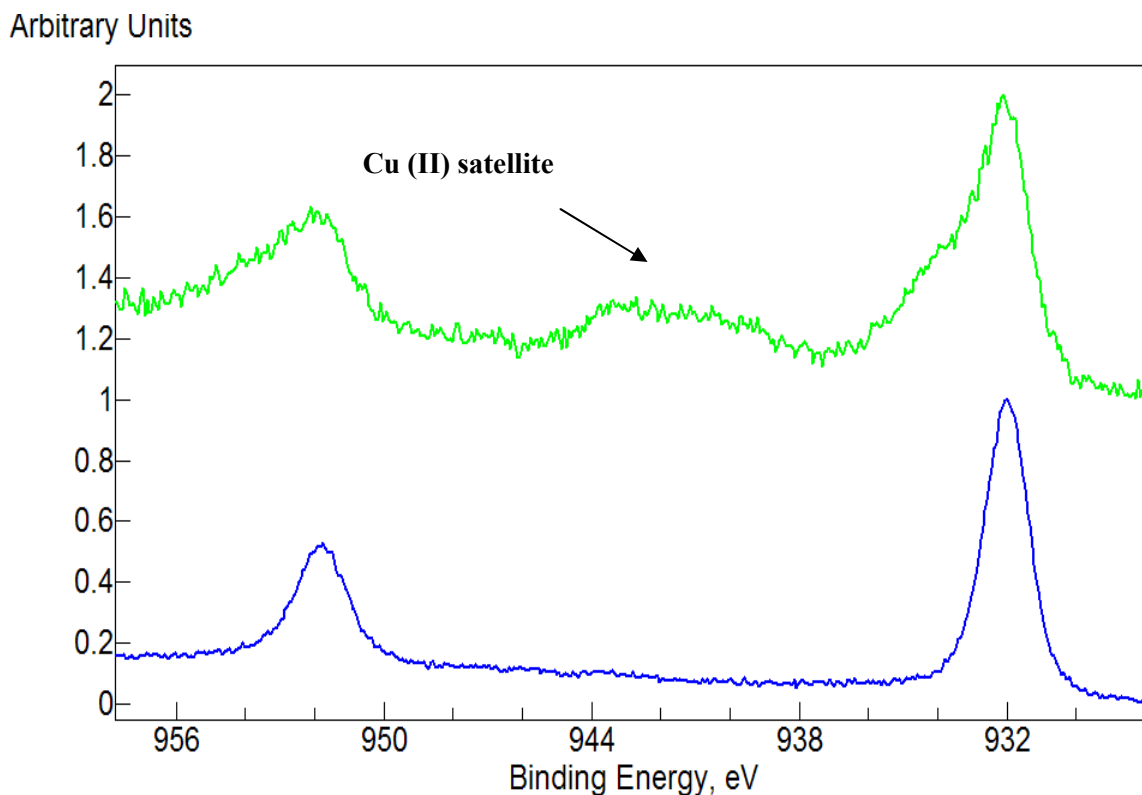


Figure 16. Cu 2p region after competitive adsorption between 1,4-benzenedithiol and terephthalic acid at a concentration of 5 mM for 24 hours (bottom) and 1 week (top). Note satellite peak in top spectrum.

If present, a standing up phase OOTF of 1,4-benzenedithiol should be identifiable in PM-IRRAS by the absorption peaks of the phenyl ring, which occur at approximately 1012, 1550 and 1600 cm^{-1} .^[129] In addition, when oxidized sulfur species are present, a distinct sulfonate peak is expected in PM-IRRAS at approx. 1169 cm^{-1} .^[86, 129] However, no peaks corresponding to the phenyl ring, thiol or sulfonate groups were observed in the PM-IRRAS analysis after competitive adsorption between 1,4-benzenedithiol and

terephthalic acid for 24 hours. Extending the adsorption time to 1 week had no effect on the PM-IRRAS results. This demonstrates that when 1,4-benzenedithiol adsorbs on ambient Cu, it forms a lying down phase OOTF bonding through both terminal groups. Difunctional molecules may become kinetically trapped in lying down configuration if the interaction between their terminal functional groups and the substrate is strong enough, even though the standing up phase would be energetically more favorable. This appears to be the case for benzene dithiol on ambient Cu. To investigate whether the failure to obtain a standing up phase is due to a strong interaction between the phenyl ring and the ambient Cu surface, a concentrated (50 mM) solution of 1,6 hexanedithiol was allowed to self-assemble on ambient Cu for 72 hours, for comparison. Also in this case, the XPS spectra (not shown) confirmed that dithiol was present, with incipient oxidization of thiol to sulfonate. However, no peaks were observed in the methylene or sulfonate stretch regions, ruling out the presence of both standing up and hairpin bonded species. This demonstrates that 1,6-hexanedithiol adopts a flat configuration on ambient Cu. A lying down configuration has also been described for 1,8-octanedithiol on Au and Ag substrates.^[24]

4.2.4 Isocyanide versus carboxylic acid

Figure 17 shows the XPS analysis after competitive adsorption between 1,4-phenylene diisocyanide (CN- ϕ -NC) and terephthalic acid, at a concentration of 5 mM for 24 hours. The carbon and nitrogen peaks detected at approx. 284.8 eV and 400 eV, respectively, are consistent with adsorption of phenylene diisocyanide. Both carbon and nitrogen peaks are highly asymmetric, requiring three peaks to obtain $\chi^2 < 2$.

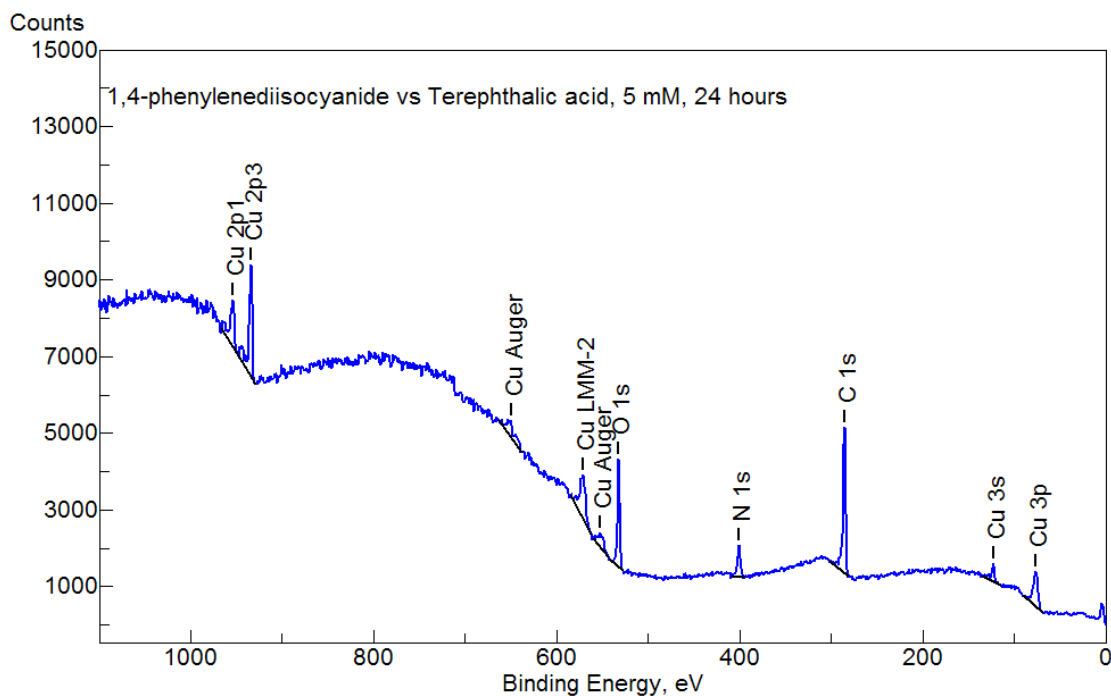


Figure 17. XPS analysis after competitive adsorption between 1,4-benzenedithiol and terephthalic acid.

The peak fit for the carbon C1s peak, shown in Figure 18a, has significant asymmetry on the high binding energy side, and can be fitted with three peaks, at 284.8 eV, 286.1 eV, and 287.6 eV. Carbon atoms in isocyanide groups experience a relatively strong upward chemical shift. For example, in methyl isocyanide (gas phase), the isocyanide group causes a high chemical shift of 2.5 eV on the carbon of the adjacent methyl group, while the carbon of the isocyanide group itself is shifted an additional 0.7 eV.^[131] In the present case of chemisorbed, π -conjugated diisocyanide, chemical shifts are affected by the donation of σ -electrons from the bonded isocyanide group to surface Cu atoms, back-bonding of electrons from Cu to the antibonding π^* orbitals of the bonded isocyanide group, and conjugation effects.^[119] The broad binding energy peak at 287.6 eV is tentatively assigned to carbon in both bound and free isocyanide groups, the middle

binding energy peak at 286.1 to carbon atoms adjacent to isocyanide groups, and the main peak at 284.8 eV to aromatic carbon, as usual.

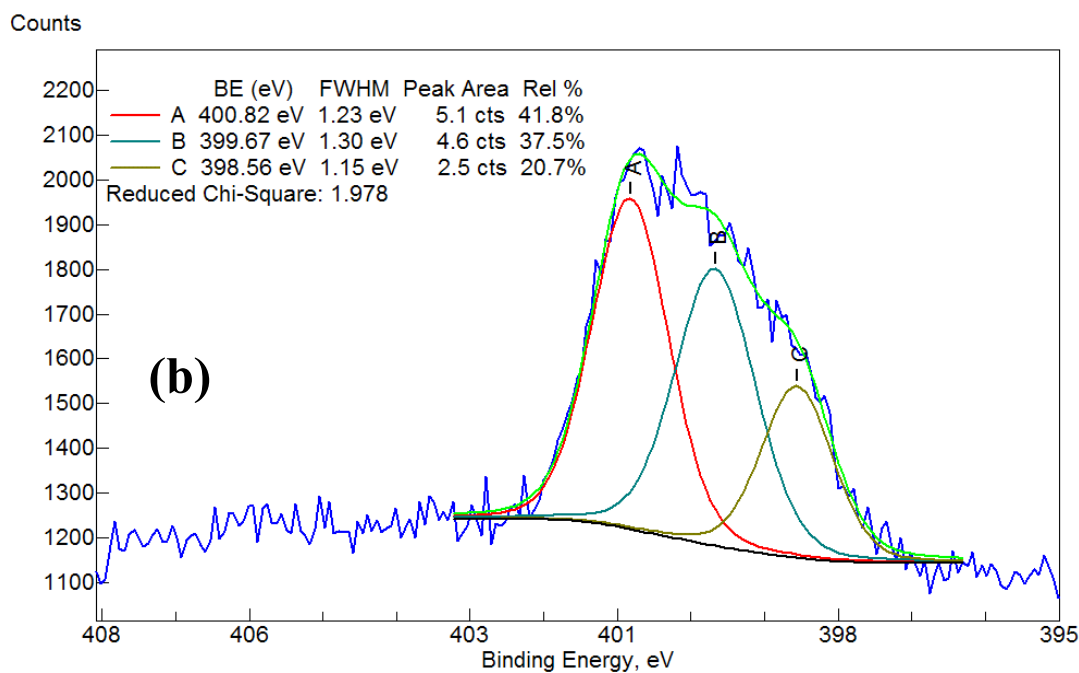
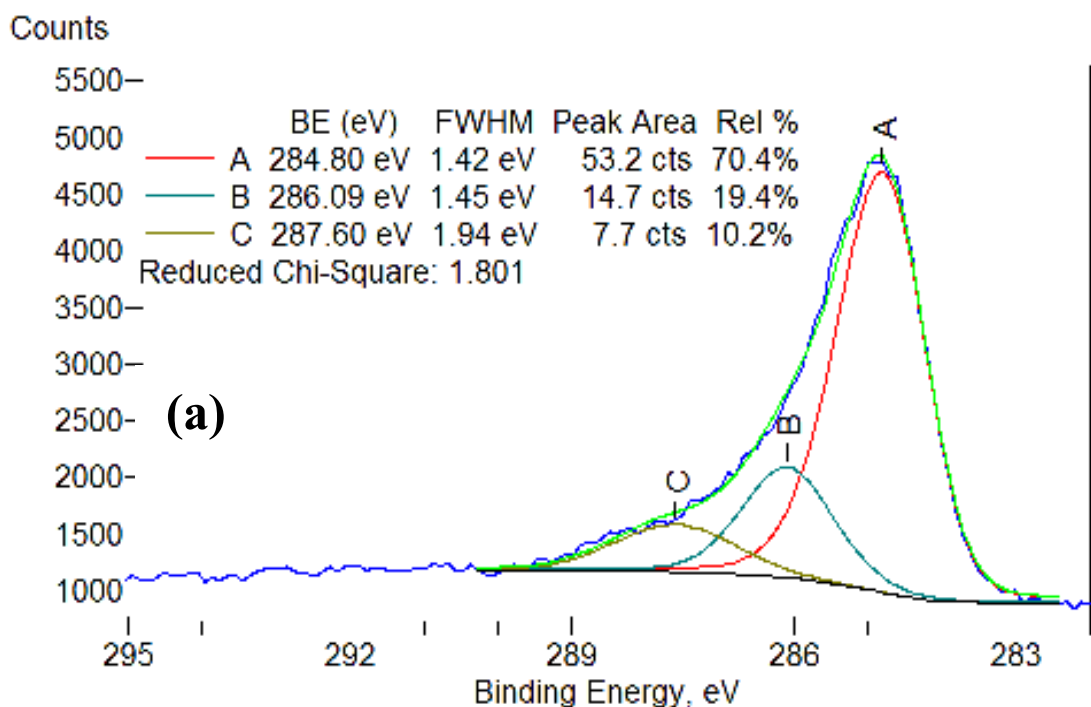


Figure 18. (a) Peak fitting of carbon C1s peak of Figure 17. (b) Peak fitting of nitrogen N1s peak of Figure 17.

The broad, high binding energy peak has some intensity in the region 288 to 289 eV, which might indicate the presence of carboxylic carbon. However, no absorption peaks for COO⁻ or COOH groups were detected in the PM-IRRAS spectrum. This demonstrates that coadsorption of terephthalic acid in the OOTF is negligible, and that 1,4-phenylene diisocyanide preferentially adsorbs over terephthalic acid. This indicates that the isocyanide group has a higher affinity for ambient Cu than the carboxylic acid group. Hence, the order of preferential adsorption is -NC > -COOH > -CN > -NCS.

The N1s peak, shown in Figure 18b can be fitted with three peaks, at 400.8 eV, 399.7 eV and 398.6 eV. The peaks at 400.8 eV and 399.7 eV are tentatively assigned to bonded and free isocyanide group, respectively. The peak at 398.6 eV may indicate that some isocyanide groups have converted to imine groups as a result of rehybridization.^[26, 132, 133] Possible explanations for this are oligomerization of terminal isocyanide groups to polyisocyanide, which has already been described on Au and Pt, or μ^2 - η^1 bridge-bonding, which has been observed on Pt at high coverage.^[77, 85, 119, 134] In the PM-IRRAS spectrum, Figure 19, there is no peak intensity in the range of 1580 to 1800 cm⁻¹ which could be assigned to an imine stretch, and hence the presence of an μ^2 - η^1 bridge-bonded configuration is unlikely.^[77, 85, 134, 135] The low binding energy peak at 398.6 eV is therefore presumed due to the presence of polyisocyanide. Based on the absence of peak intensity in the imine region of PM-IRRAS, its most likely source is polyisocyanide adsorbed on top of the OOTF. This has previously been suggested for 1,4-phenylene diisocyanide on Au based on angle resolved XPS and UPS data.^[136] When the competitive adsorption between 1,4-phenylene diisocyanide (CN- ϕ -NC) and terephthalic acid was conducted with higher initial concentrations and longer adsorption periods, the

Cu peak intensity was attenuated, consistent with increased adsorption of polyisocyanide on the surface of the OOTF, as shown in Figure 19.

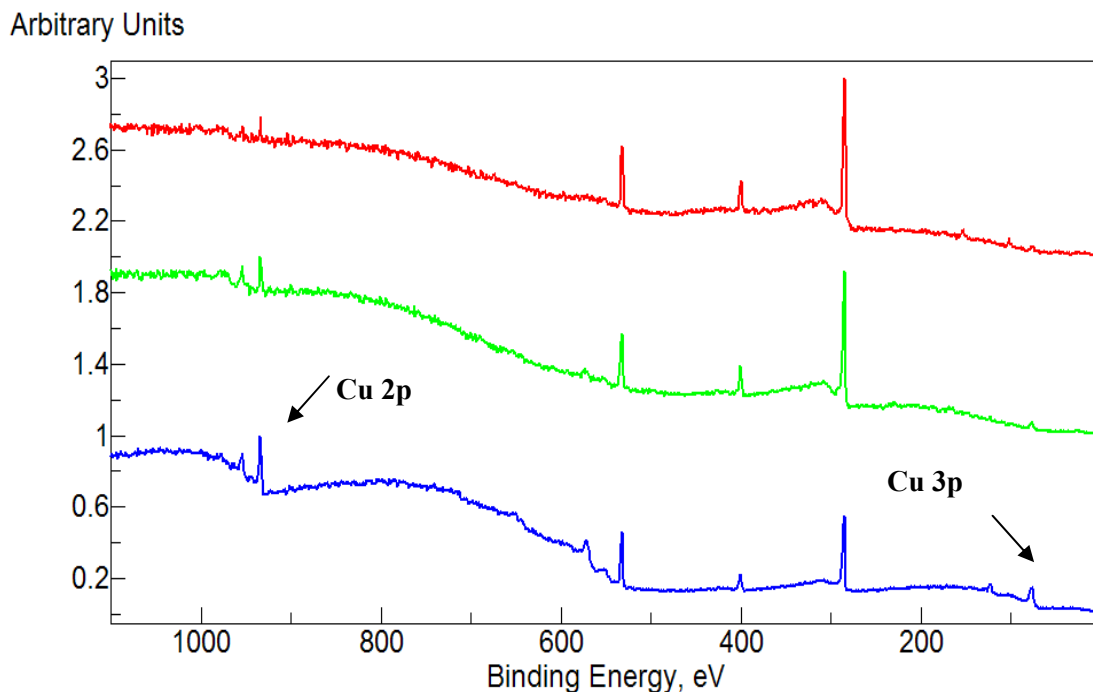


Figure 19. XPS spectra after competitive adsorption between 1,4- phenylene diisocyanide and terephthalic acid at a concentration of 5 mM, 24 hours. (bottom), 5 mM, 1 week (middle), and saturated solution, 72 hours (top).

Figure 20 shows the PM-IRRAS spectrum after competitive adsorption between 1,4-phenylene diisocyanide (CN- ϕ -NC) and terephthalic acid. At a concentration of 5 mM for 24 hours (bottom), very weak, but distinguishable peaks were observed at 1500 cm^{-1} and 1600 cm^{-1} . These peaks are identified as vibration modes of the phenyl ring.^[23, 129] In addition, a single, broad isocyanide peak is seen around 2160 cm^{-1} . In the PM-IRRAS spectrum after competitive adsorption from a 50 mM (saturated) solution for 72 hours (top), the ring stretching peaks have increased significantly in intensity,

demonstrating that the phenylene diisocyanide has adopted a more surface-perpendicular configuration on the ambient Cu surface. In spectrum 13b, the isocyanide peak is resolved as two peaks, at 2165 cm^{-1} and 2125 cm^{-1} , corresponding to surface-bonded and free isocyanide groups, respectively. This spectrum is comparable to those previously obtained for 1,4-phenylene diisocyanide on Ag and Au.^[23, 137] The observation of only a single, broad isocyanide peak in spectrum 20a (bottom) at 2160 cm^{-1} may be attributed to an overlap between free and bonded isocyanide stretching vibrations for the following reasons: (1) With flexible backbone diisocyanides, a single isocyanide stretching vibration may be observed, if the diisocyanide is adsorbed through both terminal groups, in η^1 bonding configuration (i.e. “hairpin” bonding).^[85] This would be consistent with the single broad peak at 2165 cm^{-1} . However, hairpin bonding configuration is not possible with phenylene diisocyanide due to the rigidity of the conjugated structure.^[134] (2) The peak position observed in PM-IRRAS can not be reconciled with a flat, $\eta^2(\text{C,N})$ bonding configuration through a single terminal group. In this configuration, the dipole moment for the $\eta^2(\text{C,N})$ bond is parallel to the surface, hence IR-silent, and a single peak would be observed for the pendant isocyanide group at 2125 cm^{-1} .^[136] However, this is inconsistent with the PM-IRRAS peak at 2165 cm^{-1} . (3) A significant overlap of free and bonded isocyanide peaks has previously been observed for 1,4-phenylene diisocyanide on Ag and Au, due to high asymmetry on the low frequency side of the bonded isocyanide stretch.^[23, 137]

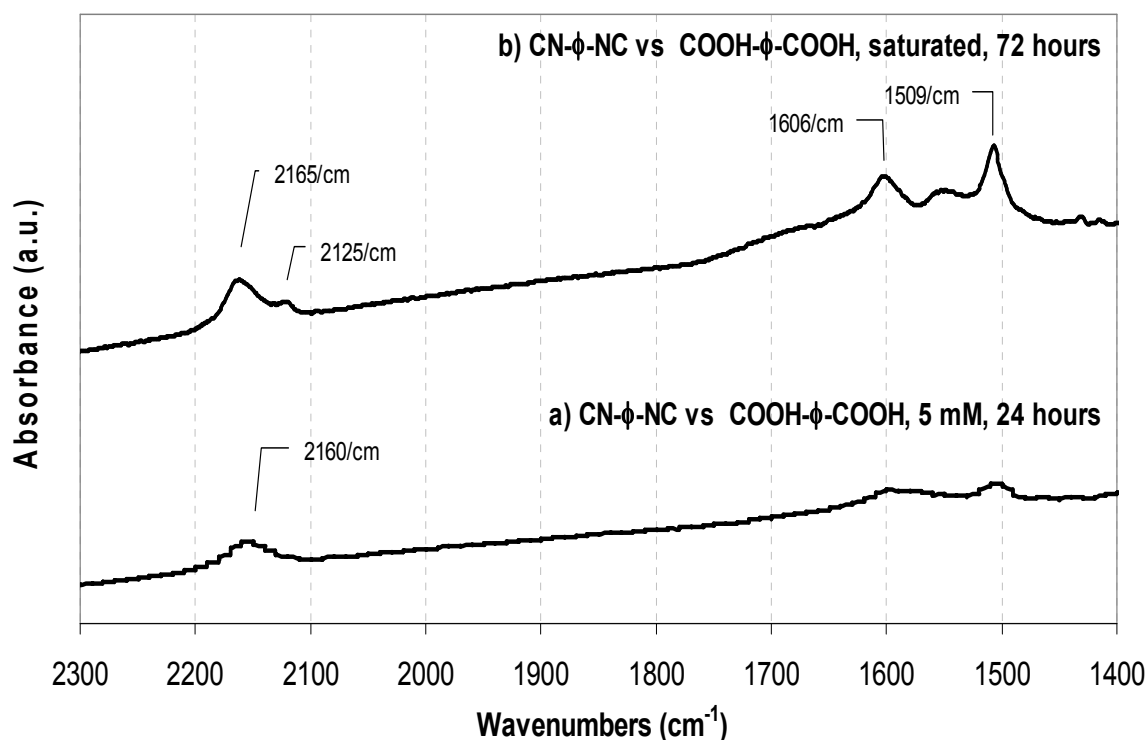


Figure 20. PM-IRRAS spectrum after competitive adsorption between 1,4- phenylene diisocyanide and terephthalic acid.

Hence, the resolution of the single peak of spectrum 20a into two peaks in 20b (top) is probably the result of an increased packing order due to increased concentration and time of adsorption. Interestingly, in spectrum 20b, the free isocyanide stretching peak (2125 cm⁻¹) is much smaller than the bonded isocyanide peak (2165 cm⁻¹) although these peaks should be comparable in intensity. A similar disparity between peaks has also been observed for 1,4-phenylene diisocyanide on Au.^[119, 134] The position of $\nu(\text{CN})$ for the bonded isocyanide group is blue-shifted to 2165 cm⁻¹ compared to 2128 cm⁻¹ for 1,4-phenylene diisocyanide in dichloromethane, while the free group is slightly red-shifted to 2125 cm⁻¹. These shifts are close to those of phenylene diisocyanide on Au and Ag, reported as 2180 cm⁻¹ and 2120 cm⁻¹.^[23, 134] The fact that the pendant isocyanide group exhibits a slight red-shift at 2120 cm⁻¹ indicates that it experiences the increased electron

density in the antibonding π^* orbital of the bonded isocyanide group, due to π -conjugation.^[18, 77, 80, 85, 118, 137-140]

4.2.5 Isocyanide versus thiol

High chemical reactivity between 1,4- phenylene diisocyanide and 1,4-benzenedithiol interfered with competitive adsorption of this two-component system. A 5 mM THF solution of 1,4-phenylene diisocyanide and 1,4-benzenedithiol became cloudy during overnight agitation for 24 hours, changing from clear to a dark orange color, with a significant amount of particulate matter precipitating from solution. This is presumed mainly due to oligomerization of phenylene diisocyanide to polyisocyanide. The PM-IRRAS spectrum, shown in Figure 21, exhibited significant peak intensity in the range of 1650 to 1720 cm^{-1} , while the intensity in the isocyanide stretch region was practically negligible, with a barely discernible peak at approx 2160 cm^{-1} . Strong and distinct peaks were also observed at 1510, 1610, and 1032 cm^{-1} , for the in-plane vibrations of the phenyl ring, and in the sulfonate stretch region 1130 to 1230 cm^{-1} . This is consistent with the formation of a mixed OOTF.

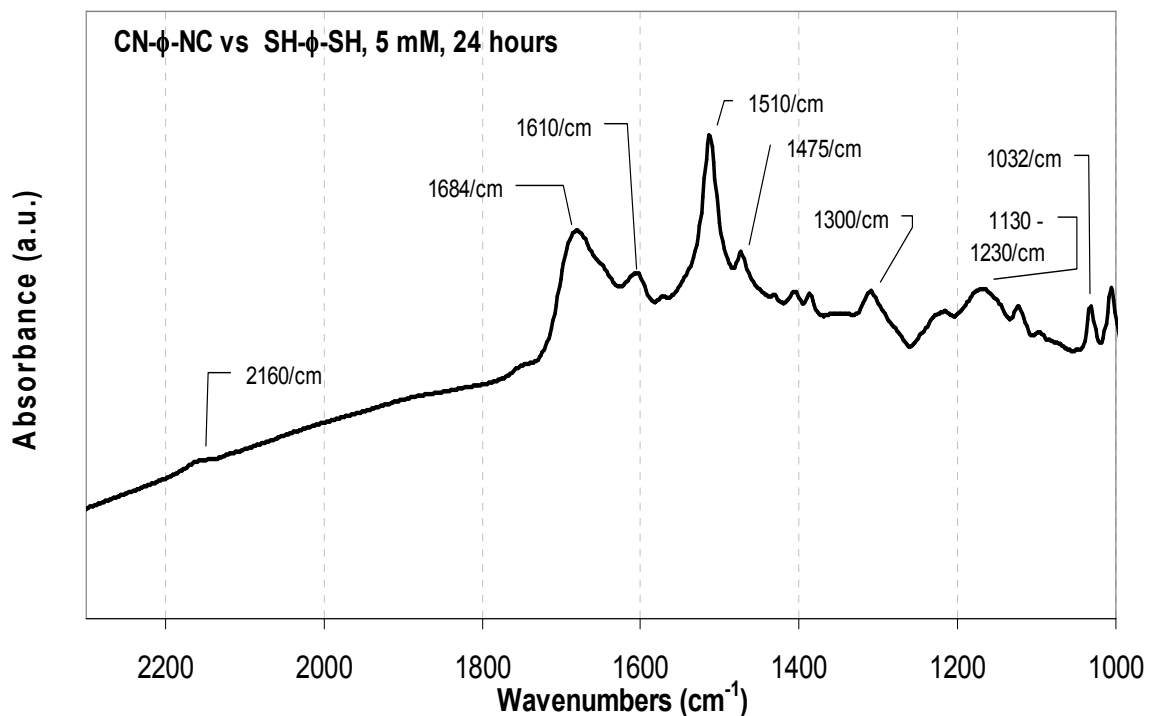


Figure 21. PM-IRRAS scan after competitive adsorption between 1,4- phenylene diisocyanide, and 1,4-benzenedithiol.

Since the reactivity of the two-component system of phenylene diisocyanide and benzenedithiol interfered with the self-assembly process, competitive adsorption was also studied between corresponding aliphatic chain adsorbents, 1,6-hexanedithiol and 1,6-diisocyanohexane. The XPS spectrum of this system shown in Figure 22 is consistent with the conclusion that co-adsorption of dithiol and diisocyanide has taken place to form a mixed OOTF. Both nitrogen and sulfur peaks were observed, with comparable intensity. This is consistent with a mixed OOTF.

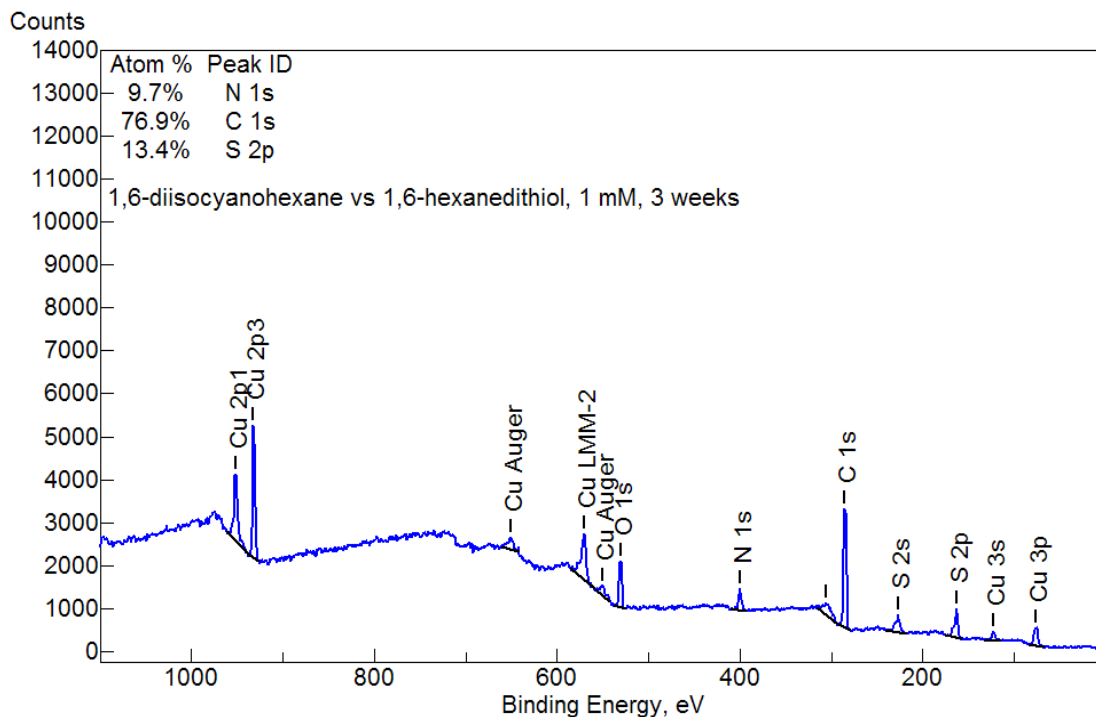


Figure 22. XPS analysis after competitive adsorption between diisocyanohexane and hexanedithiol at a concentration of 1 mM, for 3 weeks.

The peak fit for the C1s peak, shown in Figure 23a, exhibits three peaks at 284.8 eV, 286.0 eV and 286.8 eV corresponding to aliphatic carbon, carbon adjacent to isocyanide, thiol or sulfonate groups, and carbon in isocyanide groups, respectively. The N1s peak, shown in Figure 23b, can be fitted with three peaks at 400.3 eV, 399.2 eV, and 398.3 eV, corresponding to nitrogen in bonded isocyanide groups, free isocyanide groups, and imine groups, respectively. The peak fit for the sulfur 2p peak is shown in Figure 23c. Significantly, the main 2p_{3/2} peak of the 2p_{3/2} / 2p_{1/2} doublet is centered at 162.4 eV, which is indicative of thiol bonded directly to the ambient Cu substrate as thiolate. The doublet with 2p_{3/2} centered at 167.2 eV indicates oxidation of thiol to sulfonate.

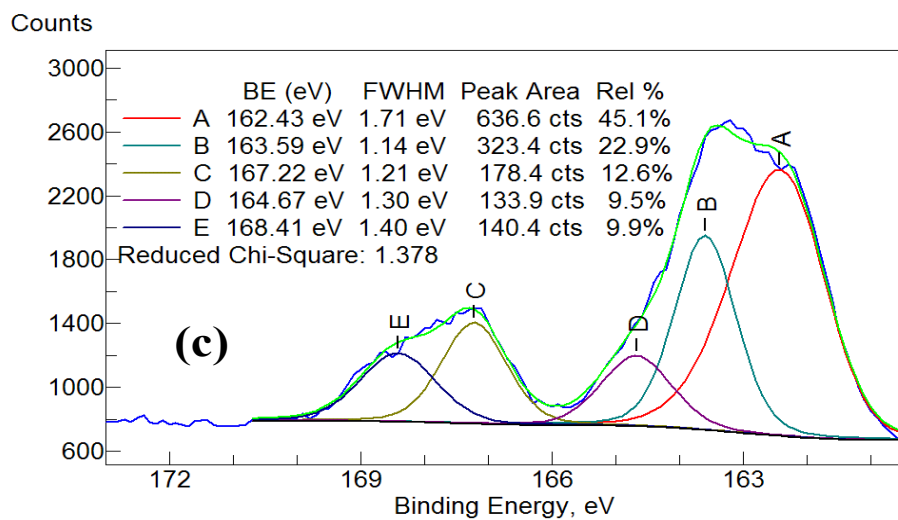
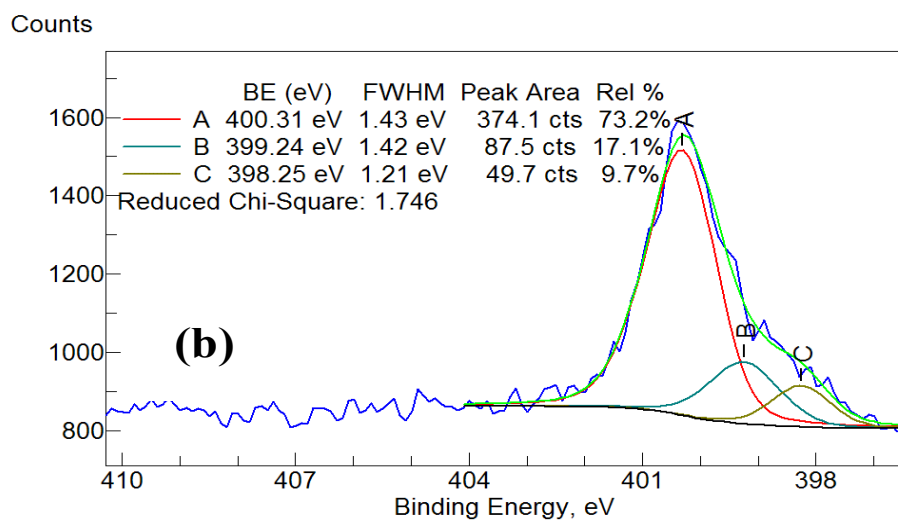
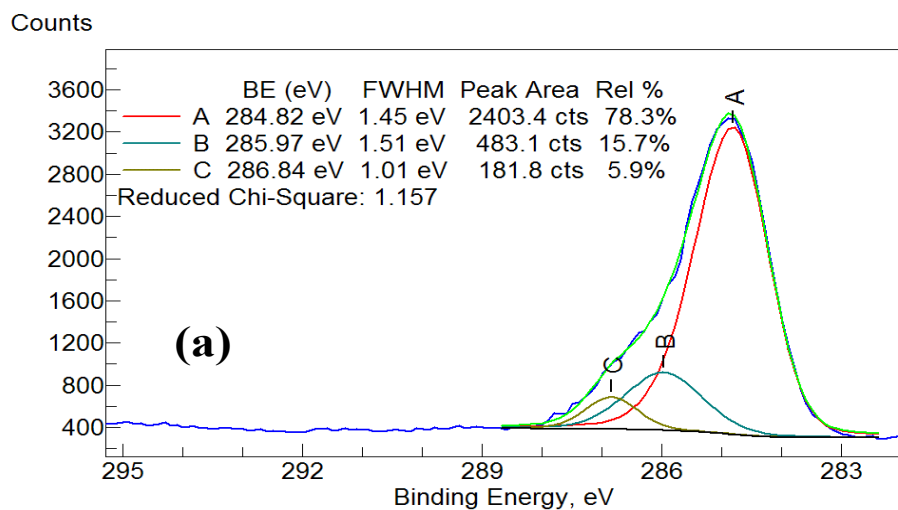


Figure 23. (a) Peak fitting of carbon C1s peak of Figure 22 (b) Peak fitting of nitrogen N1s peak of Figure 22. (c) Peak fitting of sulfur S2p peak of Figure 22.

The PM-IRRAS spectrum for this system is shown in Figure 24a (bottom). There is a strong isocyanide peak at 2189 cm^{-1} . This peak position is higher than that of bulk 1,6-diisocyanohexane at 2146 cm^{-1} , hence it is assigned to η^1 bonded isocyanide groups.^[28] Peaks were observed at 1352 and 1460 cm^{-1} for the methylene wagging and scissors vibrations, and at 2866 cm^{-1} and 2935 cm^{-1} corresponding to the symmetric and asymmetric stretching vibrations of the methylene groups of the hexane backbone.^[21, 85, 124, 141] The positions of the latter peaks indicate a relatively disordered OOTF.^[85, 124] This is consistent with hairpin bonding configuration. The formation of some polyisocyanide is evident from the weak and broad, but distinguishable, peak centered at 1650 cm^{-1} which is in the range expected for an imine stretch. A similar imine peak has been observed between 1580 and 1680 cm^{-1} after self-assembly of diisocyanohexane on Au.^[85] The broad peak at 1207 cm^{-1} is assigned to the stretching vibrations of sulfonate groups, the presence of which was concluded from the XPS sulfur peak. These peak assignments are supported by the PMIRRAS spectra obtained after adsorption from a pure solution of 1,6-diisocyanide at a concentration of 50 mM for 72 hours, shown in Figure 24b (top). Comparing spectra 17a and 17b, the spectra are very similar with the exception of the peaks at 1036 cm^{-1} and 1207 cm^{-1} . This supports the assignment of these peaks to co-adsorbed 1,6-hexanedithiol, which has presumably been induced to adopt a standing up configuration by neighboring diisocyanide molecules. Taken together, the presence of both roughly equal amounts of sulfur and nitrogen in XPS, in conjunction with the identification of thiolate bonds in XPS and surface-bonded isocyanide groups in PM-IRRAS, demonstrates that competitive self-assembly of these two molecules leads to coadsorption of dithiol and diisocyanide as distinct species. This indicates that the

isocyanide and thiol functional groups have similar affinity for ambient Cu. Hence, the final order of preferential adsorption is $-\text{NC} \approx -\text{SH} > -\text{COOH} > -\text{CN} > -\text{NCS}$.

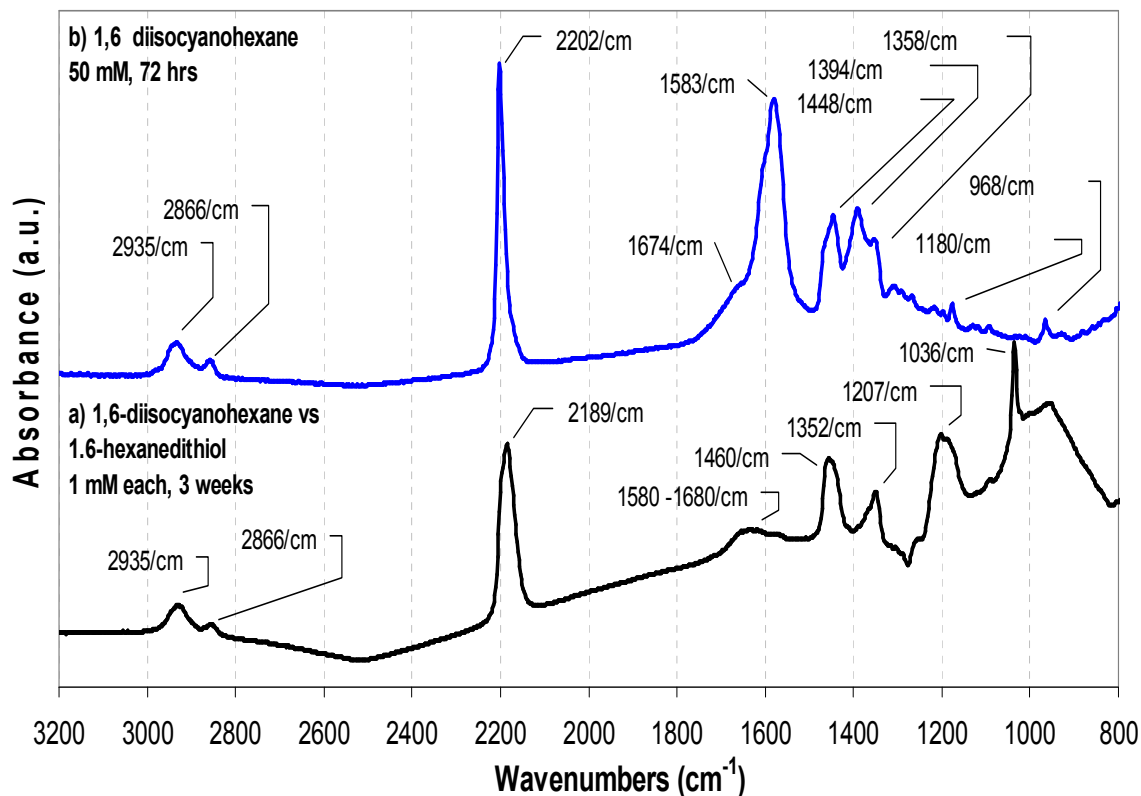


Figure 24. PM-IRRAS analysis after competitive adsorption between diisocyanohexane and hexanedithiol at a concentration of 1 mM, for 3 weeks (bottom) and adsorption from a solution containing only concentrated 1,6- hexanedithiol at a concentration of 50 mM, for 72 hours (top).

4.3 Conclusions

In conclusion, of the difunctional molecules studied in this work, diisocyanide and dithiol have the strongest affinity for ambient Cu. Dithiols tend to become kinetically trapped in a flat configuration on the substrate. In contrast, 1,4- phenylene diisocyanide and 1,4- terephthalic acid both adopt a standing up phase configuration, in which the molecules bonds to the ambient Cu substrate through one terminal functional group, with the other terminal group disposed away from the substrate. The functionalization of Cu

nanoclusters (proposed for future work) should therefore focus on the use of PDI or its oligomeric analogs. Further studies are required to characterize what appears to be a topochemical polymerization of free isocyanide functions of the diisocyanide OOTF.

CHAPTER 5

COMPETITIVE SELF-ASSEMBLY OF PHENYLENE DIISOCYANIDE AND TEREPHTHALIC ACID

5.1 Chapter overview

This chapter compares the competitive self-assembly of 1,4- phenylene diisocyanide (PDI) and 1,4- terephthalic acid (TPA) on Cu, Pt and Ni. In the previous chapter, it was shown that both PDI and TPA adopt a standing up phase configuration on Cu. The self-assembly of these linker molecules was performed also on Pt and Ni substrates. The goal was to determine which of the two linker molecules has the strongest affinity for each substrate and to investigate the feasibility of producing chemically sticky OOTFs on Ni or Pt. For ease of reference, some the results of self-assembly on Cu are reproduced in this chapter, and related to the results of self-assembly on Pt and Ni.

5.2 Competitive self-assembly on nickel

Figure 25 shows the XPS survey spectrum after competitive adsorption between PDI and TA at a concentration of 25 mM, for 18 hours. The presence of carbon and nitrogen peaks at approx. 285 eV and 400 eV, respectively, are consistent with adsorption of PDI. Several factors must be considered in the assignment of these peaks. (1) The isocyanide group may bond to a metal surface through the carbon atom in a terminal fashion, through the carbon atom, or possibly by an inclined $\sigma+\pi$ coordination bond. Alternately, it may undergo hybridization, to enable either a bridge bonding $\mu^2-\eta^1$ configuration, where the terminal carbon bonds to two metal atoms, or η^2 (C,N) di-sigma bonding where both carbon and nitrogen atoms bond to metal atoms.^[16, 28, 78, 118, 133, 142]

These bonding schemes are illustrated as bonding types III and IV, respectively, in Figure 26.^[143]

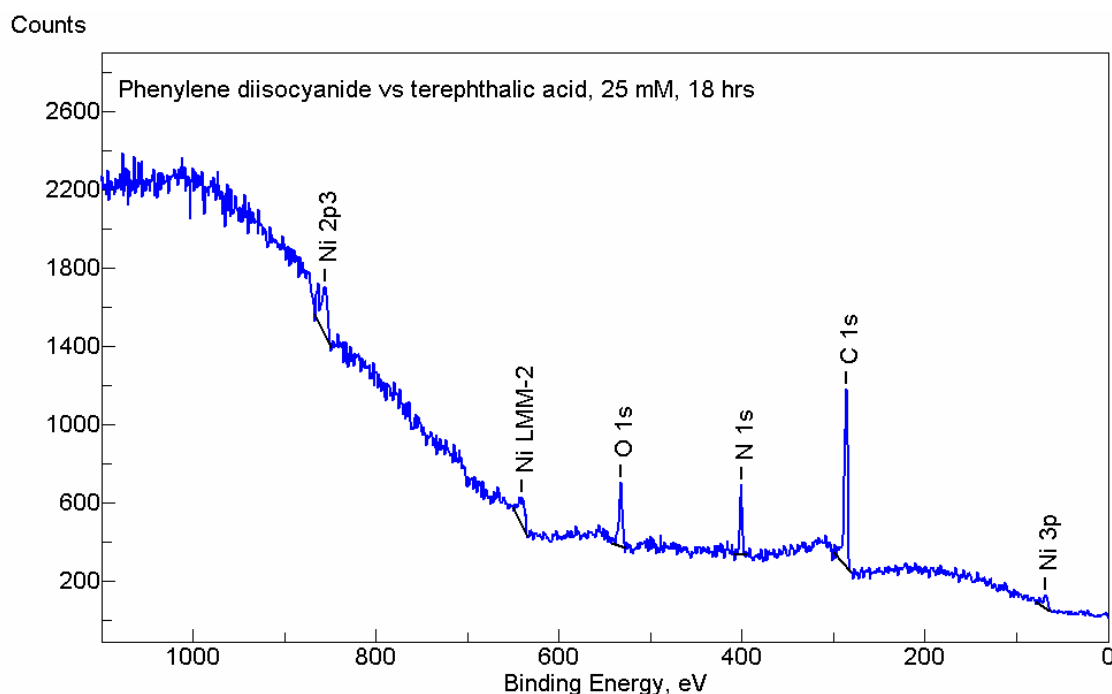


Figure 25. XPS analysis after competitive adsorption between phenylene diisocyanide and terephthalic acid on Ni.

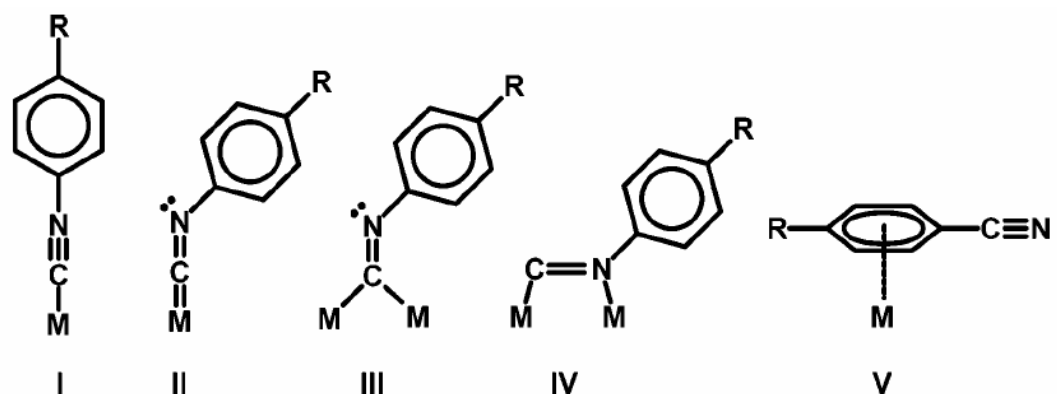


Figure 26. Range of bonding types for aryl isocyanides.^[143]

(2) Aromatic isocyanides are likely to exhibit strong conjugation effects, allowing the isocyanide - metal interaction at one end of the molecule to affect the free isocyanide group.^[119, 134] For example, the isocyanide - metal interaction, may lead to π -electron

donation from the isocyanide group to surface Ni atoms, but also back-bonding of electrons from Ni to the antibonding π^* orbitals of the bonded isocyanide group. (3) The free isocyanide group disposed away from the substrate may undergo oligomerization to form polyisocyanide.^[85] (4) Strong β -substituent effects are expected for the isocyanide group. Both the carbon and nitrogen peaks are highly asymmetric and require three peaks to obtain $\chi^2 < 2$.

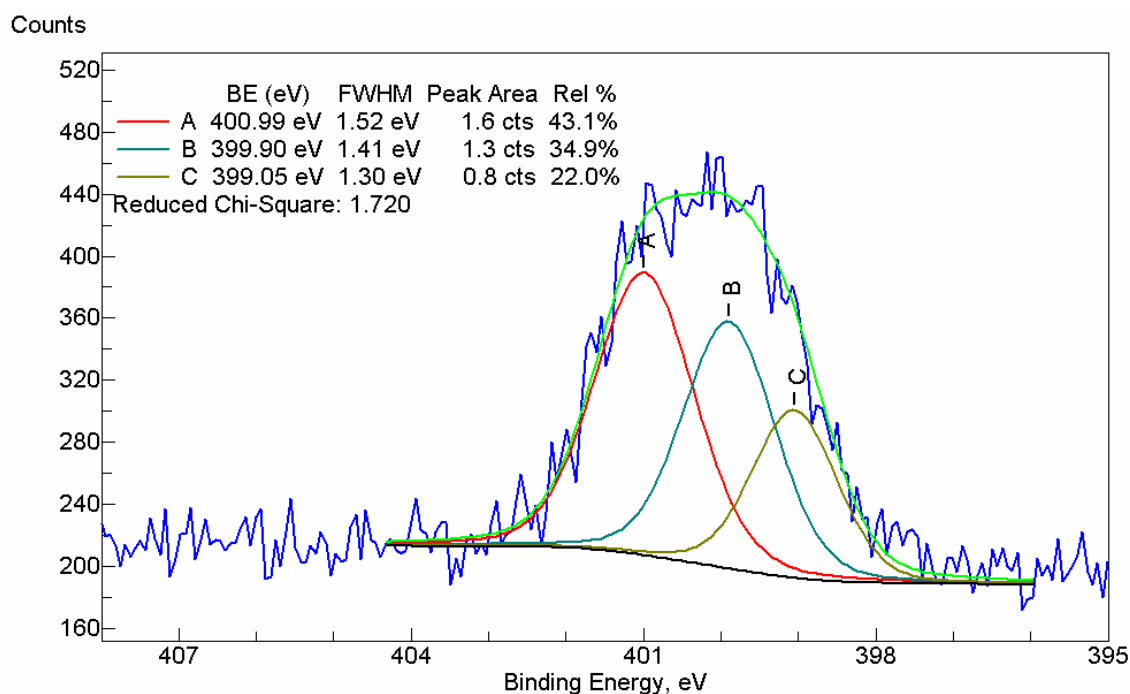


Figure 27. Peak fitting of nitrogen C1s peak of Figure 25.

The C1s peak, shown in Figure 28 can be fitted with three peaks, at 284.8 eV, 286.0 eV, and 287.1 eV. Carbon atoms in isocyanide groups experience a relatively strong upward chemical shift. For example, in methyl isocyanide (gas phase), the isocyanide group causes a chemical shift of 2.5 eV on the carbon of the adjacent methyl group, while the carbon of the isocyanide group itself is shifted an additional 0.7 eV.^[131] Therefore, the highest binding energy peak at 287.1 eV is tentatively assigned to carbon

atoms in free isocyanide groups, while the middle binding energy peak at 286.0 to carbon atoms in either rehybridized surface - bonded isocyanide groups or in polyisocyanide. These peaks are referenced to the main peak at 284.8 eV, which is assigned to aromatic carbon. Significantly, there is no significant peak intensity in the region of 288 to 289 eV, which indicates that no adsorption of carboxylic acid has occurred.^[144] The oxygen peak of Figure 25 is assigned to minor degree of oxidation, presumably of Ni to NiO. The N1s peak, shown in Figure 28 can be fitted with three peaks, at 401.0 eV, 399.9 eV and 399.1 eV.

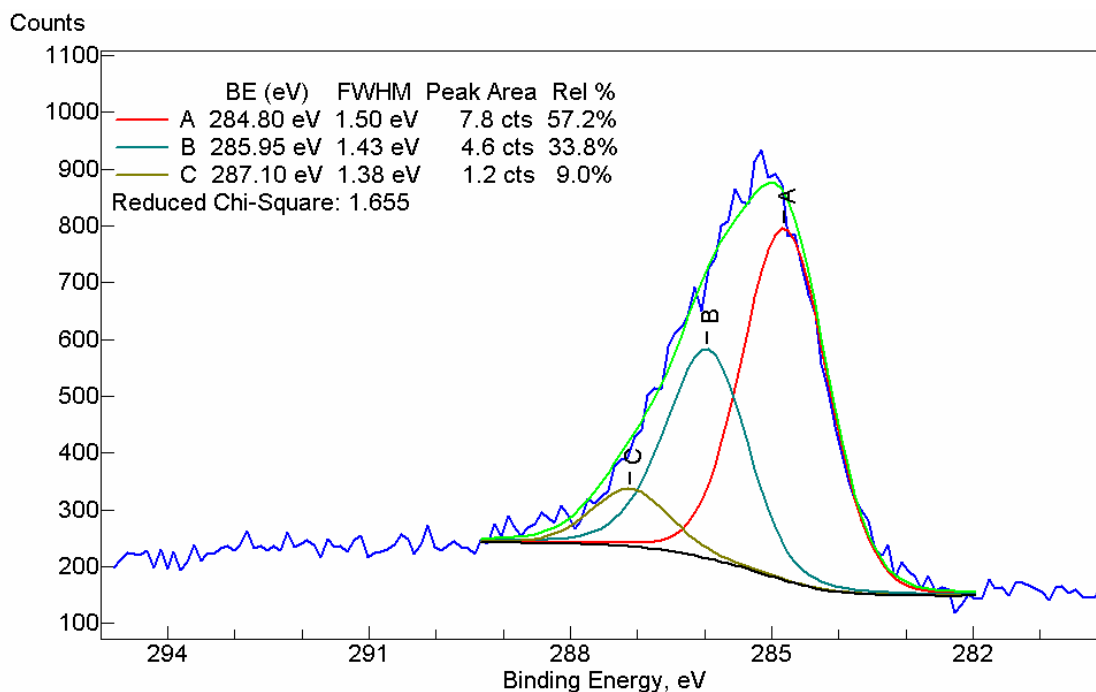


Figure 28. Peak fitting of carbon N1s peak of Figure 25.

The lowest binding energy peak at 399.1 eV is tentatively assigned to nitrogen atoms in imine groups, assuming that some of the pendent isocyanide groups have undergone rehybridization and oligomerization to polyisocyanide.^[23, 85] The peaks at 401.0 eV and 399.9 eV are assigned to nitrogen in free isocyanide groups, and surface

bonded isocyanide groups, respectively. This assignment assumes rehybridization of the surface bonded isocyanide group to allow either μ^2 - η^1 bridge bonding or η^2 (C,N) di-sigma bonding on the Ni surface.^[77, 78] Rehybridization of cyanide groups leading to a reduction in bond order is associated with a shift of N1s to lower binding energy compared to the free cyanide group, and the same should reasonable be expected for the isomeric isocyanide group.^[26, 133, 142] In summary, XPS data demonstrates that PDI preferentially adsorbs over TA on Ni, and this indicates that the isocyanide group has a higher affinity for ambient Ni than the carboxylic acid group.

The PM-IRRAS spectrum, Figure 29, revealed a single peak in the region expected for the isocyanide stretch, at 2120 cm^{-1} . In addition, peak intensity was observed at 1596 and 1500 cm^{-1} , as expected for the in-plane stretching vibrations of the phenyl backbone.

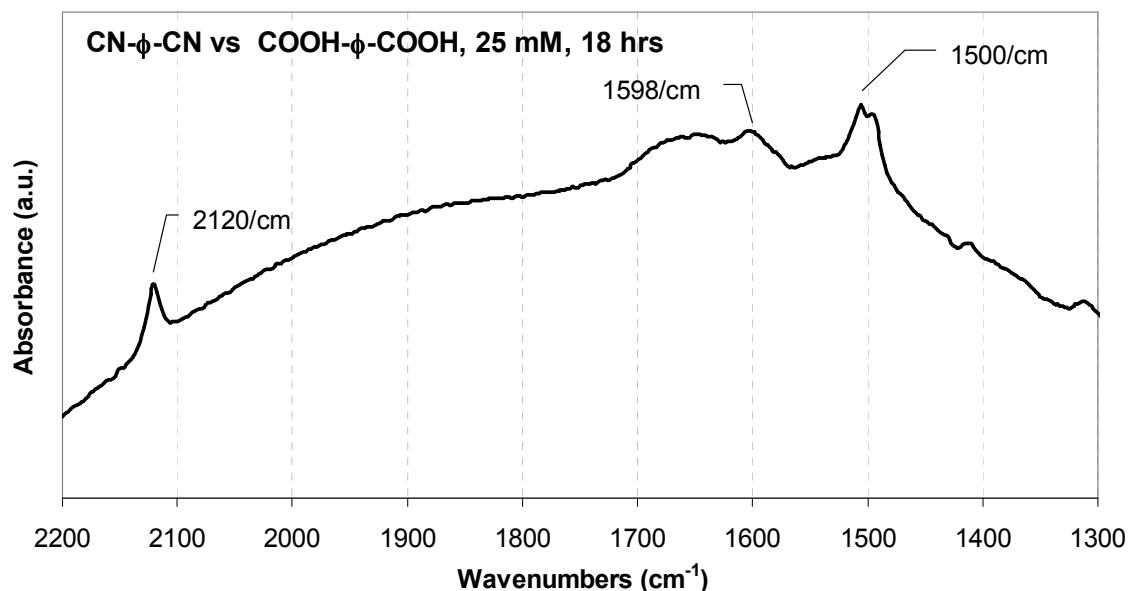


Figure 29. PM-IRRAS analysis after competitive adsorption between phenylene diisocyanide and terephthalic acid on Ni.

If PDI adsorbs with both isocyanide groups, with the phenyl ring lying flat and parallel to the surface, these isocyanide and ring stretch vibrations are all IR-silent in PM-IRRAS mode. On the other hand, when bonding in η^1 terminal configuration, two isocyanide peaks should be observed for PDI, corresponding to bonded and free isocyanide groups, respectively. Therefore, the presence of a single isocyanide peak in conjunction with ring stretch vibrations is consistent with the assumption that the isocyanide groups bond to the metal surface in either bridge bonding μ^2 - η^1 configuration, or in η^2 (N,C) configuration with one isocyanide group bonded to the Ni surface through both carbon and nitrogen atoms, but with the phenyl ring bent and tilted away from the

surface. In the bridge bonding $\mu^2\text{-}\eta^1$ configuration, an imine peak should be observed in the range of 1600 to 1680 cm^{-1} , in addition to the free isocyanide stretch.^[145] In the η^2 (N,C) configuration, one isocyanide group is surface parallel, hence IR-silent, and only the free isocyanide group protruding away from the surface has an IR-visible vibration. The observed isocyanide peak position at 2120 cm^{-1} is consistent with a free isocyanide stretch. There is a slight red-shift compared to 2128 cm^{-1} for 1,4-phenylene diisocyanide in dichloromethane which suggests slightly increased electron density in the antibonding π^* orbital of the bonded isocyanide group, due to π -conjugation throughout the PDI molecule.^[18, 77, 80, 136, 137] The peak intensity observed in the imine stretch region 1620 to 1700 cm^{-1} is consistent with bridge bonding $\mu^2\text{-}\eta^1$ configuration. It is also in the range expected for polyisocyanide. Oligomerization of free isocyanide groups to form polyisocyanide upon adsorption of PDI on Au has previously been described.^[77, 80, 85, 131, 136, 137, 144] Significantly, the presence of the free isocyanide peak confirms that PDI has formed a sticky surface on Ni.

5.3 Competitive self-assembly on copper

Figure 30 shows the XPS analysis after competitive adsorption between PDI and TA at a concentration of 5 mM for 24 hours. The carbon and nitrogen peaks detected at approx. 285 eV and 400 eV, respectively, are consistent with adsorption of PDI. The carbon C1s peak (Figure 31) and the nitrogen N1s (Figure 32) are found to be highly asymmetric, as in the case of PDI on Ni. Each requires three peaks to obtain $\chi^2 < 2$. The N1s peak, shown in can be fitted with three peaks, at 400.8 eV, 399.6 eV and 398.5 eV.

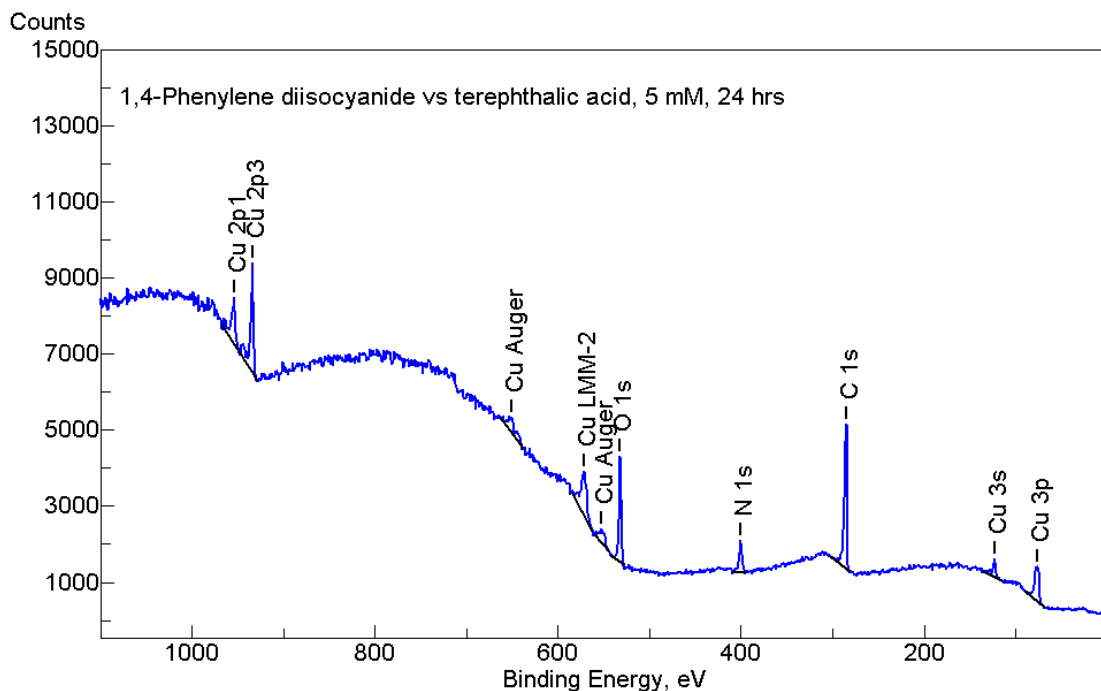


Figure 30. XPS analysis after competitive adsorption between phenylene diisocyanide and terephthalic acid on Cu.

In contrast to the case of PDI on Ni, the high binding energy peak is assigned to surface-bonded isocyanide, while the middle binding energy peak is assigned to free isocyanide group. This assignment assumes η^1 terminal bonding of isocyanide groups on the Cu surface, similar to that on Au and Ag.^[23, 28] As before, however, the peak at 398.5 eV is assigned to isocyanide after rehybridization to imine.

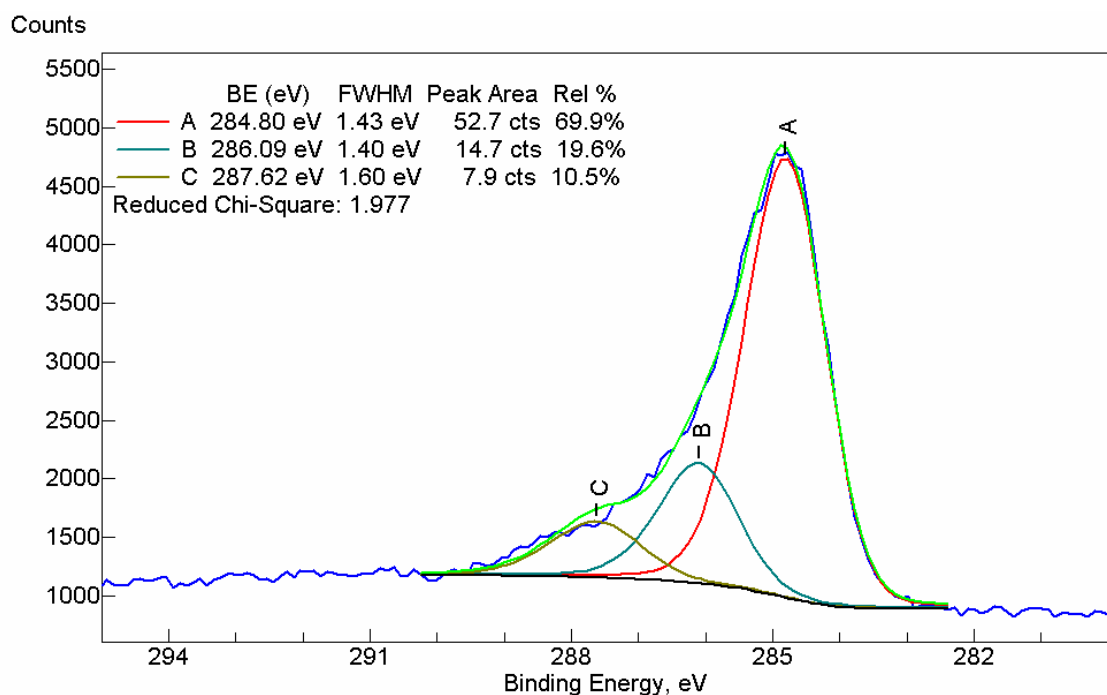


Figure 31. Peak fitting of carbon C1s peak of Figure 30.

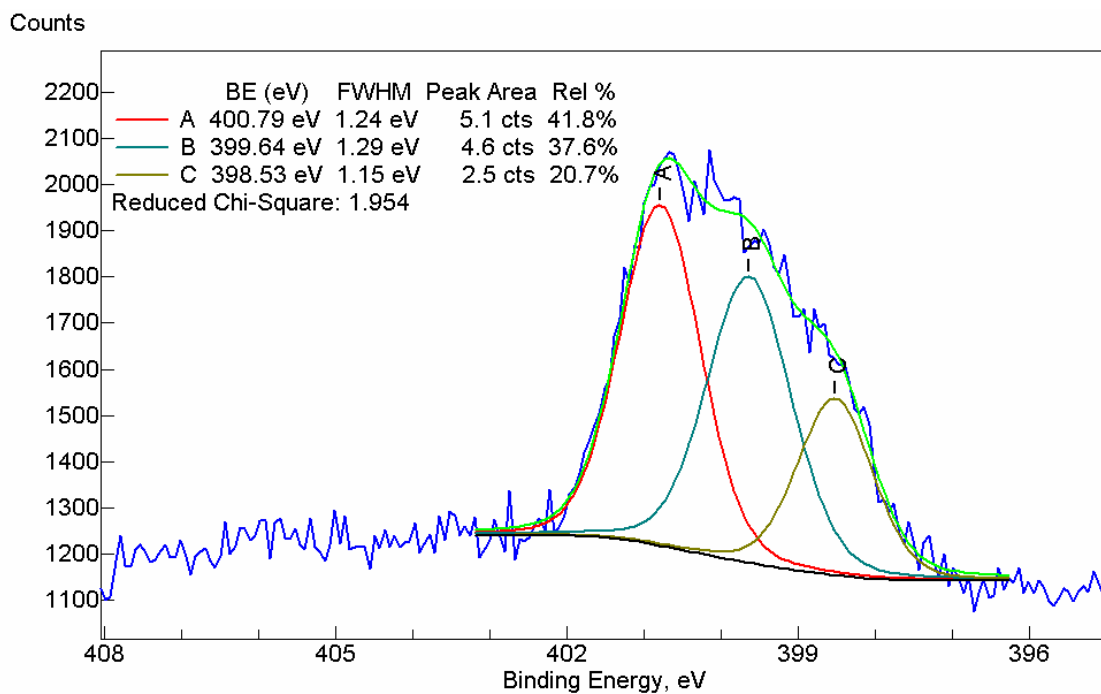


Figure 32. Peak fitting of nitrogen N1s peak of Figure 30.

The C 1s peak can be fitted with three peaks, at 287.6 eV, 286.1 eV and 284.8 eV. The high binding energy peak is assigned to carbon atoms in both surface bonded and free isocyanide groups, while the middle binding energy peak is assigned to carbon atoms adjacent to isocyanide groups. The peak at 284.8 eV is assigned to aromatic carbon atoms. The high binding energy peak is relatively broad, and contains some intensity in the region 288 to 289 eV, which might indicate the presence of carboxylic carbon. However, no absorption peaks for COO⁻ or COOH groups were detected in the PM-IRRAS spectrum (Figure 33), hence, coadsorption of terephthalic acid in the OOTF is negligible. Hence, the oxygen peak of Figure 30 is assigned to minor degree of oxidation of Cu to Cu₂O, as expected.^[86] In summary, the XPS data demonstrates that PDI preferentially adsorbs over TA on Cu, which indicates that the isocyanide group has a higher affinity for Cu than the carboxylic acid group.

The PM-IRRAS spectrum, Figure 33a, shows the PM-IRRAS spectrum after competitive adsorption between PDI and TA, at a concentration of 5 mM for 24 hours.

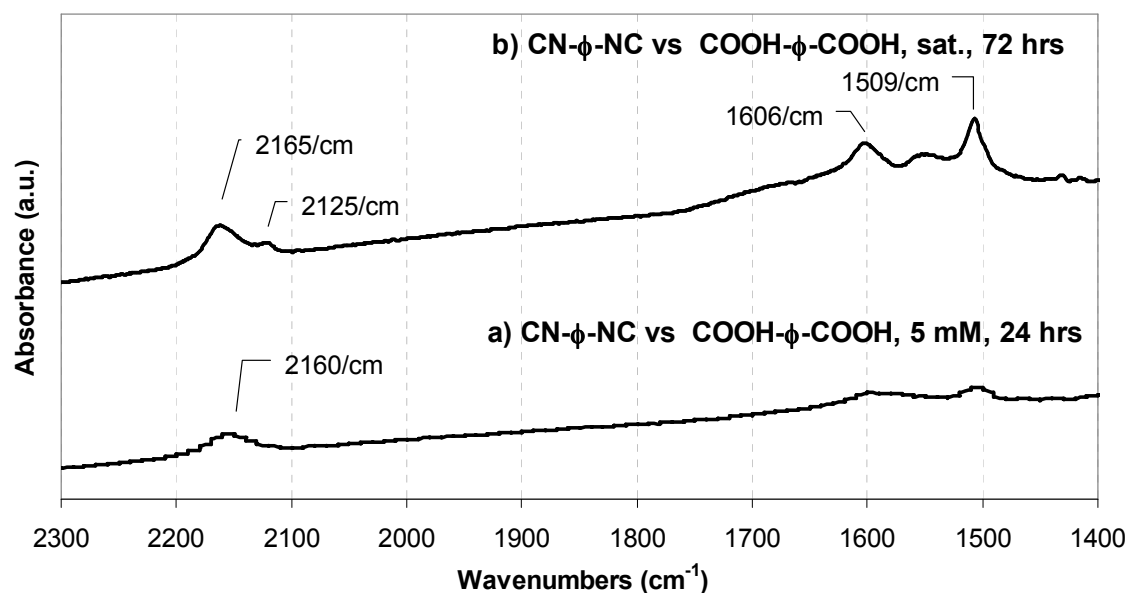


Figure 33. PM-IRRAS spectrum after competitive adsorption between 1,4- phenylene diisocyanide and terephthalic acid.

As in the case of PDI on Ni, peak intensity was observed at 1500 cm^{-1} and 1600 cm^{-1} and assigned to vibration modes of the phenyl ring.^[23, 129] There is no significant peak intensity in the range of 1580 to 1800 cm^{-1} and hence, the XPS peak at 398.5 eV assigned to polyisocyanide must be due to a small amount of polyisocyanide adsorbed on top of the OOTF, as previously proposed for 1,4-phenylene diisocyanide on Au.^[85, 136] In the isocyanide stretching region, a single, broad isocyanide peak is seen around 2160 cm^{-1} , corresponding to an η^1 terminal surface bonded isocyanide group. This single peak can not be due to hairpin bonding through both terminal groups, due to the inherent rigidity of the PDI molecule. The single isocyanide peak at 2160 cm^{-1} can also not be reconciled with $\eta^2(\text{C,N})$ bonding through a single terminal group, with the phenyl ring and one free isocyanide groups disposed away from the surface. This would yield a single peak closer to approx. 2120 cm^{-1} for the free isocyanide vibration, as in the case of PDI on Ni, rather than the observed stretch at 2160 cm^{-1} . Hence, the peak position observed in PM-IRRAS is most likely due to an overlap of free and η^1 terminal bonded isocyanide peaks. As discussed in the previous chapter, to confirm this, competitive adsorption from a 50 mM (saturated) solution was conducted for 72 hours. In the resulting PM-IRRAS spectrum, Figure 33b, the ring stretching peaks have increased significantly in intensity, and the isocyanide peak is more clearly resolved into two peaks, at 2165 cm^{-1} and 2125 cm^{-1} , corresponding to surface-bonded and free isocyanide groups, respectively. The resolution of the single peak of spectrum 33a into two peaks in 7b (top spectrum) is probably the result of an increased packing order due to increased concentration and time of adsorption. The position of $\nu(\text{CN})$ for the bonded isocyanide group is blue-shifted to 2165 cm^{-1} compared to 2128 cm^{-1} for 1,4-phenylene diisocyanide in dichloromethane,

while the free group is slightly red-shifted to 2125 cm^{-1} . The red shift of the free isocyanide group is close to that observed for PDI on Ni. The vibration peaks are close to those of phenylene diisocyanide on Ag, reported as 2180 cm^{-1} (surface-bonded isocyanide group), and 2118 cm^{-1} (free isocyanide).^[23] On Au, these peaks have been observed at 2180 cm^{-1} (surface-bonded isocyanide group) and 2121 cm^{-1} (free isocyanide), respectively.^[134]

5.4 Competitive self-assembly on platinum

Figure 34 shows the XPS survey spectrum after competitive adsorption between PDI and TA at a concentration of 5 mM, for 24 hours.

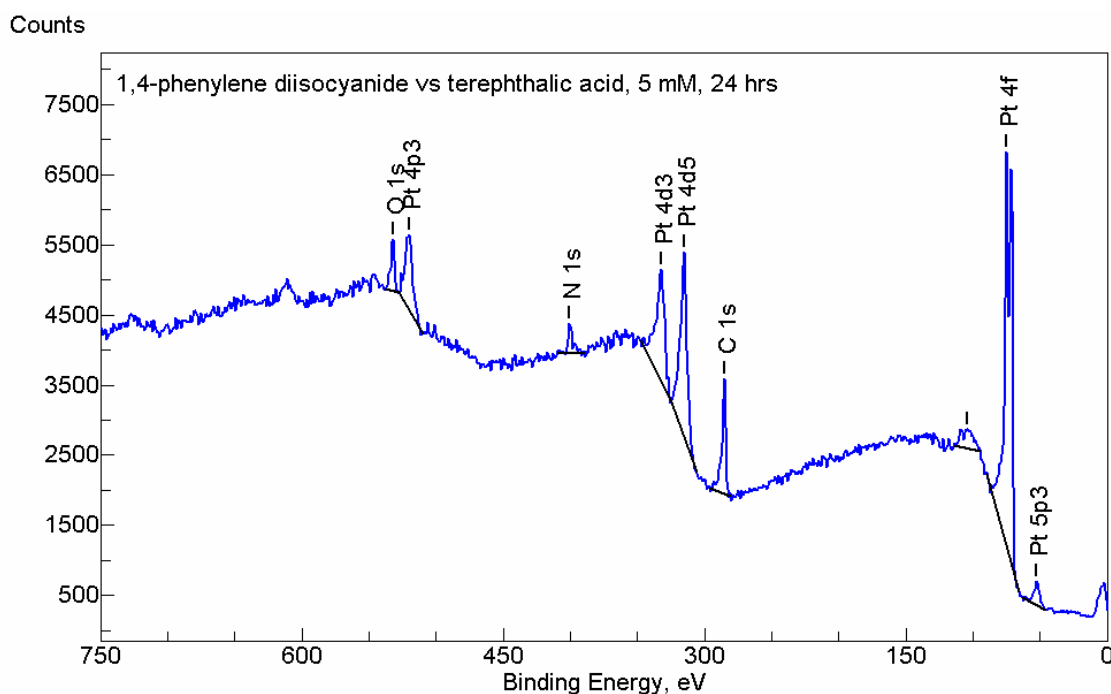


Figure 34. XPS analysis after competitive adsorption between phenylene diisocyanide and terephthalic acid on Pt.

The presence of carbon and nitrogen peaks at approx. 285 eV and 400 eV, respectively, are consistent with adsorption of PDI. In this case, however, an oxygen peak was observed at 531 eV, which can not be assigned to oxidation of the metal substrate. Figure 35 shows the Pt 4f_{5/2} and 4f_{3/2} peaks at 74.5 eV and 71.2 eV, as expected for metallic Pt^[146]

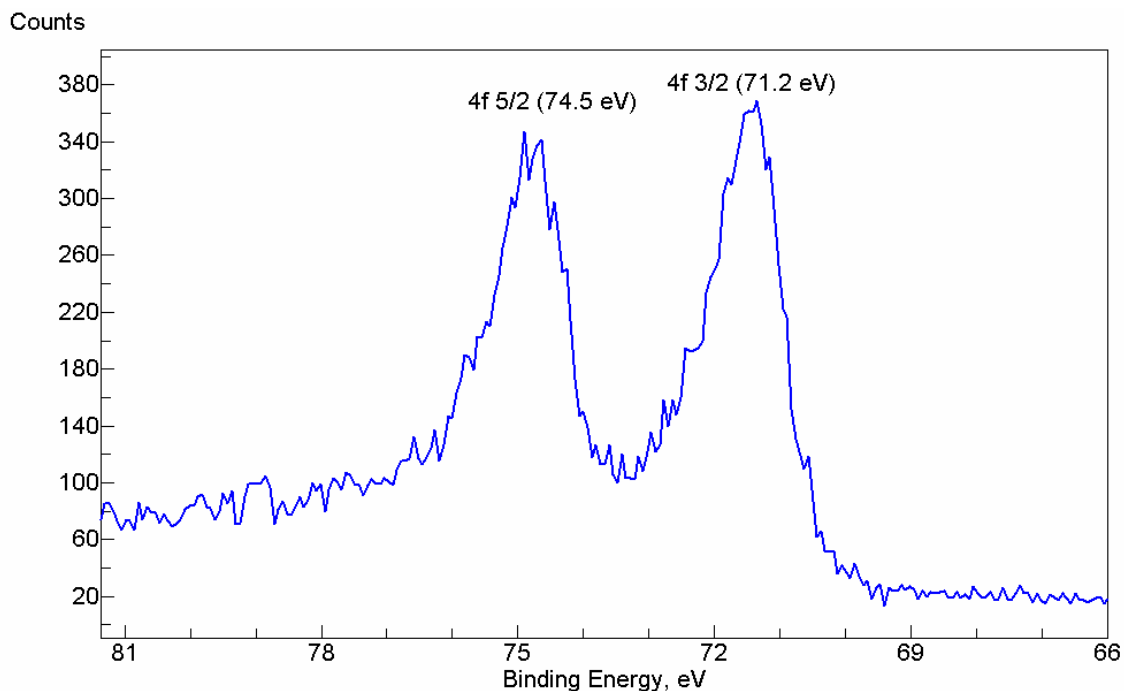


Figure 35. Peak positions for Pt 4f_{5/2} and 4f_{7/2} peaks of Figure 34.

The peak fit for the C1s peak, shown in Figure 36, requires four peaks to obtain $\chi^2 < 2$. The peaks at 284.8 eV, 286.1 eV, and 287.1 eV are assigned to aromatic carbon atoms, carbon atoms adjacent to isocyanide groups, and carbon atoms in surface bonded and free isocyanide groups. The smallest peak, at 288.5 eV, occurs in the region expected for carbon in carboxylate groups.^[126] Hence, this peak, in conjunction with the oxygen peak of Figure 34, is consistent with coadsorption of a small amount of TA with PDI. The PM-IRRAS spectrum revealed no peaks, which could be assigned to the nitrile group, the

carboxylic acid group, or to the phenyl backbone, and hence all PDI and TA present on the Pt surface are adsorbed in a flat, surface parallel configuration.

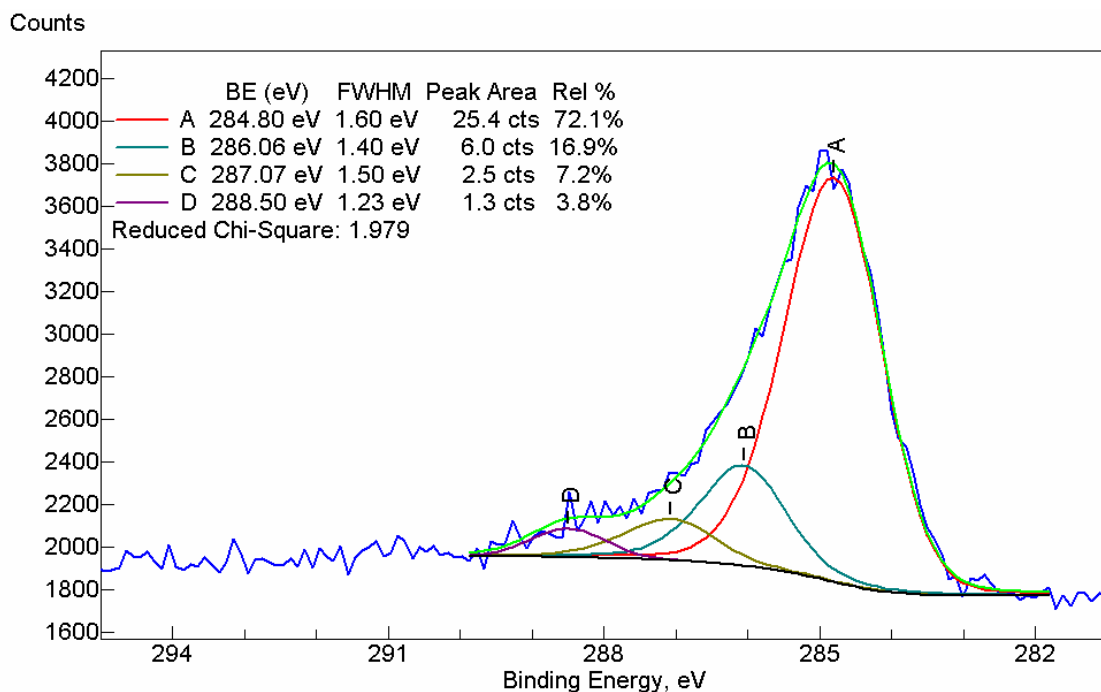


Figure 36. Peak fitting of carbon C1s peak of Figure 34.

Taken together, the XPS and PM-IRRAS data show that both TA and PDI adsorb flat on the Pt surface. This is apparently due to the combination of aromatic bonding and the difunctionality of PDI and TA.

The flat adsorption of PDI on Pt is inconsistent with its behavior on Cu, Ni and many other substrates, and hence deserves further comment. On one hand, the flat adsorption is consistent with that reported by Vong et. al. for PDI adsorbed on silica supported Pt catalyst.^[147] On the other hand, it is inconsistent with the conclusions drawn by Gruenbaum et al. who reported a terminal bonded adsorption configuration for SAMs of PDI on surface roughened Pt electrodes.^[148] However, there appear to be significant problems with the SERS (Surface Enhanced Raman Spectroscopy) spectral analysis,

upon which the conclusion of that paper was based. Some of the main problems are: 1) two peaks were observed in the isocyanide stretching region, at 2122 cm^{-1} (strong) and 1912 cm^{-1} (weak), and these were assigned to “atop bound” and “bridging bound” isocyanide groups, respectively, both of which are terminal bonding modes. Due to the rigidity of the PDI molecule, if it is terminal bonded by either of these modes, the pendant isocyanide group must be free, and its vibration peak should be observable in the SERS spectrum. However no peak assignment was made for the free isocyanide group, nor was the fate of the pendant isocyanide group discussed. 2) The assignment of the 2122 cm^{-1} peak is based on a frequency comparison with a complex formed by PDI and Pt_3 clusters, reported by Bradford et al. In these Pt_3 clusters, PDI exhibits extremely high fluxionality, constantly migrating around the Pt_3 triangle by moving between terminal and edge-bridging bonding modes, even down to as low as -80°C . However, this fluxional interaction between PDI and Pt_3 clearly is not analogous to the chemisorption of PDI onto Pt, after formation of a SAM.^[149] 3) The frequency of the supposedly “atop bonded” peak at 2122 cm^{-1} was recognized as being very close to that of free isocyanide. In fact, the frequency for the free terminal isocyanide group was found to be 2120 cm^{-1} and 2125 cm^{-1} for PDI on Ni and Cu, respectively, as described above, and was also reported in the narrow range of $2119\text{ cm}^{-1} - 2122\text{ cm}^{-1}$ for PDI on Au, Ag, Co and Pd.^[16, 23, 28, 150] To explain this, Gruenbaum et. al. suggest that σ -donation and π -back-donation contribute equally to the NC-Pt bond. In other words, the red-shift from π -back-donation and blue-shift from σ -donation cancel each other so that no net shift is observed. Aside from being a questionable interpretation of data at face value, it has been shown that when the isocyanide group undergoes terminal, on-top bonding to Pt, its stretching

vibration blue-shifts by at least 40 cm^{-1} .^[18, 80, 85, 151, 152] 4) The peak at 2122 cm^{-1} were not found to vary with applied electrode potential. This is consistent with a free isocyanide group, but not a terminal bonded isocyanide. Taken together, the conclusion in the paper by Gruenbaum et. al., of a standing up phase of PDI on Pt, does not appear to be supported by the data. Therefore, the demonstration of a standing up phase of difunctional linker molecules on Pt will require further research.

5.5 Conclusions

In conclusion, the competitive self-assembly between 1,4-phenylene diisocyanide (PDI) and terephthalic acid (TA) results in the preferential adsorption of PDI over TPA both on Cu and Ni substrates. Moreover, PDI bonds in a terminal fashion through one isocyanide group on both Ni and Cu. The functionalization of Cu and Ni nanoclusters (proposed for future work) should therefore focus on the use of PDI or its oligomeric analogs.

In contrast, the competitive self-assembly between 1,4-phenylene diisocyanide (PDI) and terephthalic acid (TA) on Pt results in adsorption of PDI with a small amount of coadsorption of TA, flat on the surface. Since neither of these difunctional molecules form sticky OOTFs, neither are effective for controlling the interface of Pt substrate by the self-assembly technique. The identification of linker molecules capable of achieving this aim is proposed for future studies.

CHAPTER 6

REACTIVE MOLDING OF CELLULOSE WHISKER NANOCOMPOSITES

6.1 Chapter overview

This chapter discusses the results of reactive molding of cellulose whisker nanocomposites. This was achieved by in-situ polymerization, using a furfuryl alcohol (FA) as a polymerizable solvent medium to produce cellulose whisker – polyfurfuryl alcohol (CW-PFA) nanocomposites. Cellulose whiskers are not commercially available, and therefore they were synthesized by hydrolysis with sulfuric acid. The results of characterizing the morphology of the cellulose whiskers are shown. The polymerization of FA to PFA in the presence of CW is then discussed. To characterize the polymerization behavior and to investigate how the presence of CW influences the polymerization of FA, FTIR spectra were collected before and during the resinification process. Finally, characterization of the thermal stability of the CW-PNC, as measured by TGA, is discussed and compared to pure polymer. The results provide a useful qualitative measure of CW dispersion in the cured PNC. The mechanical properties of CW-PFA were not measured, because adequate specimens for mechanical testing could not be produced with the available lab equipment.

6.2 Morphology of cellulose whiskers

Concentrated suspensions of CW were prepared from acid hydrolysis of MCC according to the procedure described in chapter 3. The CW exhibited birefringence when viewed through crossed polars. This behavior is illustrated in Figure 37, which shows flow birefringence (top) and birefringence at rest (bottom) of a concentrated suspension of cellulose whiskers.^[113]

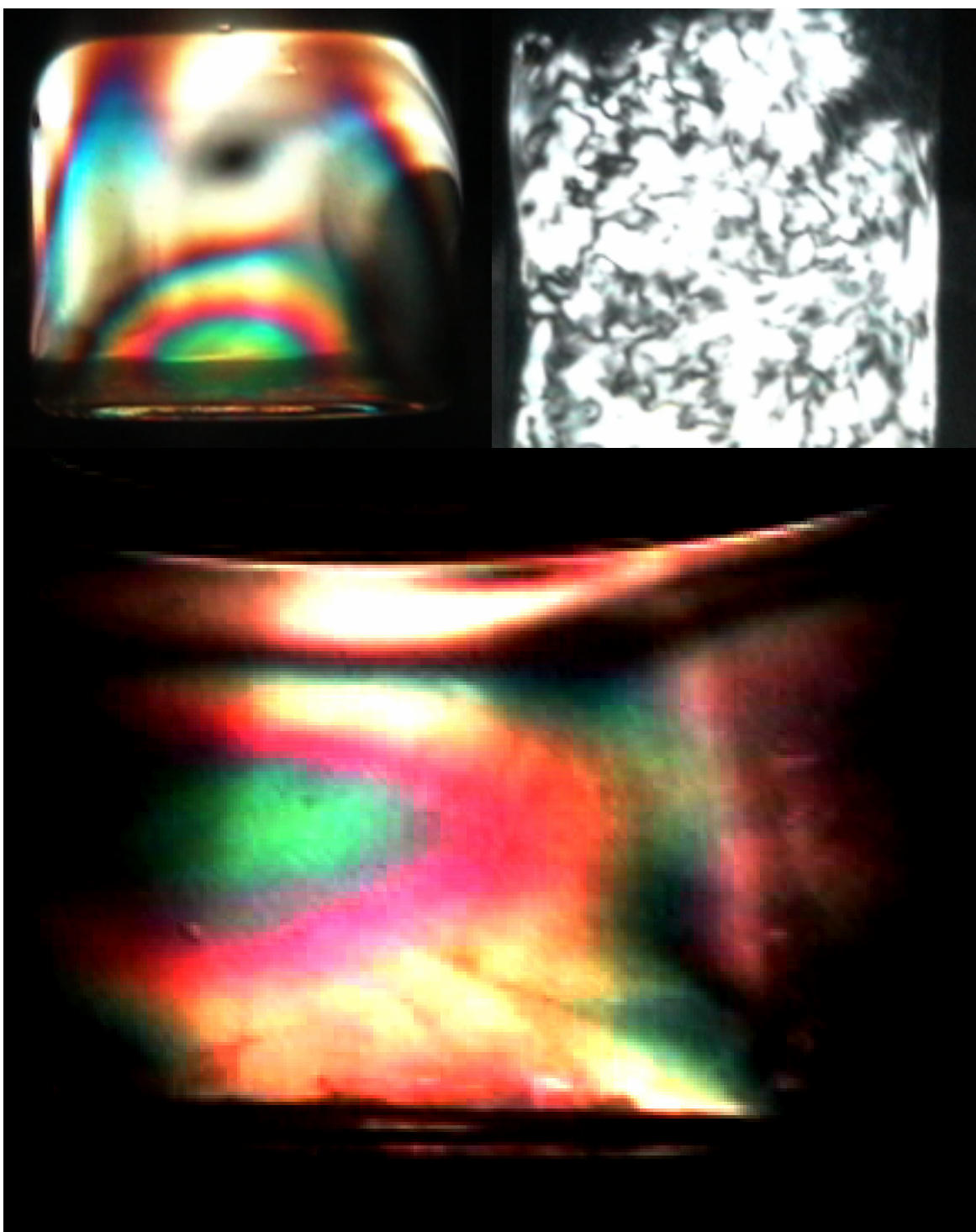


Figure 37. Birefringence of suspensions of cellulose whiskers, viewed through crossed polars. Flow birefringence (top) and birefringence at rest (bottom).

The birefringence of the CW suspensions is attributed to the liquid crystalline behavior of the CW, and proves that whiskers have been successfully refined from the MCC precursor. The dispersion of CW is also evident from the gallery of TEM and AFM images in Figure 38 - 42 .

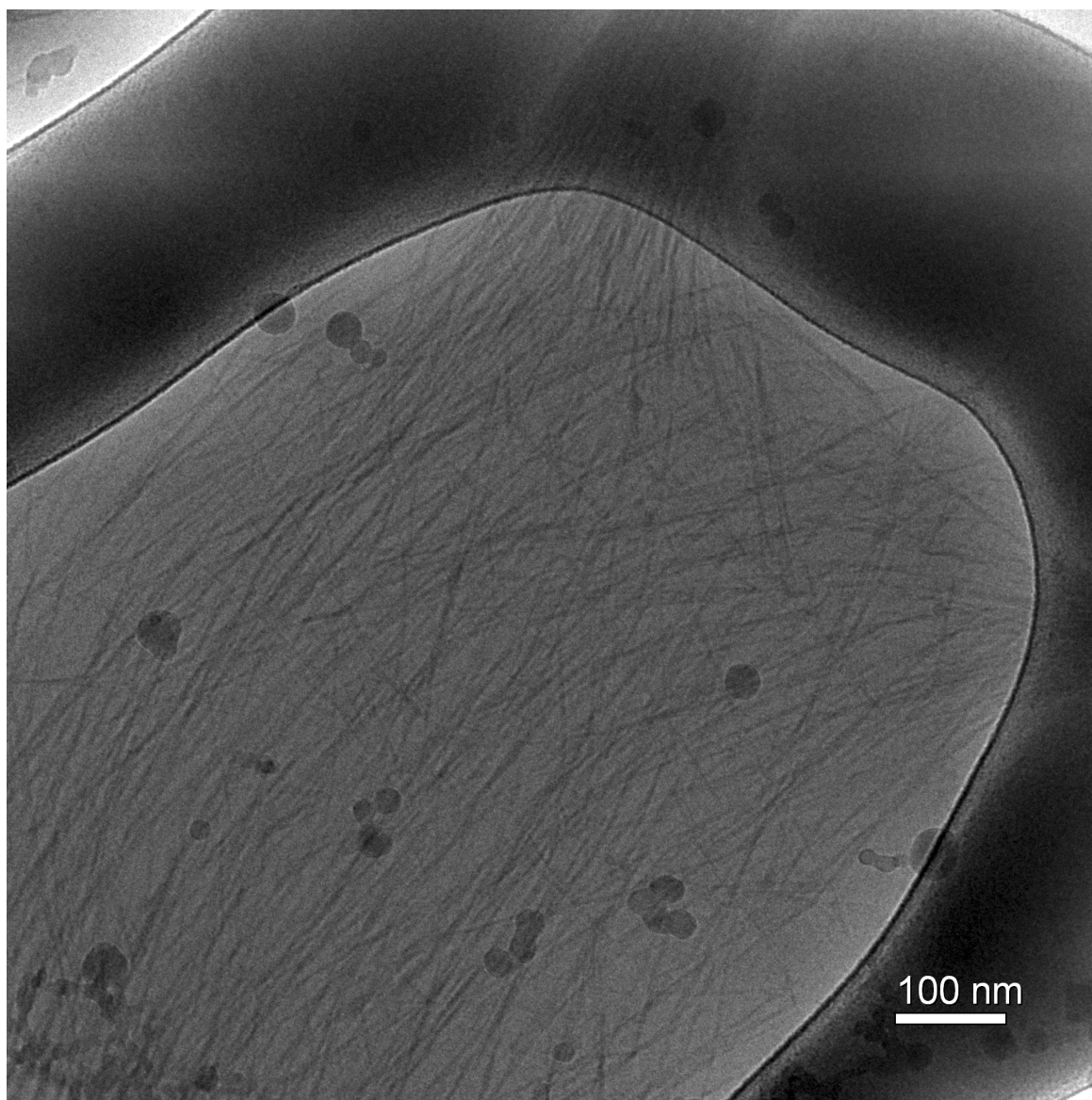


Figure 38. TEM images of a suspension of cellulose whiskers. Magnification factor is $\times 21,000$. Horseshoe shaped border is the lacey carbon backing of the TEM grid.

Figure 38 -39 are TEM images of a cellulose suspension, taken by the cryo-TEM method. This method used liquid N₂ to freeze a sample of the CW suspension and maintain the frozen state throughout the TEM imaging process.^[114] The results therefore prove that the CW are well dispersed and stable in suspension.

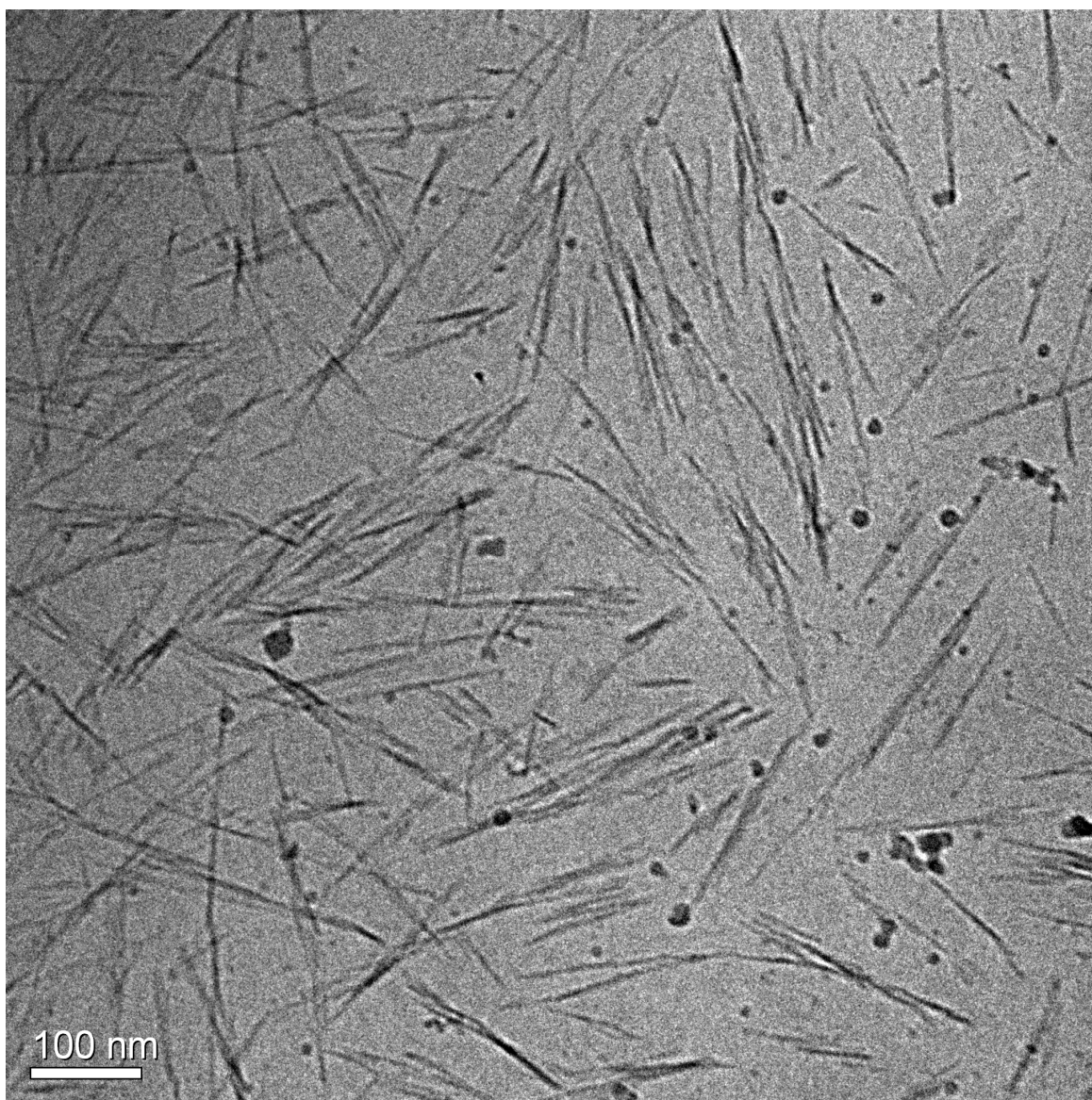


Figure 39. Cryo-TEM images of a suspension of cellulose whiskers.

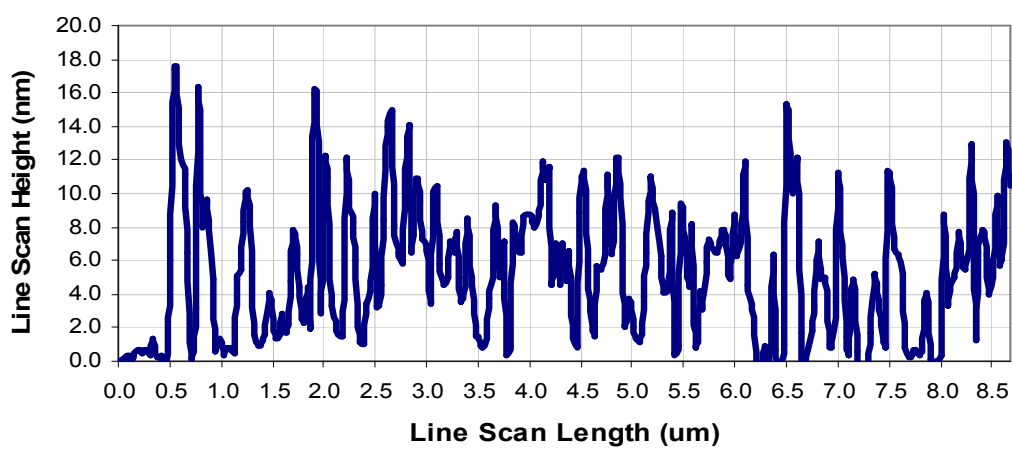
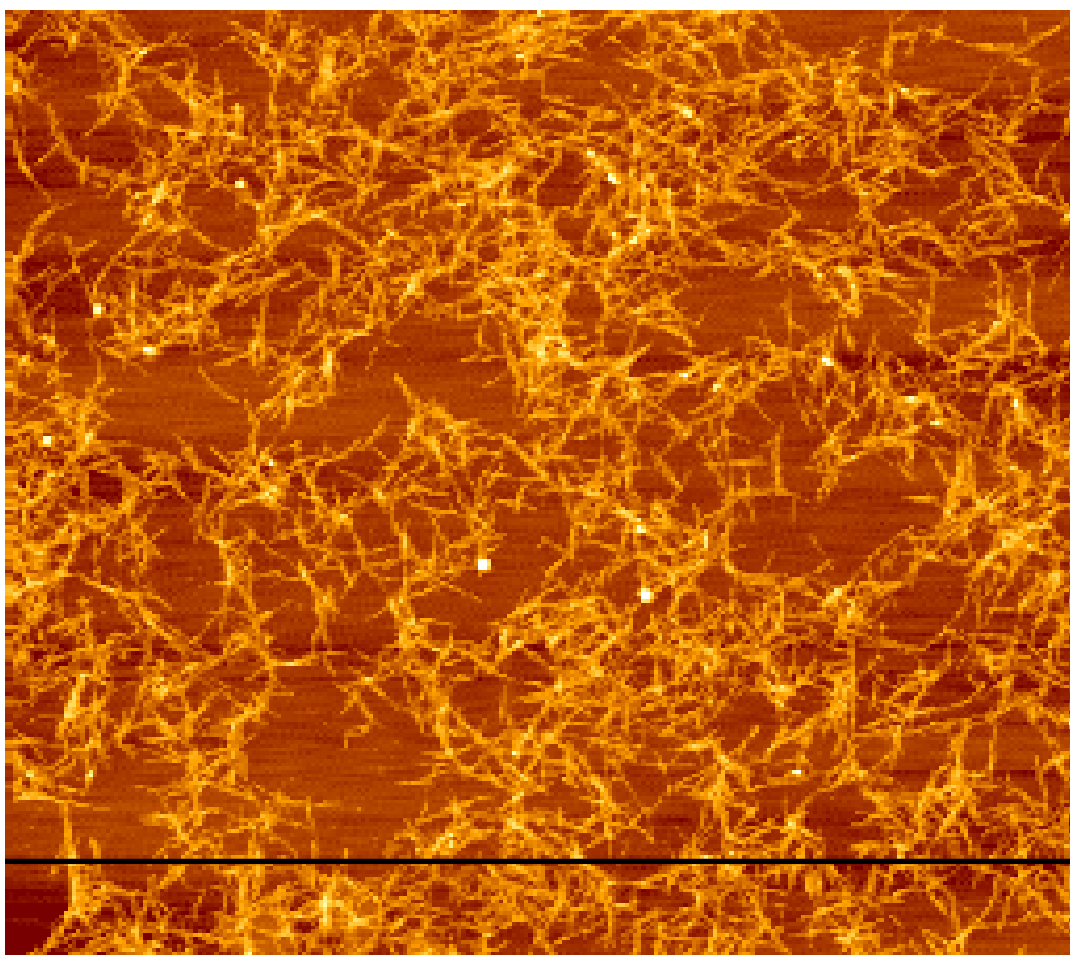


Figure 40. AFM phase contrast images of cellulose whiskers from acid hydrolysis of microcrystalline cellulose.

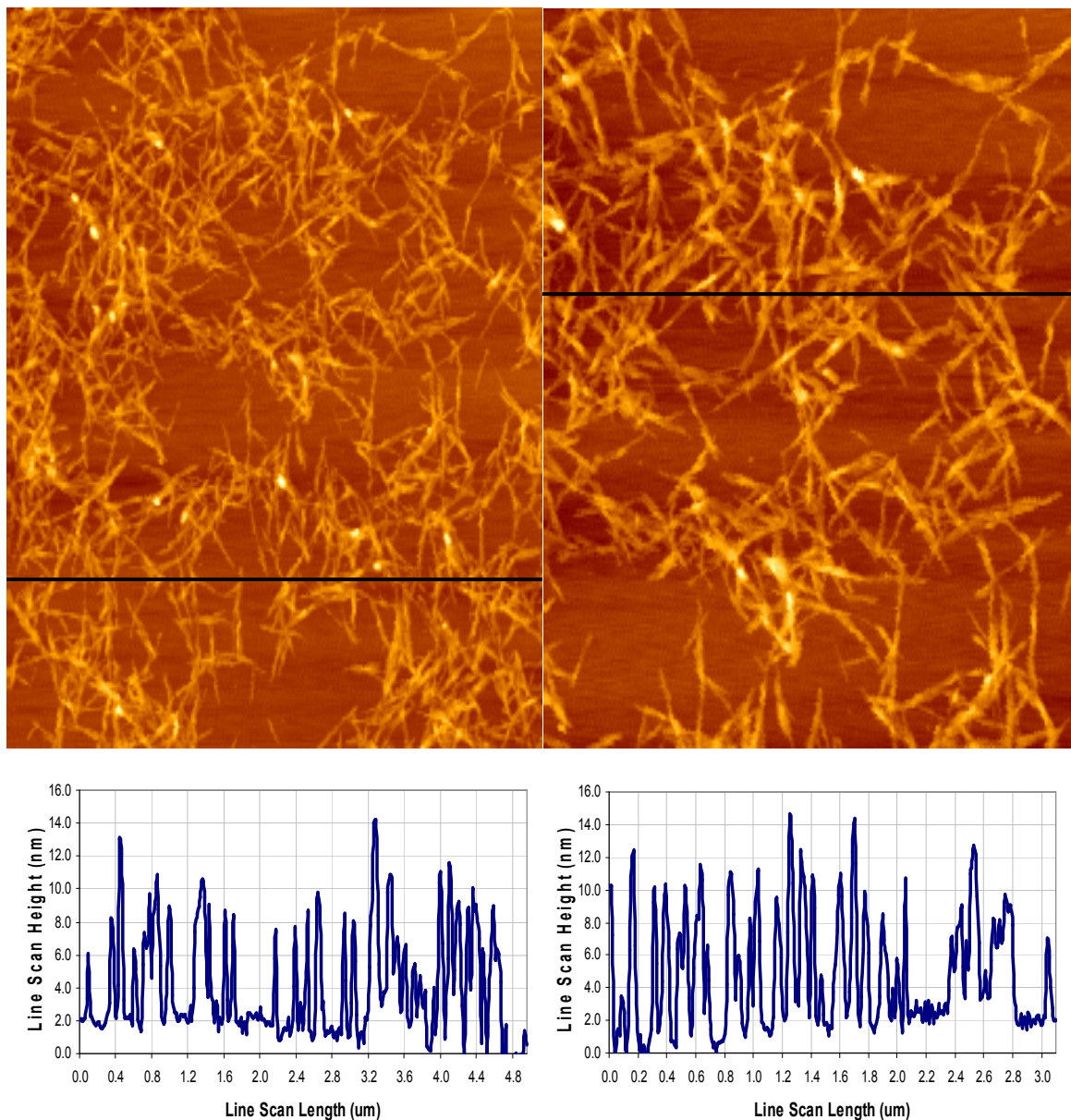


Figure 41. AFM phase contrast images of cellulose whiskers from acid hydrolysis of microcrystalline cellulose.

Figure 40 - 42 are AFM images of a film of dried cellulose whiskers. Like the TEM images, the AFM images show that the CW are well dispersed. From these figures, it can be seen that the average diameter of the CW whiskers is around 10 nm, and that the aspect ratio is in the range of 50 – 100. This is consistent with the literature.^[9, 57]

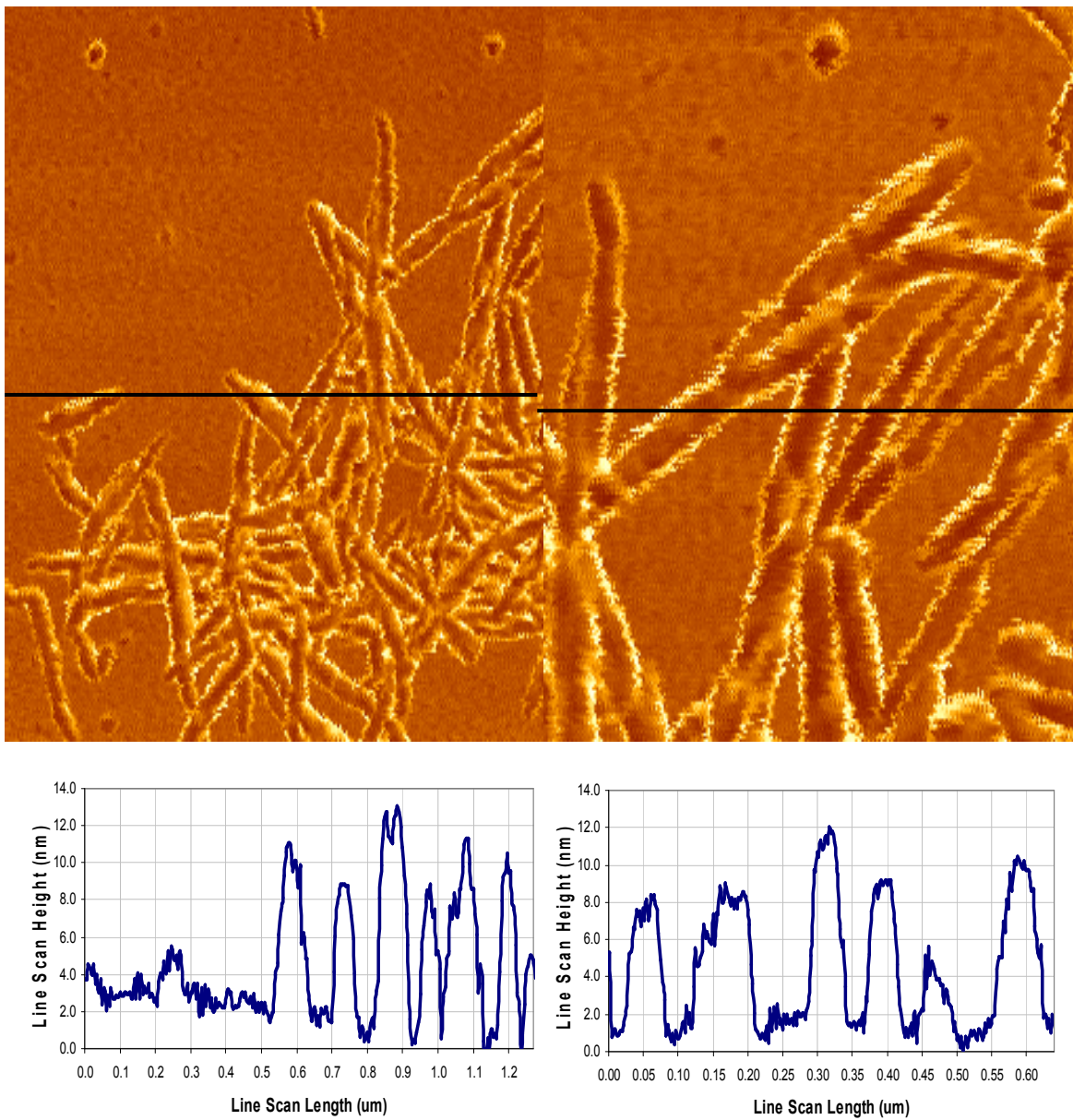


Figure 42. AFM phase contrast images, with line scans, of cellulose whiskers from acid hydrolysis of microcrystalline cellulose.

6.3 Resinification of furfuryl alcohol in the presence of cellulose whiskers

CW has a richly hydroxylated surface, and when sulfuric acid is used in the CW synthesis, the CW surface also contains sulfonic acid residues originating from the hydrolysis step. The sulfonic acid groups carry a negative charge, and this is critical for providing electrostatic stabilization of the CW dispersion in the FA.^[9, 11] However, the esterification reaction is reversible, and the deesterification of sulfonic acid groups from the CW surface at elevated temperature can be exploited to catalyze the in-situ polymerization of FA in close proximity to the CW.^[153] By wrapping PFA around the CW, the initial dispersion can be preserved in the PFA resin and in the cured nanocomposite. To explore this approach, 1.0 phr freeze-dried CW was dispersed in FA by means of a brief ultrasonication treatment (Fisher 500W, 25 – 50% amplitude, 15 min.) followed by heating to 50°C for 1 h. At this temperature, the CW – FA mixture was stable, and the rate of polymerization was negligible. However, increasing the reaction temperature to the 60-100°C range triggered the polymerization of FA. Within 2-3 minutes at 100°C, the mixture turned from yellow to dark brown due to rapid accumulation of PFA particles and within 2 hours the gel point was reached. After 9 hours at 60°C or 4 hours at 75°C, a fluid resin is obtained. Under identical experimental conditions, neither microcrystalline cellulose (MCC) nor silica gel induced the polymerization of FA, demonstrating that neither the ultrasonication treatment, nor the presence of a high, hydroxyl-rich surface area is sufficient to explain the rapid polymerization of FA in the presence of CW. Rather, it is the sulfonic acid residues at the CW surface that are responsible for triggering the polymerization. This mechanism is shown schematically in Figure 43.

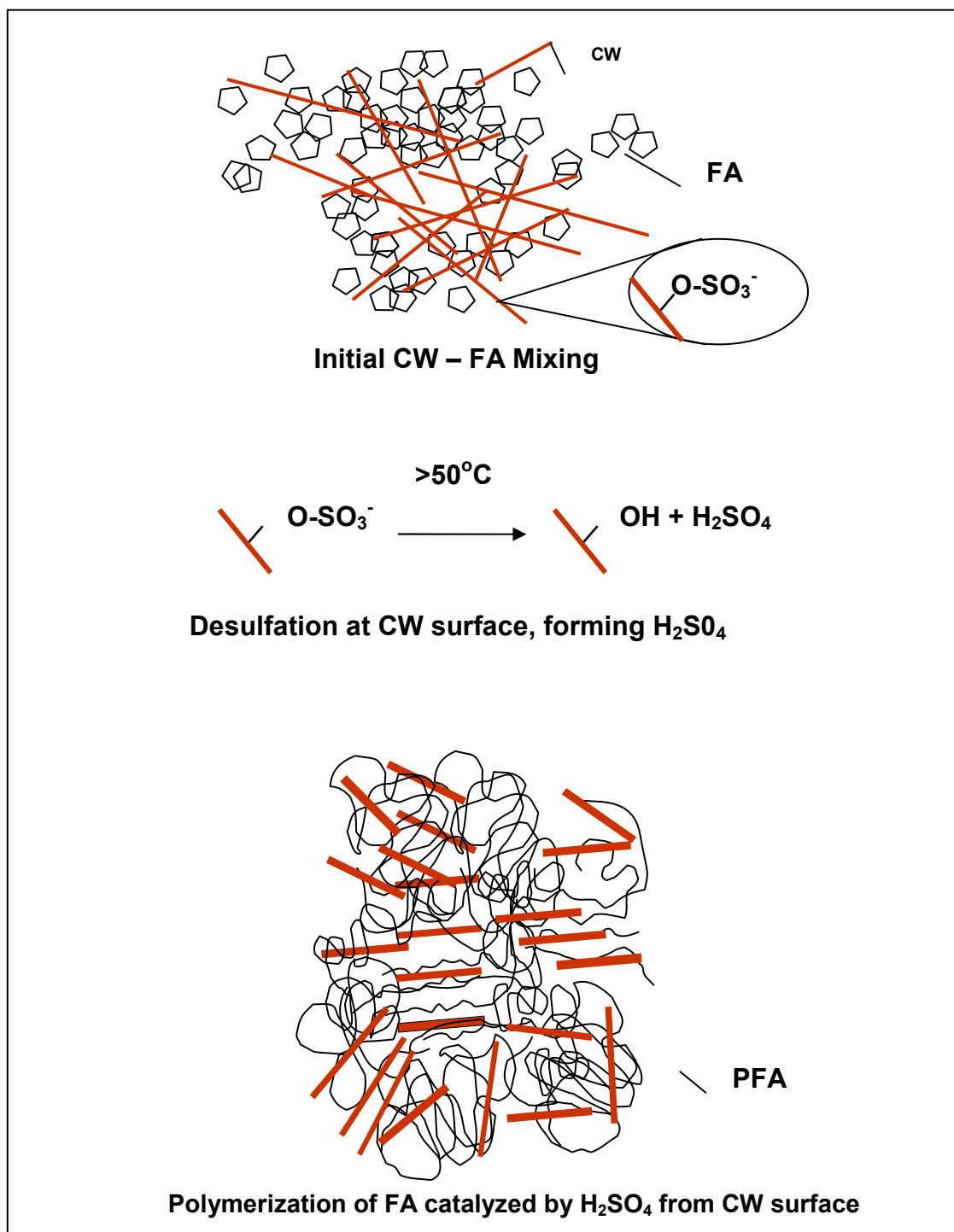


Figure 43. Proposed mechanism for polymerization of furfuryl alcohol in the presence of cellulose whiskers.

The most plausible explanation for this reaction is that at room temperature and up to 50°C, the sulfonic acid groups at the CW surface are stable. However, increasing the temperature to the 60°C-100°C range leads to the de-esterification of the sulfonic acid groups, detaching them from the CW surface, and allowing them to combine with H₂O from the condensation polymerization of FA and reform sulfuric acid.^[153-156] The sulfuric acid then catalyzes the polymerization of FA in close proximity to, and around the CW, trapping the fine CW dispersion in the PFA resin.

The rapid progress of resinification is evident from the FTIR spectra, shown in Figure 43, for FA with 0.75 phr CW after 1h at 50°C (spectrum a) and after reacting the CW – FA mixture at 100°C for 30min, 1h, and 2h (spectra b, c and d, respectively). The spectrum for GAI-PFA after 12 hrs resinification at 100°C (spectrum e) is included for comparison. The polymerization of FA is typically accompanied by significant increases in the intensity of the peak at 1562 cm⁻¹, assigned to the skeletal vibration of 2,5 disubstituted furan rings, and at 1712 cm⁻¹, assigned to the C=O stretch of γ -diketones formed from hydrolytic ring opening of some of the furan rings along the PFA chain.^[102, 104] At the same time there is a decrease in peak intensity (not shown) for the broad peak in the hydroxyl stretching region (3200 – 3600 cm⁻¹) and for the peak at 3120 cm⁻¹, assigned to the in plane stretch of the hydrogen at the C5 position of the furan ring.^[115]

The intensity of the sharp peaks at 1504 cm⁻¹, assigned to ring stretching of the furan ring serves as an internal reference peak for semiquantitative analysis. Table 1 shows the results of applying the internal referencing method to the peaks at 1562 cm⁻¹ and 1712 cm⁻¹ for the spectra in Figure 44. Internal referencing of the 1562 cm⁻¹ peak to the 1500 cm⁻¹ peak indicates that in less than 1 h at 100°C, the degree of polymerization

of the CW – PFA resin is comparable to GAl-PFA resin after 12 h resinification at 100°C. This is also apparent from internal referencing of the 1712 cm⁻¹ peak to the 1500 cm⁻¹ peak.

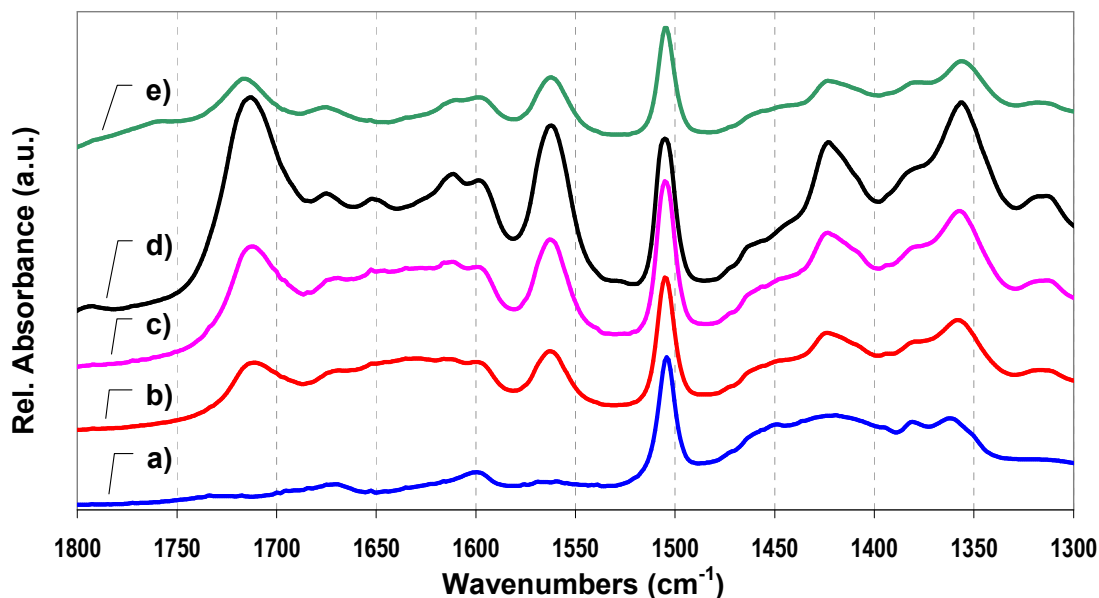


Figure 44. FTIR spectra for a) CW - FA at 50°C for 1h; CW PFA resin after reaction at 100°C for b) 30min.; c) 1h; d) 2h; and for comparison, e) resinification of FA with γ -Al at 100°C for 12h

Table 1. Internal referencing of the 1562 cm⁻¹ and 1712 cm⁻¹ peaks from Figure 44.

Peak height ratio I/I _{ref}	GAl-PFA 12h/100°C	CW-PFA 0.5h/100°C	CW-PFA 1h/100°C	CW-PFA 2h/100°C
I ₁₅₆₂ /I ₁₅₀₀	0.527	0.465	0.663	1.107
I ₁₇₁₂ /I ₁₅₀₀	0.424	0.455	0.697	1.349

Figure 45 compares the FTIR spectra for CW PFA, compared with pure FA and with GAl PFA. In the 1800 cm⁻¹ to 1300 cm⁻¹ region, it can be seen that the growth of the γ -diketone peak at 1710 cm⁻¹ with increasing polymerization is characteristic both of

Lewis acid (γ -Al) catalyzed GAl -PFA and of CW - PFA catalyzed by the sulfonic (Brönstedt) acid residues from the whiskers.

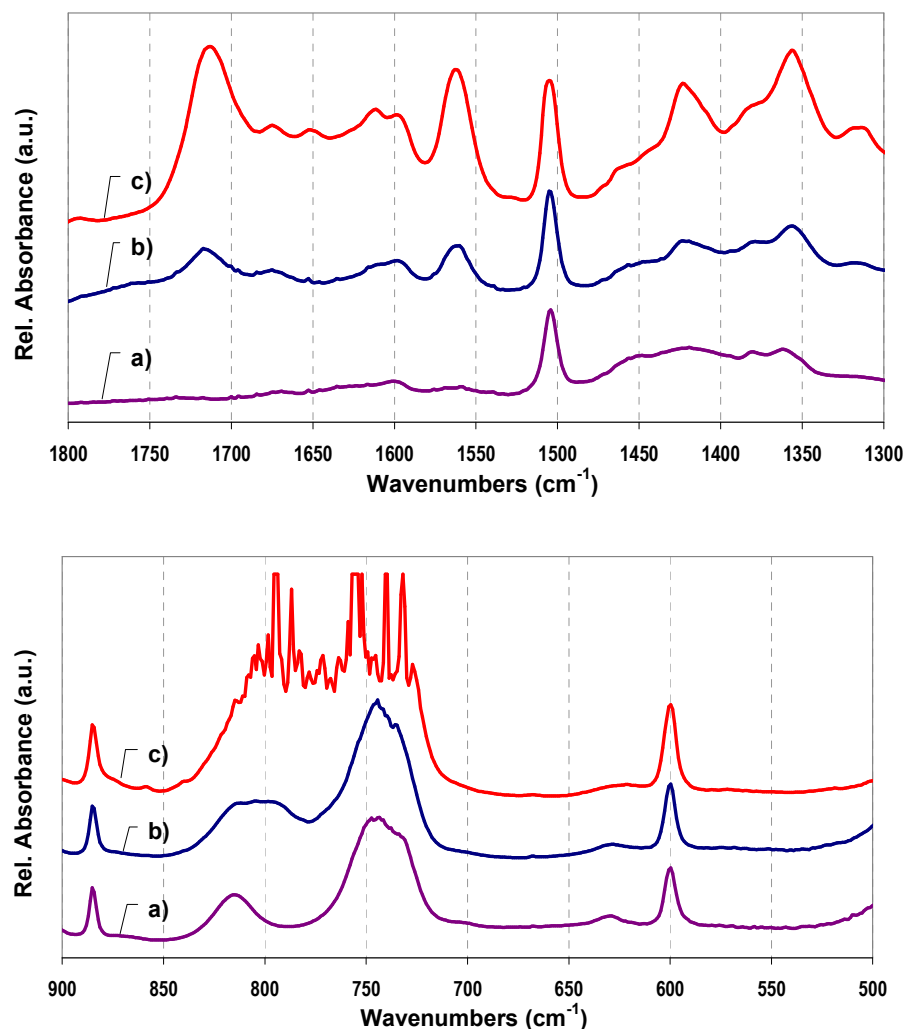


Figure 45. FTIR spectra for a) pure FA; b) GAl PFA resin; c) CW PFA resin

6.4 Thermal resistance of cellulose whisker – furfuryl alcohol nanocomposites

When dispersed in a composite matrix, the high surface area of the CW filler translates to high interfacial area between matrix and filler, leading to the immobilization of the matrix polymer at the nanoparticle surface. As a result, significant enhancements in thermal and mechanical performance are expected for CW PNCs as

compared to pure polymer matrix. Therefore, thermogravimetric analysis (TGA) provides a useful qualitative measure of CW dispersion in the cured PNC. Figure 46 shows non-oxidative degradation in a nitrogen flow of GAl-PFA (spectrum a), and CW-PFA (spectrum b) composite samples. These were prepared by oven-curing at 130°C for 75 min, and then at 210°C for 105 min. For comparison, the spectra for the MMT-PFA nanocomposites, which will be the focus of the next chapter, are also shown. These are coded 30B-MMT PFA (spectrum c) and NaMMT-PFA (spectrum d).

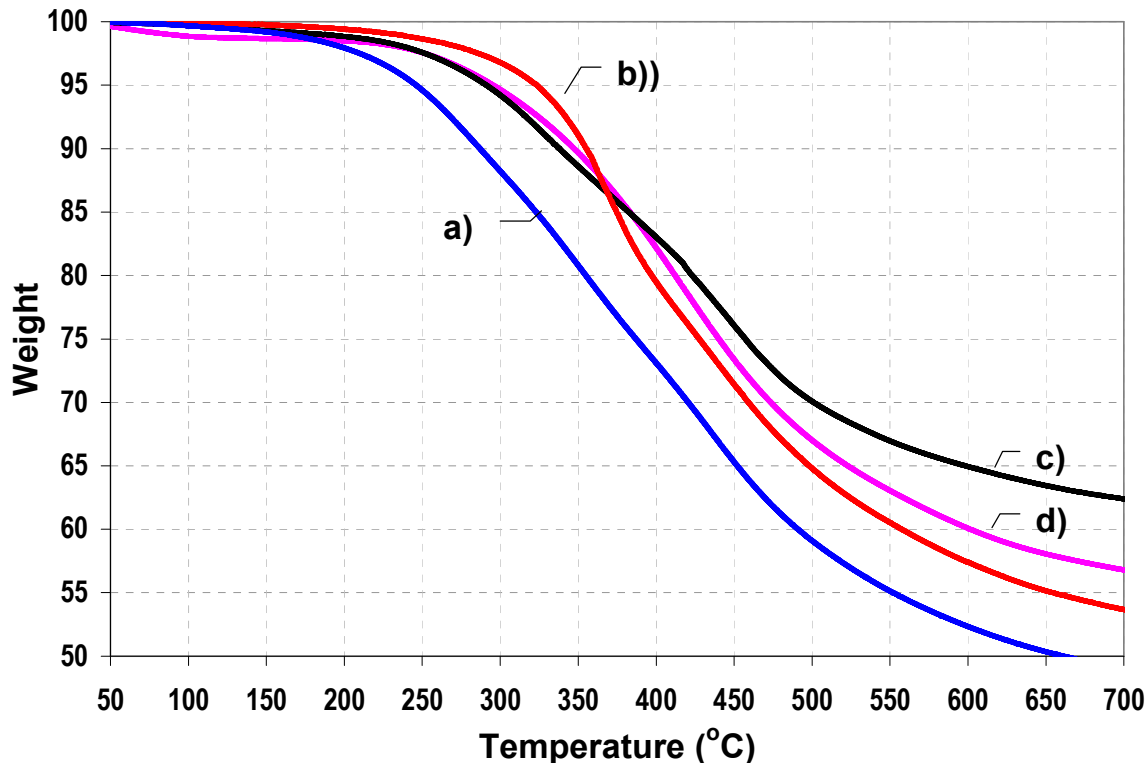


Figure 46. TGA scans collected at 10°C/min showing onset of degradation for the case of non-oxidative degradation in N₂ for cured PNCs of a) GAl-PFA, b) CW-PFA, c) 30BMMT-PFA and d) NaMMT PFA

In CW-PFA, the onset of degradation (temperature at 5% weight loss) is 323°C, which is 77°C higher compared to Gal-PFA, and remarkably, also 20°C – 30°C higher compared to the MMT-PFA nanocomposites. The residual weight of CW-PFA is 6% higher at 500°C and 4% higher at 800°C compared to pure PFA. Table 2 summarizes the main TGA results.

Table 2. Temperature at onset of decomposition and weight retention at 500°C and 800°C for cured PFA nanocomposites.

	Gal-PFA	CW-PFA	NaMMT-PFA	30BMMT-PFA
Onset of degradation (5% weight loss) in N₂ flow				
	246°C	323°C	302°C	295°C
Weight retained after non-oxidative degradation in N₂				
500 °C ^a	59%	65%	67%	70%
800 °C ^b	48%	52%	55%	60%

^aStandard deviation for residual weights is 1.0%. ^bStandard deviation for residual weights is 1.3%.

Mechanical testing is second way to confirm the increased thermo-mechanical performance expected for CW PNCs. A Teflon mold was used to prepare DMA samples of cured CW-PFA. Unfortunately all samples were contained large voids and blisters and were not suitable for mechanical testing. Mechanical testing by nanoindentation is proposed for future work.

6.5 Conclusions

Completely bio-based PNCs with enhanced properties can be produced by using in-situ polymerization techniques to disperse nanoparticles of CW in a thermosetting PFA matrix. The resinification of FA to PFA occurs rapidly in the presence of CW,

because CW plays a dual role in the in-situ polymerization process, by first catalyzing the polymerization, thereby eliminating the use of strong mineral acid catalysts, and then enhancing the thermal stability of the consolidated PNCs. Therefore, in-situ polymerization with CW offers an attractive processing route for producing PFA matrix nanocomposites without the use of strong mineral acids, solvents or surfactants.

In CW-PFA nanocomposites, the ability of CW to increase the thermal stability of a PNC by restricting the thermal motion of the matrix polymer is evident from the TGA data. CW PNCs show a high increase in the temperature at onset of degradation of nearly 80°C compared to PFA, at only 1.0 wt%. This is attributed to effective immobilization of PFA at the CW surface, and promises increased mechanical properties. Future studies should focus on mechanical testing of the CW-PFA nanocomposites.

CHAPTER 7

REACTIVE MOLDING OF MONTMORILLONITE NANOCOMPOSITES

7.1 Chapter overview

This chapter discusses the results of reactive molding of nanocomposites from naturally occurring montmorillonite clay. This was achieved by in-situ polymerization, using a furfuryl alcohol (FA) as a polymerizable solvent medium to produce montmorillonite– polyfurfuryl alcohol (MMT-PFA) nanocomposites. Surface modified montmorillonite clay is commercially available, as well as natural sodium montmorillonite. Since FA is hydrophilic, while PFA is hydrophobic, the intercalation process was studied both with naturally occurring hydrophilic sodium montmorillonite (NaMMT), and with an organomodified montmorillonite (30BMMT). The morphology of the MMT was characterized by AFM, and the results are shown here.

The in-situ intercalative polymerization of FA to PFA in the presence of MMT is then discussed. To characterize the polymerization behavior and to investigate how the presence of MMT influences the polymerization of FA, FTIR spectra were collected before and during the resinification process. The dispersion of MMT in the PFA matrix is shown both direct and indirectly. Direct evidence is presented from x-ray diffraction (XRD) which was used to monitor the process of intercalation and exfoliation of the MMT at various stages of resinification. The dispersion is indirectly evidenced in increased thermal stability of the MMT-PFA nanocomposite, as measured by TGA. The thermal stability is discussed and compared to pure polymer and CW-PFA. Also, an important difference between oxidative and non-oxidative degradation of NaMMT-PFA nanocomposite is discussed, and a mechanism proposed to explain the difference in terms of acid-catalyzed degradation.

7.2 Morphology of montmorillonite clay

The morphology of the MMT used in the preparation of MMT – PFA nanocomposites was examined by AFM, by drying dilute aqueous suspensions on a smooth silicon wafer. Figures 47 - 48 highlight the lamellar morphology of the MMT.

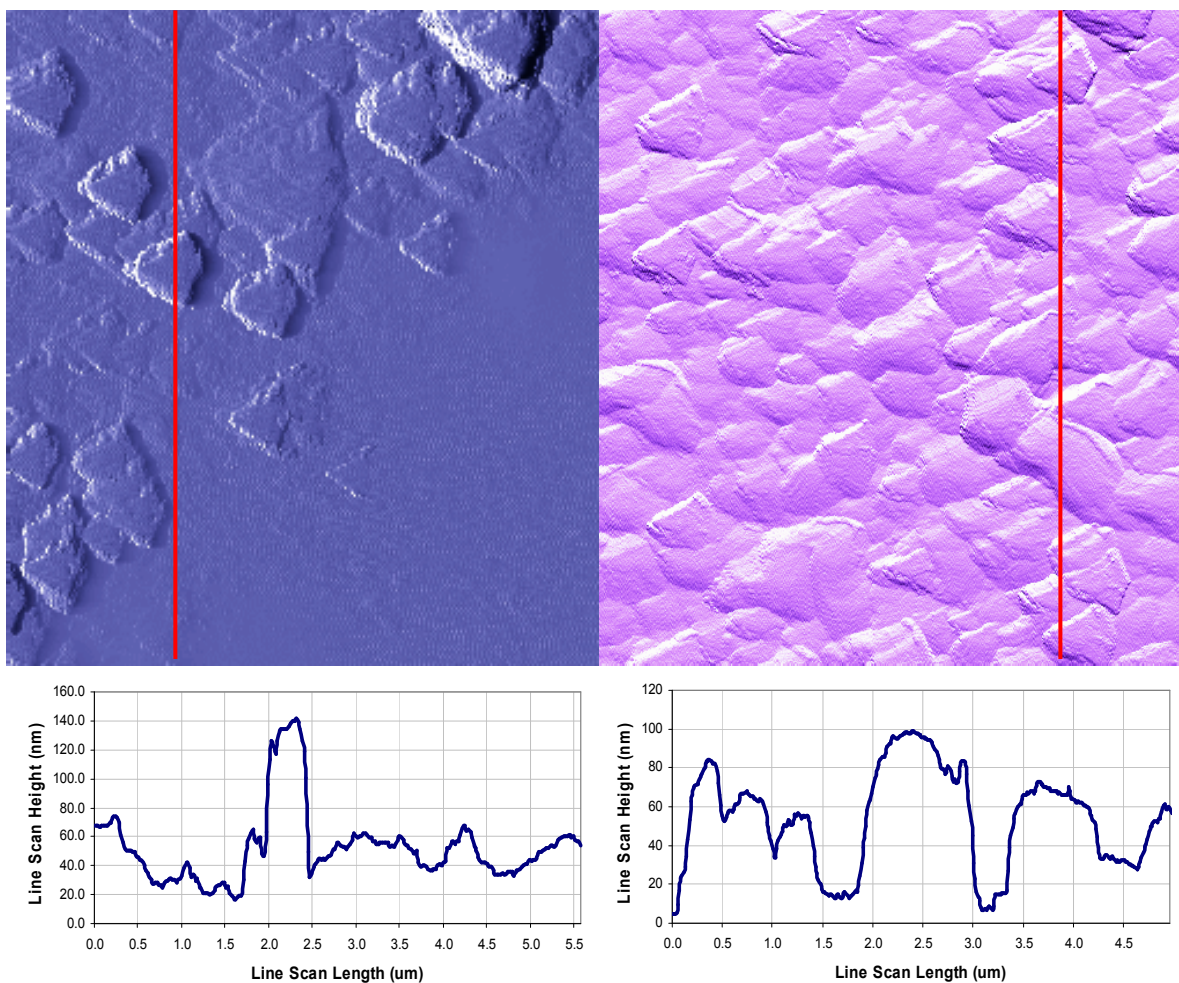


Figure 47. AFM phase contrast images of large tactoids of MMT.

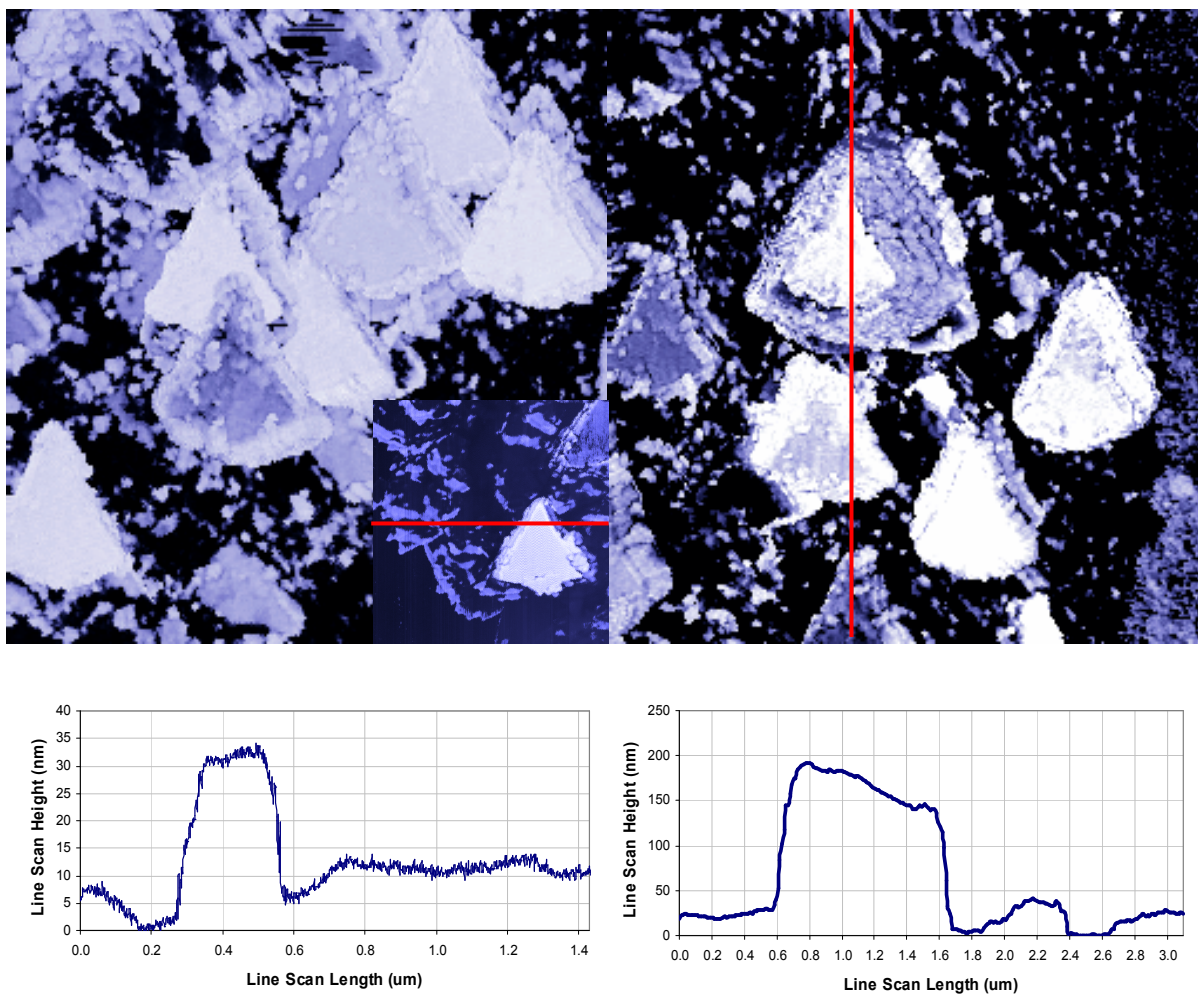


Figure 48. AFM phase contrast images of large tactoids of MMT.

The line scan shows that large tactoids spanning 0.6 - 1.0 μm in length. Since the thickness of an individual platelet is approximately 1 nm, the aspect ratio of these plates is 20 – 100 upon complete exfoliation.^[10, 157] The tactoid height varies between 150 and 200 nm, hence the largest tactoids (bottom right hand image) contain approx. 150 and 200 silicate layers prior to exfoliation. As shown in Figure 47 - 48, large tactoids tend to have a regular “arrowhead” shape.

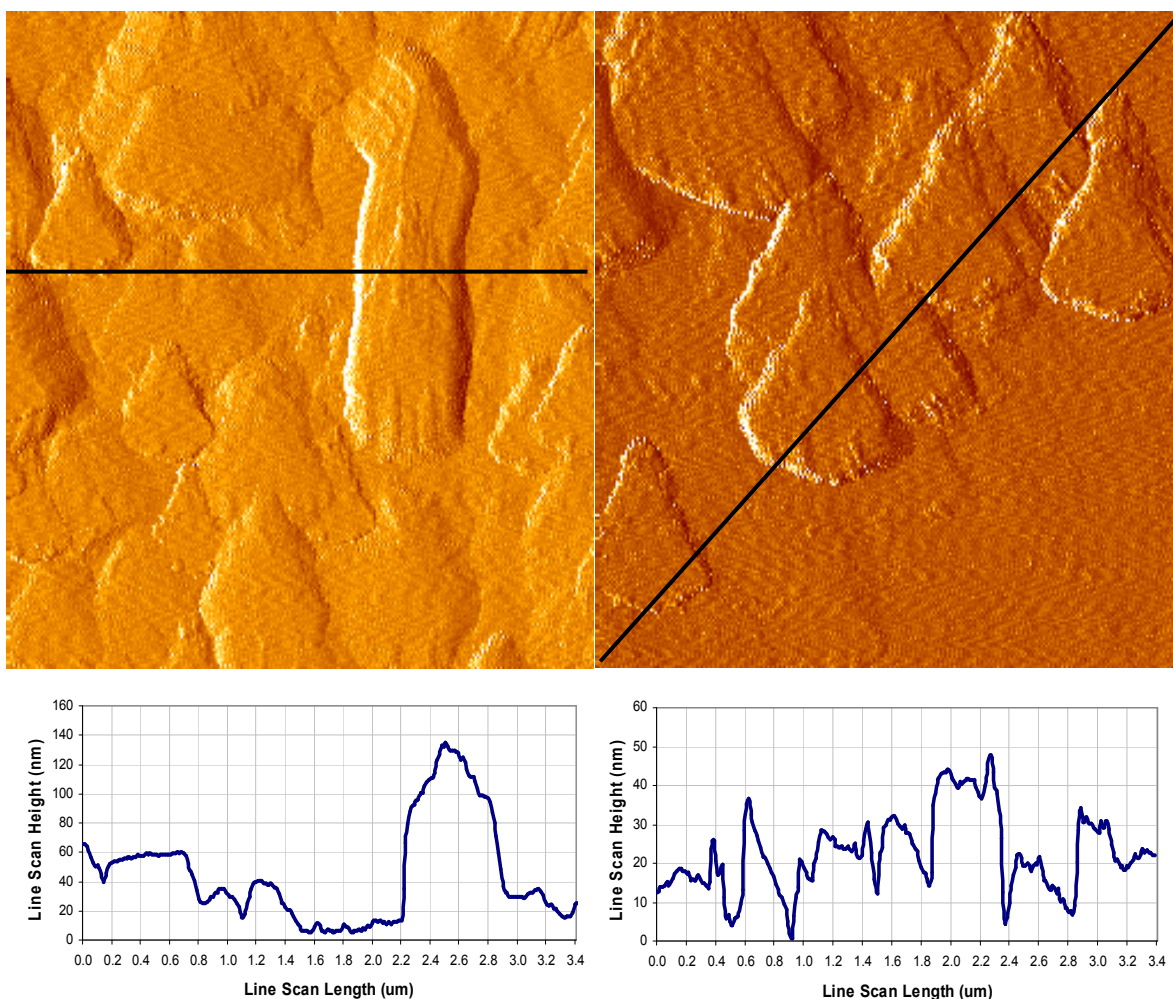


Figure 49. AFM phase contrast images of medium size tactoids of MMT in the process of exfoliation.

Figure 49 shows several tactoids in the process of exfoliation, for example note the tactoid in the top left image, which is bisected by the line scan. Previously studies have noted that tactoids disperse as a deck of cards thrown on a table, because they cleave along the (001) basal surface, i.e. they exfoliate as platey crystals. Note from the line scan of top right hand image that several tactoids are actually highly tilted. Figures 50 – 51 show several tactoids which have been almost completely exfoliated. As the

tactoids exfoliate, the platelets tend to fracture, and the regular arrowhead morphology predominant among larger tactoids disintegrates to yield an array of irregular shapes.^{[158,}
^{159]} As can be seen from the line scans, some tactoid are only 3-4 platelets high.

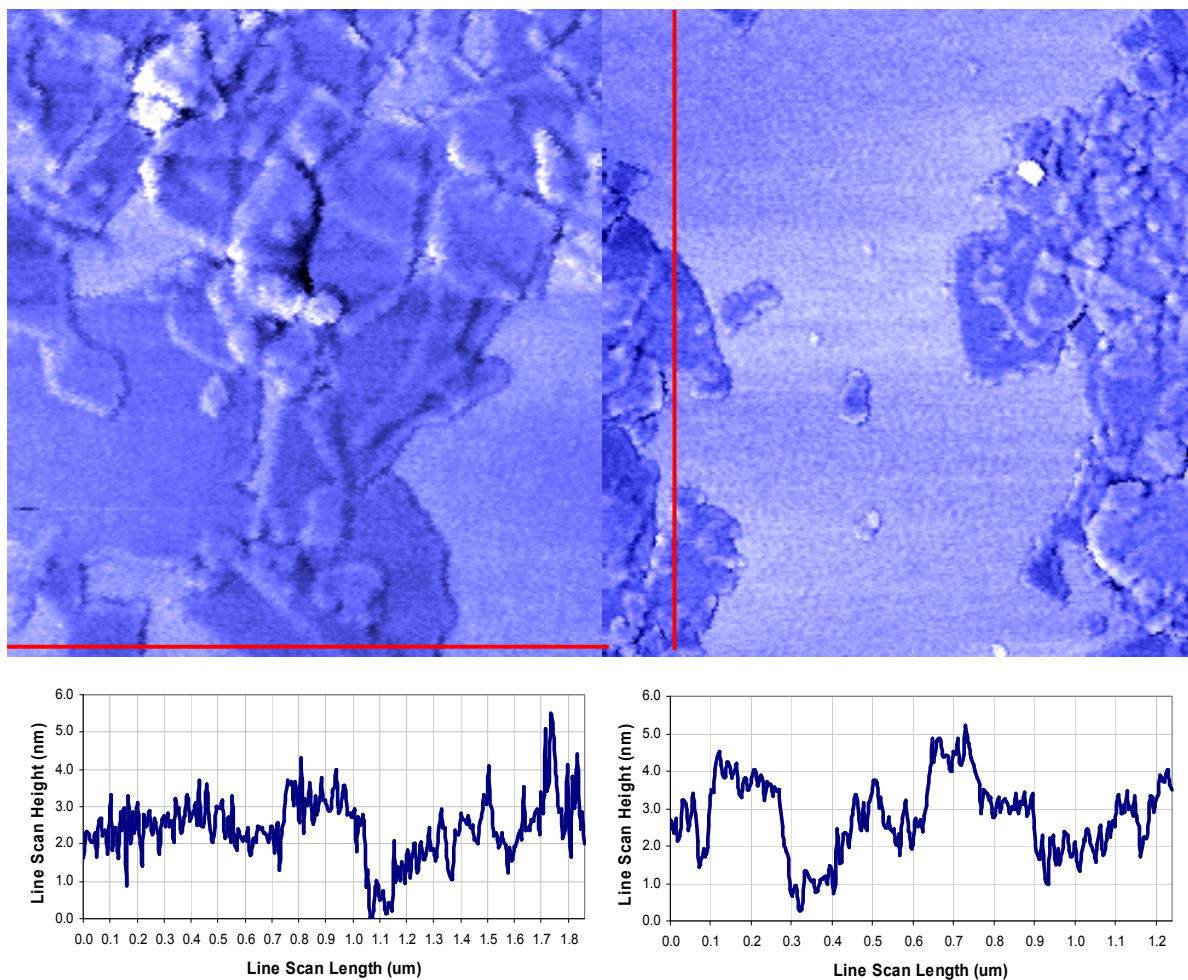


Figure 50. Exfoliated tactoids of montmorillonite. Note the irregular shapes of exfoliated platelets compared to the larger tactoids in Figures 48 – 49.

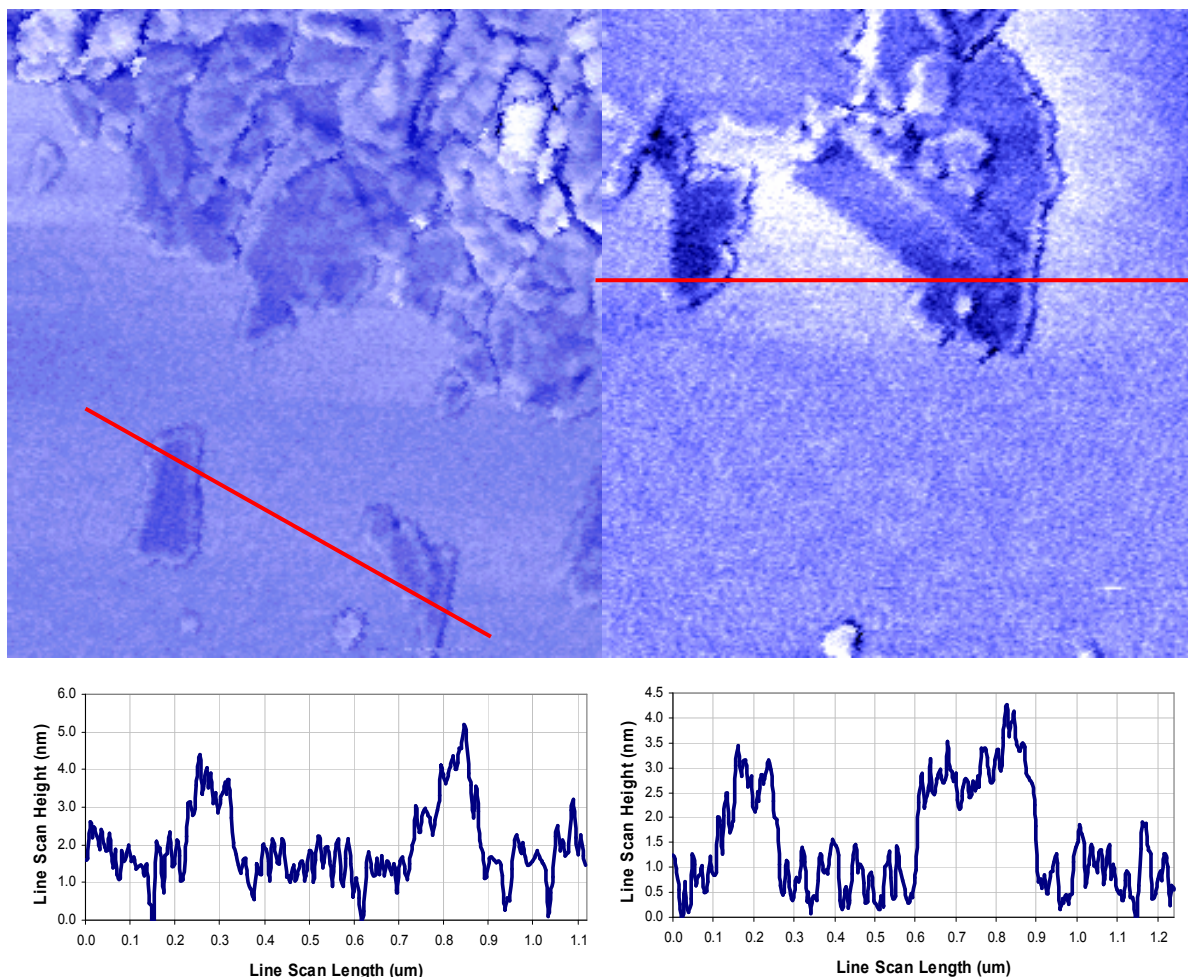


Figure 51. Exfoliated tactoids of montmorillonite.

7.3 Resinification of furfuryl alcohol in the presence of montmorillonite

Preliminary DSC surveys indicated that MMT possesses sufficient catalytic activity (attributed to Lewis acidity) to effect the polymerization of FA to PFA above approximately 140°C. Figure 52 shows typical DSC spectra for FA with 10 phr NaMMT, FA with 10 phr 30BMMT, and pure FA. In the presence of MMT clay, exothermic curing is observed in the region 130 – 210°C. The exotherm is interrupted by a strong endothermic peak above 160°C, due to loss of water from polymerization and volatiles (the DSC pans could not be sealed tightly enough to avoid through-leakage). In contrast, for uncatalyzed, pure FA, no exotherm is observed, but only endothermic loss of volatiles.

Effect of MMT catalyst on resinification of FA

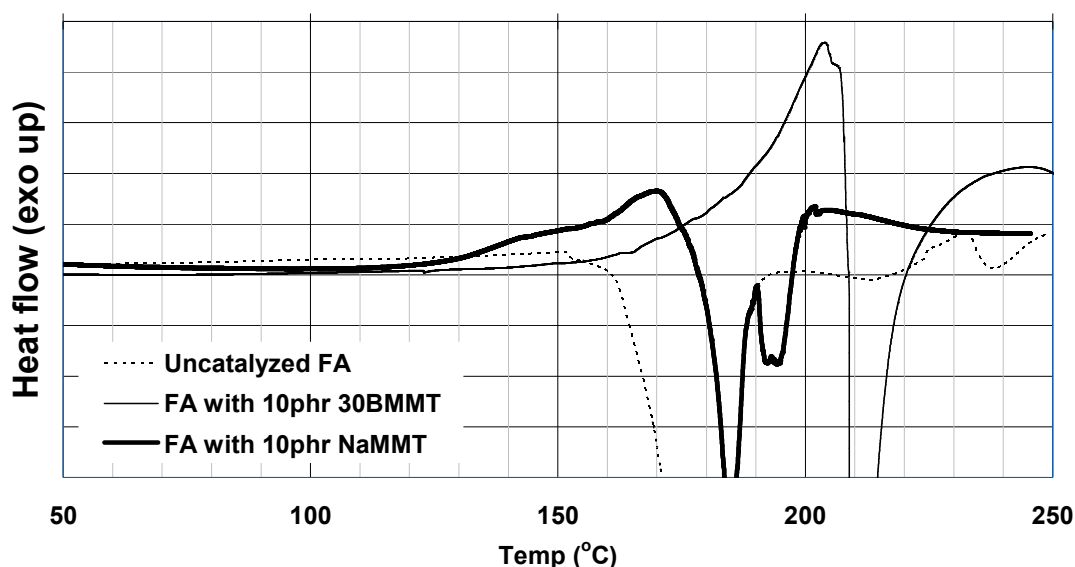


Figure 52. DSC spectra collected at 10°C/min, using sealed DSC pans, comparing uncatalyzed FA with FA catalyzed with 10 phr MMT.

Therefore, the FA – MMT system was heated to 150°C, at which temperature both NaMMT - FA and 30BMMT – FA mixtures resinified, reaching the gel point within 1 – 2 hrs. Intercalation and exfoliation of MMT leads to an increase in the d_{001} spacing (i.e. the basal spacing) of the MMT tactoids, which can be calculated from the position of the main diffraction peak in x-ray diffraction (XRD) and from Bragg's law, $2d\sin\theta = \lambda$. Therefore, XRD was employed to monitor the degree of intercalation and exfoliation of the MMT at various stages of resinification. The change in the d_{001} spacing (i.e. the basal spacing) of the MMT tactoids was calculated from the position of the diffraction peak using Bragg's law, $2d\sin\theta = \lambda$. The interlayer gallery spacing was then estimated by subtracting 10 Å (the thickness of a single platelet) from the calculated basal spacing.

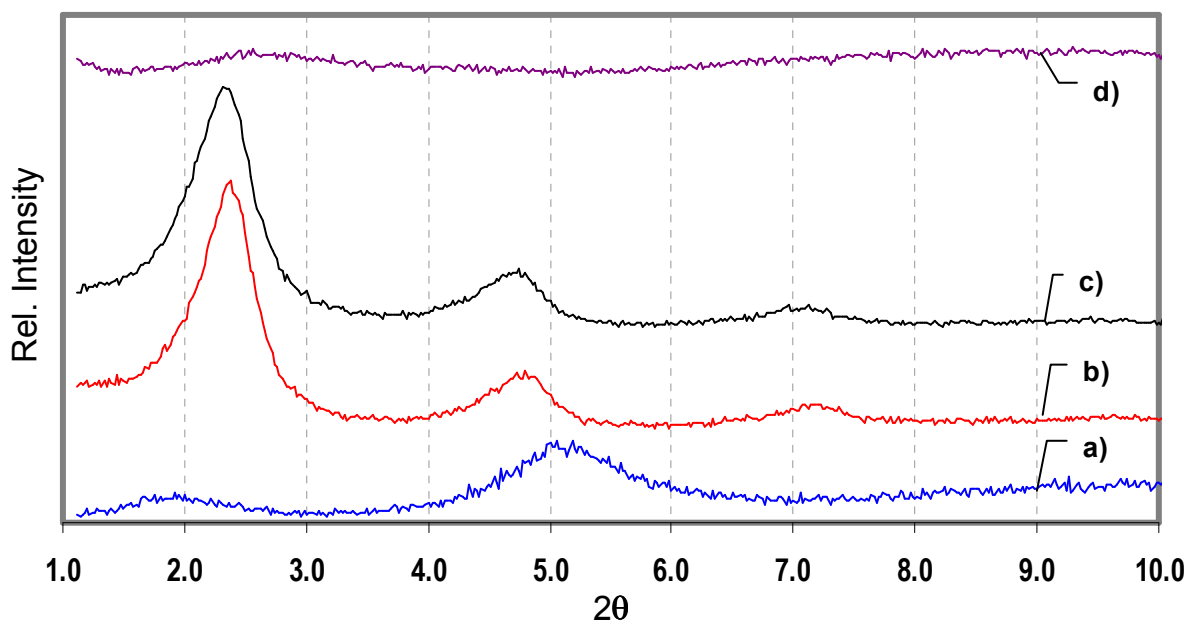


Figure 53. XRD patterns showing intercalation and exfoliation of MMT as a function of polymerization of PFA: a) 30BMMT; b) intercalated 30BMMT PFA resin; c) 30BMMT PFA resin after first stage cure; d) fully cured and exfoliated 30BMMT PNC.

Figure 53, patterns a) – c) shows the diffraction patterns collected for 30BMMT– PFA resin. Prior to intercalation, 30B MMT powder (pattern a) has a basal spacing of $d_{001} = 17.2 \text{ \AA}$ ($2\theta = 5.1^\circ$) and hence an interlayer gallery spacing of approx. $7.2 \text{ \AA}$. This spacing is due to the organic modifier being oriented roughly parallel to the platelets. In the initial 30BMMT – FA mixture, the basal spacing increases by approx. $20 \text{ \AA}$, evidenced by a dramatic shift in the main diffraction peak from $5.1 \text{ \AA}$ to $2.4 \text{ \AA}$, showing that 30BMMT readily solvates FA. Interestingly, this basal spacing remains nearly constant as the intercalated FA undergoes resinification. At the gel point of the 30BMMT PFA resin (pattern b), some 30BMMT tactoids remain intact albeit with a slightly increased basal spacing of $18.3 \text{ \AA}$ ($2\theta = 4.8^\circ$). However most of the 30BMMT is intercalated with PFA, as evidenced by the intense diffraction peak at $37.1 \text{ \AA}$ ($2\theta = 2.4^\circ$), which corresponds to an interlayer gallery spacing of $27 \text{ \AA}$. 30BMMT PFA resin produced using 2 phr PTSA/acetic acid as a cocatalyst was also found by XRD to be intercalated, with nearly the same basal spacing ($37 \text{ \AA}$). At this stage, the organic modifier is envisioned as forming

a paraffinic monolayer, in which the tallow chain of the organomodifier is extended away from the clay surface, to optimize salivation by the intercalating monomer or polymer.^[38] The observed basal spacing is very close to that described for 30BMMT intercalated with epoxy precursor (DGEBA), and for octadecyl ammonium - modified MMT intercalated with polyols with molecular weights ranging from 700 - 3000 g/mol.^[37, 160] In the latter case, the interlayer gallery expansion was shown to depend on the chain length of the organic modifier, rather than the molecular weight of the intercalating polyol. The diffraction peaks at $2\theta = 2.4^\circ$ and 4.8° were still observed in the 30BMMT PNC after the first stage of curing at 130°C , however in the final cured 30BMMT PNC (pattern c), no diffraction peaks are observed in the XRD patterns, showing that the 30BMMT has been completely exfoliated throughout the matrix. The exfoliation has presumably been effected by stiffening of the PFA due to extended crosslinking and molecular weight increase which characterize the second stage of curing.

In the case of NaMMT, exfoliation is achieved already upon resinification. Figure 54 shows that prior to intercalation, NaMMT powder (pattern d) has a basal spacing of $d_{001} = 11.7\text{\AA}$ ($2\theta = 7.5^\circ$) corresponding to an interlayer gallery spacing of approx. $1.7\text{\AA}$. NaMMT, like 30BMMT, readily solvates FA, and after initial mixing, it undergoes an interlayer gallery expansion to approx. $15.5\text{\AA}$ ($2\theta = 5.7^\circ$). At this stage, a monolayer of FA is most likely coordinated to the surface of the NaMMT by hydrogen bonding. As the reaction temperature increases to $130^\circ\text{C} - 140^\circ\text{C}$ (patterns e – f), resinification proceeds more rapidly, the diffraction peak broadens, its intensity decreases, and by the time the temperature reaches 150°C (pattern g), the peak vanishes, indicating complete exfoliation of NaMMT resin (pattern h).

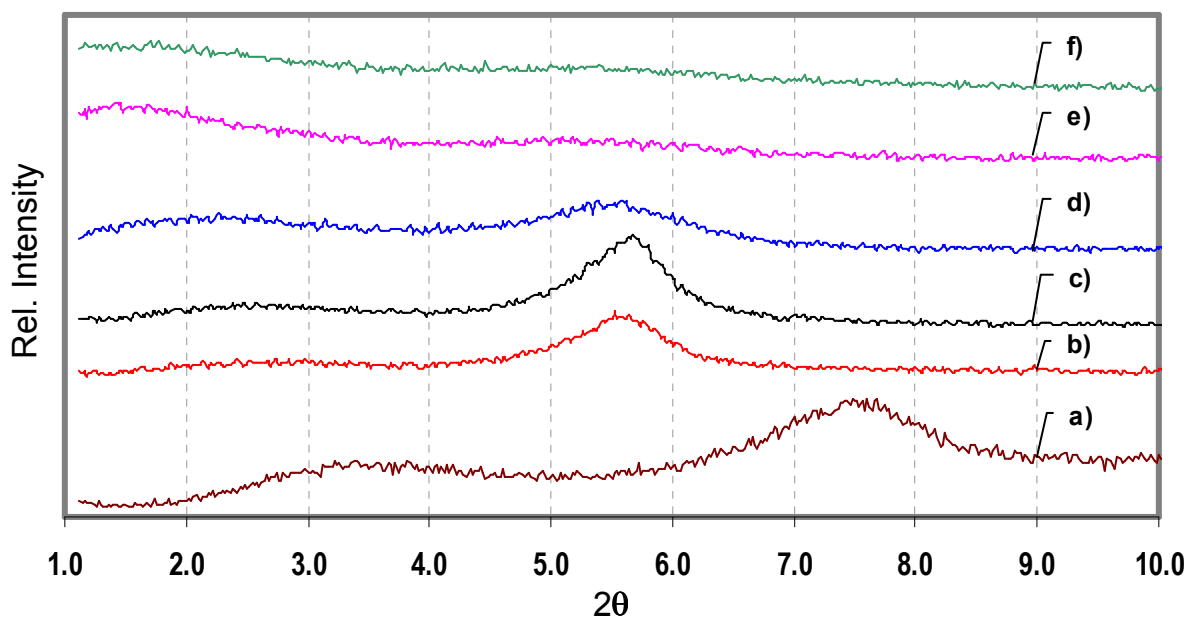


Figure 54. XRD patterns showing intercalation and exfoliation of MMT as a function of polymerization of PFA: a) NaMMT; b) after initial mixing with FA; c-e) intercalated NaMMT PFA resin at 130°C, 140°C and 150°C, respectively; f) exfoliated NaMMT PFA resin.

The in-situ intercalative polymerization process, shown schematically in Figure 55, is especially favorable for the FA – MMT combination because MMT has the ability to catalyze the polymerization of FA to PFA which in turn drives the exfoliation process observed in XRD as discussed above.

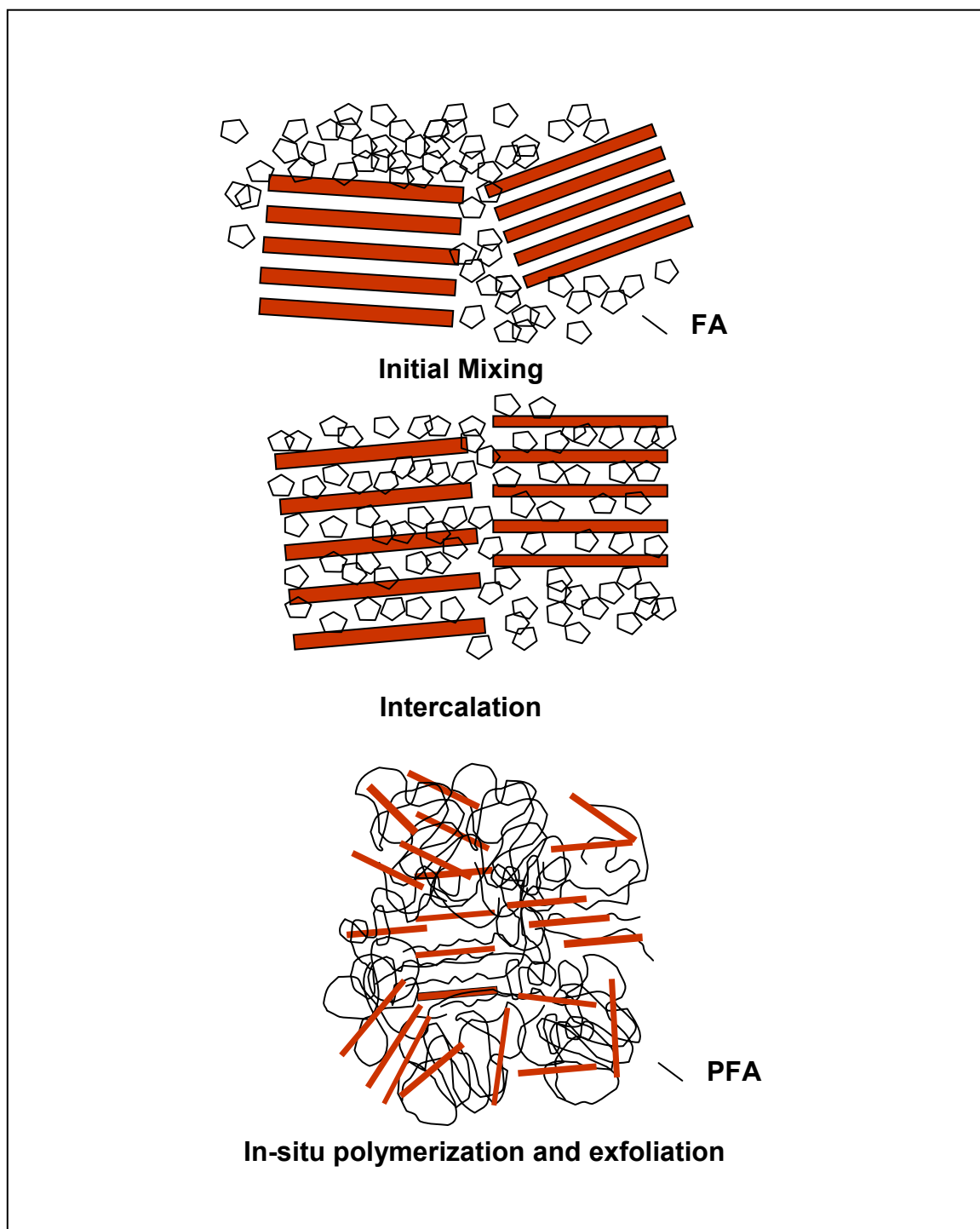


Figure 55. Schematic representation of the in-situ intercalative polymerization.

In FTIR, the polymerization of FA is normally accompanied by significant increases in the intensity of the peak at 1562 cm^{-1} , assigned to the skeletal vibration of 2,5 disubstituted furan rings. At the same time there is a decrease in peak intensity for the broad peak in the hydroxyl stretching region ($3200 - 3600\text{ cm}^{-1}$) and for the peak at 3120 cm^{-1} , assigned to the in plane stretch of the hydrogen at the C5 position of the furan ring. The intensity of the sharp peak at 1504 cm^{-1} is assigned to the ring stretching of the furan ring, and is prominent both in FA and PFA spectra. The resinification of with NaMMT is shown in Figure 56, which compares the FTIR spectra for FA with 10phr NaMMT after initial mixing (spectrum a), at 150°C (spectrum b), after 1h at 150°C (spectrum c) and the final gelled resin after 1.25h at 150°C and cooling to room temperature (spectrum d). The resinification of FA with 30BMMT is shown in Figure 57, which compares the FTIR spectra for FA with 10phr 30BMMT after initial mixing with FA (spectrum a), at 150°C (spectrum b), after 1h at 150°C (spectrum c) and the final gelled resin after 2h at 150°C and cooling to room temperature (spectrum d).

From Figures 56 - 57, several spectral features are worth noting. Typically, a strong peak at 1711 cm^{-1} , assigned to the C=O stretch of γ -diketones formed from hydrolytic ring cleavage of some of the furan rings along the PFA chain, is observed in PFA resins. However, Figure 56 - 57 show that in the $1800 - 1300\text{ cm}^{-1}$ region, for both NaMMT PFA and 30BMMT PFA the intensity of the peak at 1710 cm^{-1} is remarkably weak, especially for NaMMT PFA. The relatively high intensity of the peak at 1420 cm^{-1} , assigned to C-O-C stretching of the furan ring is consistent with the lack of ring cleavage. In the $900 - 500\text{ cm}^{-1}$ region, the two broad peaks centered at 815 cm^{-1} and 744 cm^{-1} evolve into a single band, as a polymerization progresses. This is due to a new peak forming at approx. 800 cm^{-1} . The peak at 730 cm^{-1} was in the literature originally assigned to the out of plane vibration of the C-H groups at the C5 position of the furan ring, because in the transmission spectrum, it appears to decrease with increasing polymerization relative to the peak around 800 cm^{-1} .^[102, 116]

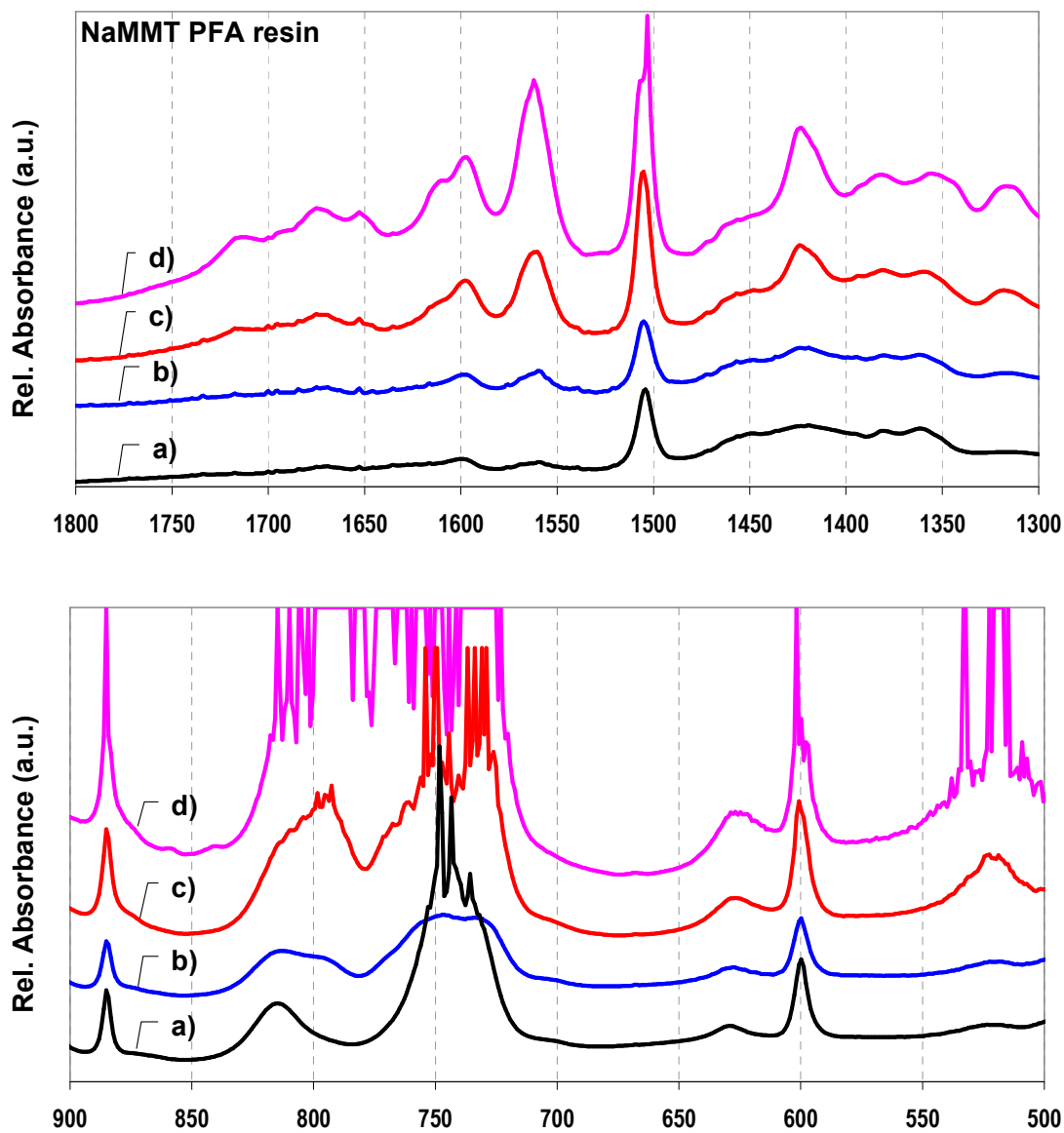


Figure 56. FTIR spectra for a) NaMMT - FA after initial mixing; b) 150°C; c) after 1h at 150°C; d) gelled resin after 1.25h at 150°C and cooling to room temperature

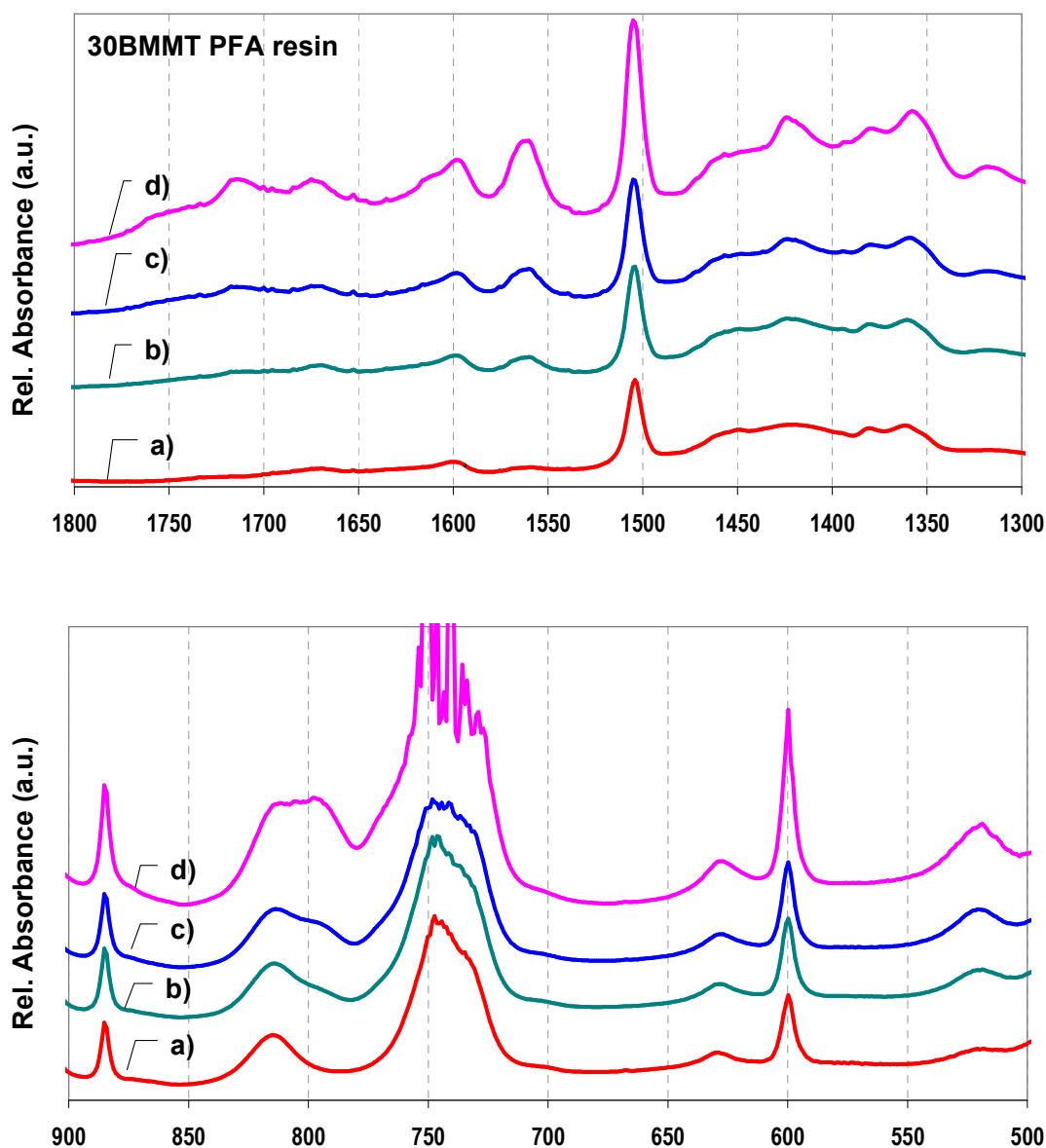


Figure 57. FTIR spectra for a) 30BMMT - FA after initial mixing; b) 150°C; c) after 1h at 150°C; d) final gelled resin after 2h at 150°C and cooling to room temperature

However in the absorbance spectra of Figure 56 and Figure 57, it can be seen that the intensity of the 730 cm^{-1} peak does not decrease with increasing polymerization. Hence the assignment of this peak to the C-H groups at the C5 position of the furan ring is questionable. Assigning the peak at 730 cm^{-1} to a ring stretching mode of the furan ring, as has been done in recent papers, is more reasonable.^[115, 161] A third feature of

interest in Figure 57 is the peak at 520 cm^{-1} assigned to the Al-O stretch in MMT.^[162] The intensity of this peak increases with increasing polymerization as expected, given that dispersion of MMT is occurring simultaneously. For NaMMT PFA, the intensity of this peak increases dramatically upon final resinification and exfoliation, and the peak can be seen to split into several peaks, at 533 cm^{-1} , 518 cm^{-1} and 508 cm^{-1} . This feature of the MMT PFA spectra is useful, as it serves to differentiate between intercalated and exfoliated MMT morphology and hence to corroborate the XRD analysis.

The intensity of the sharp peak at 1504 cm^{-1} , assigned to ring stretching of the furan ring serves as an internal reference for semiquantitative analysis. Table 3 shows the results of applying the internal referencing method to the peaks at 1562 cm^{-1} and 1711 cm^{-1} for GAl-PFA (12 hrs reaction at 100°C) and MMT PFA (1-2 hrs resinification at 150°C). For comparison, the results from chapter six for CW-PFA (2 hrs resinification at 100°C) are also included. Based on the $1710\text{ cm}^{-1}/1500\text{ cm}^{-1}$ ratios, it can be seen that the structures of CW-PFA and MMT-PFA differ in that CW PFA is characterized by very strong hydrolytic furan ring cleavage to γ -diketone, while MMT suppresses the ring cleavage. As was noted in chapter six and shown in Figure 45, catalysis with γ -Al leads to furan ring cleavage to γ -diketone. Hence, the difference can not simply be attributed to the difference between Lewis versus Brönstedt acid catalysis. An explanation for this structural difference awaits further investigation in future studies.

Table 3. Internal referencing of the 1562 cm^{-1} and 1711 cm^{-1} peaks from Figures 56 - 57.

Peak height ratio I/I_{ref}	CW PFA resin ¹	30BMMT resin ²	NaMMT resin ²	GAl-PFA resin ³
I_{1560}/I_{1500}	1.115	0.423	0.825	0.527
I_{1710}/I_{1500}	1.349	0.195	0.177	0.424

¹2 hrs reaction at 100°C

²1-2 hrs reaction at 150°C

³12 hrs reaction at 100°C

A Teflon mold was used to prepare DMA samples of cured MMT-PFA to further confirm the increased thermo-mechanical performance expected for CW PNCs.

Unfortunately, as with the CW-PFA nanocomposites, all samples contained large voids and blisters and were not suitable for mechanical testing.

7.4 Thermal resistance of montmorillonite – furfuryl alcohol nanocomposites

MMT is often used to enhance the thermal properties of a composite material. Significant increases in the onset of decomposition and char retention have been described for a range of PNCs using MMT.^[4, 8] This is generally attributed to the restricted thermal motion of polymer chains at the MMT surface. The key role of the latter mechanism helps to explain cases where PNCs in which MMT is intercalated exhibit higher thermal stability compared to corresponding PNCs in which MMT is completely exfoliated, even though the exfoliated structure provides a more tortuous path for out-diffusion. Figure 58 compares the non-oxidative degradation of MMT-PFA with that of CW – PFA and GAl-PFA. As discussed previously in chapter 6, the largest increase in the onset of degradation (temperature at 5% weight loss) is seen for CW-PFA.

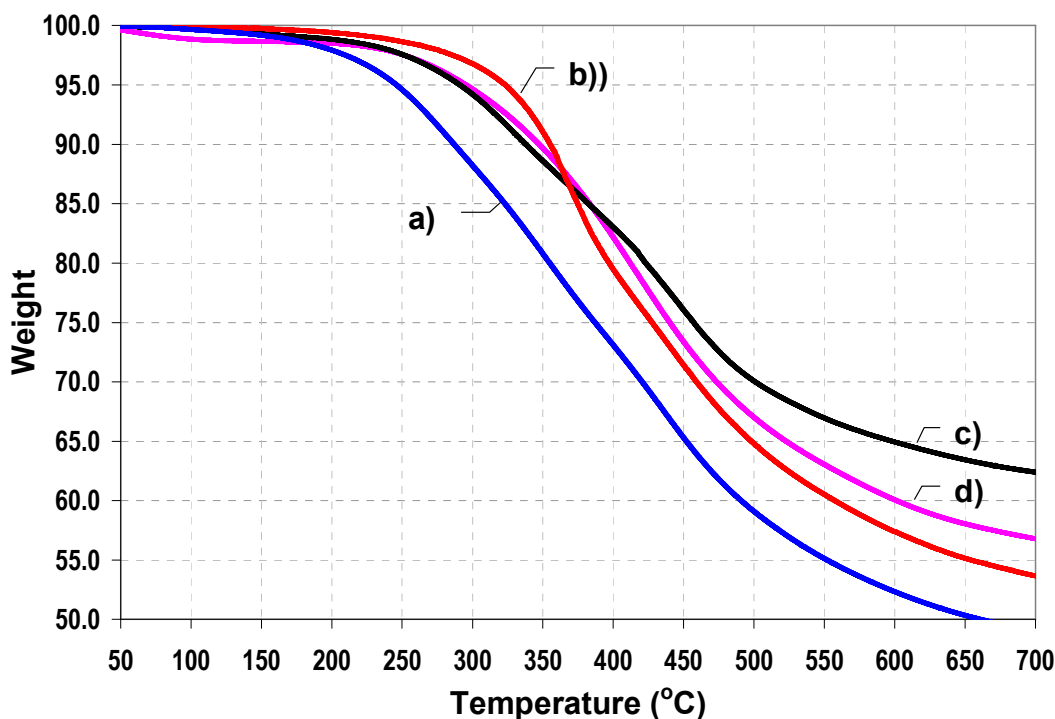


Figure 58. TGA scans collected under N₂ flow, at 10°C/min showing onset of degradation for the case of non-oxidative degradation for cured PNCs of a) GAl-PFA, b) CW-PFA, c) 30BMMT-PFA and d) NaMMT PFA

Above 400°C however, 30B-MMT PFA shows the highest thermal stability of all three PNCs. Table 4 shows weight retention at 500°C and 800°C for cured PFA nanocomposites. At 800°C, the residual mass of 30B-MMT PFA is 12% higher compared to GAl-PFA. The increased thermal resistance of the MMT-PFA nanocomposites compared to CW-PFA nanocomposites can be attributed to the retarded out-diffusion of decomposition products thanks to the ‘labyrinth’ morphology of exfoliated MMT in the matrix.^[38, 163] Above 450°C, H₂O evolved from the decomposing PFA, tends to oxidize methylene bridges between furan rings to carbonyl functions.^[164, 165] Hence the longer diffusion path in MMT-PFA PNCs translates to a greater likelihood of oxidation as opposed to mass loss. The explanation for the increased thermal resistance of 30BMMT PNC over NaMMT PNC is less straight-forward. However, since exfoliation of NaMMT occurs while the PFA is still resinous, this allows for a small amount of phase separation

of the NaMMT prior to final matrix consolidation. NaMMT has a hydrophilic surface, and is less compatible with the organophilic PFA matrix compared to 30MMMT. Phase separation of the NaMMT may therefore result in gaps in the labyrinth morphology through which diffusion is more rapid. In contrast, organophilic 30BMMT exfoliates during the late cure stage, and the exfoliated morphology of the 30BMMT is locked in place by the low mobility of the highly branched and crosslinked PFA matrix.

Table 4. Temperature at onset of decomposition and weight retention at 500°C and 800°C for cured PFA nanocomposites under non-oxidative degradation in N₂.

	GAI-PFA	CW-PFA	NaMMT-PFA	30BMMT-PFA
Onset of degradation (5% weight loss) in N ₂ flow				
	246°C	323°C	302°C	295°C
Weight retained after non-oxidative degradation in N ₂				
500°C ¹ :	59%	65%	67%	70%
800°C ² :	48%	52%	55%	60%

¹The standard deviation for the residual weights is 1.0%.

²The standard deviation for the residual weights is 1.3%.

Figure 59 shows the oxidative degradation in an air flow of GAI-PFA (spectrum a), CW-PFA (spectrum b), 30B-MMT PFA (spectrum c) and NaMMT-PFA (spectrum d) after oven-curing at 130°C for 75 min, and then at 210°C for 105 min. As in the case of non-oxidative degradation, CW-PFA shows the largest increase in the onset of degradation of all PNCs. For CW-PFA, the onset of degradation is 350°C, which is 92°C higher compared to GAI-PFA.

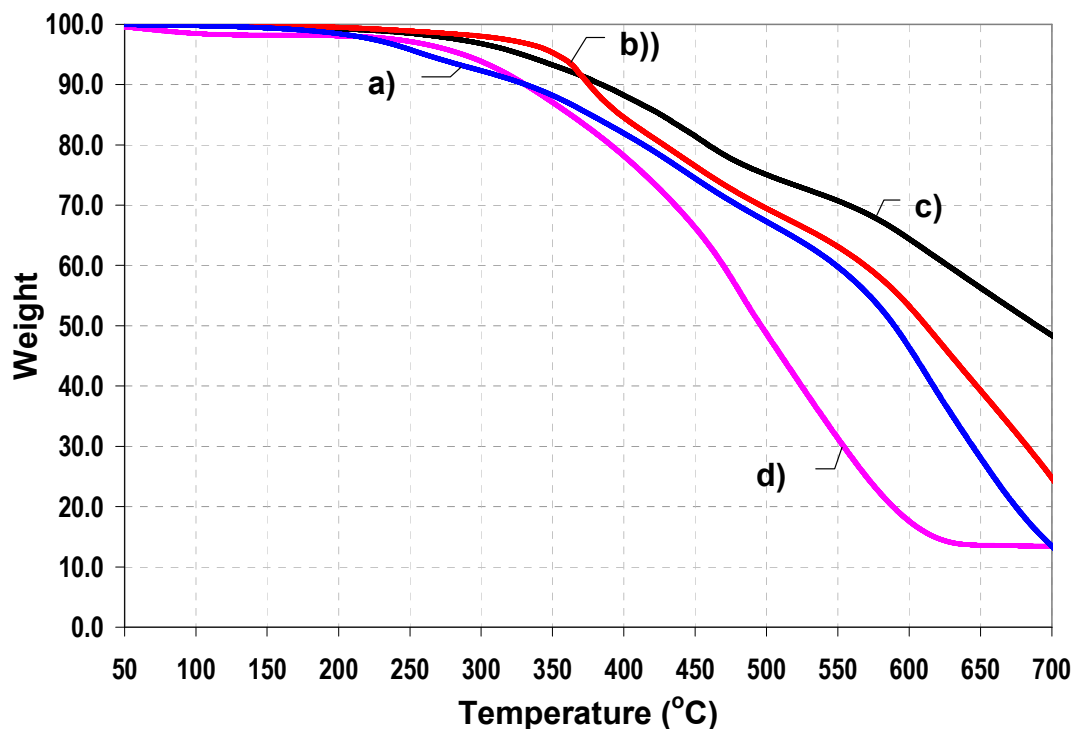


Figure 59. TGA scans collected under air flow, at 10°C/min showing onset of degradation for the case of oxidative degradation for cured PNCs of a) GAl-PFA, b) CW-PFA, c) 30BMMT-PFA and d) NaMMT PFA.

The behavior of 30BMMT is also similar compared to the case of non-oxidative degradation in that above 370°C, 30B-MMT PFA shows the highest thermal stability of all three PNCs. Table 5 shows weight retention at 500°C and 800°C for cured PFA nanocomposites. At 800°C, the residual mass of 30B-MMT PFA is 30% higher compared to GAl PFA. However, for NAMMT PFA, there is a significant difference in thermal resistance compared to the case of non-oxidative degradation. The residual weight of NaMMT PFA drops rapidly above 450°C and levels out at approx 14% above 650°C. In this case, the NaMMT appears to accelerate, rather than retard the decomposition of PFA. The main steps in the oxidative degradation of PFA are oxidation of methylene bridges to carbonyl functions, followed by chain scission.^[102, 164, 165] Degradation under HCl gas flow has been shown to accelerate the decomposition of PFA compared to degradation under argon flow.^[166] Since the surface of NaMMT contains highly acidic sites, with acidity comparable to HCl, these sites most likely accelerate the degradation of PFA. The

fact that 30BMMT does not accelerate degradation of PFA under the same conditions implies that the acidic sites at the 30BMMT surface are blocked, perhaps by decomposition products originating from the organic modifier. Regardless of the nature of the mechanism, this result highlights the importance of studying degradation under MMT modified PNCs both under oxidative and non-oxidative conditions.

Table 5. Temperature at onset of decomposition and weight retention at 500°C and 800°C for cured PFA nanocomposites under oxidative degradation in air.

	GAI-PFA	CW-PFA	NaMMT-PFA	30BMMT-PFA
Onset of degradation (5% weight loss) in air flow				
	258 °C	350 °C	288 °C	327 °C
Weight retained after non-oxidative degradation in air				
500°C ¹ :	67%	70%	39%	75%
800°C ² :	2.1%	4.8%	14%	32%

¹The standard deviation for the residual weights is .7% for NaMMT PFA, but <1% otherwise

²The standard deviation for the residual weights is 1.0%

7.5 Conclusions

In-situ intercalative polymerization of PFA with MMT offers an attractive processing route for producing PFA matrix nanocomposites without the use of solvents or surfactants. MMT plays a dual role in the in-situ polymerization process, by first catalyzing the polymerization, thereby eliminating the use of strong mineral acid catalysts, and then enhancing the thermal stability of the consolidated PNCs. A significant increase in residual weight above 400°C is seen for the MMT-PFA nanocomposites. MMT PFA also increases the onset of degradation by 50 – 60°C compared to pure PFA polymer. This is attributed to effective immobilization of PFA at the CW surface, and promises increased mechanical properties. As with the case of CW PFA, these results show how a way of simultaneously fulfilling the objectives of

increasing the use of usage of bio-based materials while realizing advanced composite materials by using nanoscale fillers.

Future work should focus on characterizing the mechanical properties MMT-PFA nanocomposites. Organomodified MMT is the best choice of MMT for future work, because above 450°C NaMMT appears to accelerate, rather than retard the decomposition of PFA.

CHAPTER 8

CONCLUSIONS

The self-assembly of linker molecules leading to the formation of sticky surfaces has been successfully achieved on Cu and Ni substrates. Of the difunctional molecules studied in this work, diisocyanide and dithiol have the strongest affinity for ambient Cu. Dithiols tend to become kinetically trapped in a flat configuration on the substrate. In contrast, 1,4- phenylene diisocyanide and 1,4- terephthalic acid both adopt a standing up phase configuration, in which the molecules bonds to the ambient Cu substrate through one terminal functional group, with the other terminal group disposed away from the substrate. On Ni, the competitive self-assembly between 1,4-phenylene diisocyanide (PDI) and terephthalic acid (TA) also results in the preferential adsorption of PDI over TPA both also on Ni, with PDI bonding in a terminal fashion through one isocyanide group. This significance of these results is in showing that surface functionalization of Cu or Ni should focus on the use of PDI or TPA or their oligomeric analogs. Similarly, the surface functionalization of nanoclusters of Cu or Ni, aimed at increasing their interaction with a polymer matrix, and hence their dispersion in a PNC, should focus on the use of PDI or TPA rather than dithiols.

The reactive molding of completely bio-based PNCs with enhanced properties has been achieved by using in-situ polymerization techniques to disperse nanoparticles of in a thermosetting PFA matrix. The in-situ polymerization with CW or MMT offers an attractive processing route for producing PFA matrix nanocomposites without the use of strong mineral acids, solvents or surfactants, because the resinification of FA to PFA is

catalyzed by CW and MMT nanoparticles. These nanoparticles also enhance the thermal stability of the consolidated PNCs and this is attributed to the nanoparticles restricting the thermal motion of the matrix polymer. CW PNCs show a high increase in the temperature at onset of degradation of nearly 80°C compared to PFA, at only 1.0 wt%.

MMT-PFA also exhibits enhanced thermal stability compared to pure PFA. The onset of degradation is 50 – 60°C higher compared to pure PFA polymer. However the most remarkable increase in thermal properties achieved with MMT-PFA nanocomposites is the increase in residual weight above 400°C. Organomodified MMT increases residual weight at 800°C by 30% compared to pure PFA. For high temperature applications, organomodified MMT should be selected rather than sodium MMT, because above 450°C NaMMT appears to accelerate, rather than retard the decomposition of PFA. This shows the importance of studying both oxidative and non-oxidative degradation of PNCs. The overall significance of these results is in showing a way to disperse nanoparticles with the use of an appropriate polymerizable solvent without the need for inert solvents or surfactants.

CHAPTER 9

RECOMMENDATIONS

Cu or Ni nanoclusters should be prepared, first as monolayer protected clusters, for example with alkane thiols, and then ligand exchanged with PDI, TPA or its oligomeric analogs. These functionalized metal nanoclusters should then be embedded in a polymer matrix bearing appropriate functional groups along its backbone, for example nitrile or hydroxyl groups. It should be confirmed that functionalized Cu or Ni nanoclusters exhibit increased interaction with the matrix polymer compared to non-functionalized nanoclusters and show better dispersion. Since none of the difunctional molecules use in this work formed sticky OOTFs on Pt, the self-assembly of alternate of linker molecules should be investigated.

Future work should focus on characterizing the mechanical properties MMT-PFA nanocomposites. The increase in thermal stability exhibited by CW-PFA and MMT-PFA nanocomposites indicates effective immobilization of PFA at the nanoparticle surface and this promises increased mechanical properties. In addition, the cause of the accelerated decomposition at high temperature observed for sodium MMT – PFA nanocomposites should be further investigated.

APPENDIX A

APPLICABILITY OF SELF-ASSEMBLY RESULTS TO CIRCUIT BOARD PRINTING

This appendix discusses how the self-assembly of difunctional molecules on copper, as described in chapter four of this thesis, has potential application in the field of microelectronics.

OOTFs formed by self-assembly of difunctional molecules that bond to the substrate through one terminal group, and collectively form a chemically reactive surface with the terminal group disposed away from the substrate function as a molecular glue. They are capable of providing a strong chemical bond to anchor either adlayers of a polymer or a top substrate to the bottom substrate. By selecting difunctional molecules with π -conjugated backbone structures, i.e. “molecular wires”, it is possible to prepare electrically conductive OOTFs.

This may provide a solution to one of the main challenges facing the continued miniaturization of integrated circuits into the nanoscale regime, i.e. increased accuracy in positioning and mounting electronics components onto printed circuit boards (PCBs). In the first stage of PCB assembly, a “solder brick” of solder paste or electrically conductive adhesive (ECA) is deposited onto the metallic pads of a board substrate. Electronic components are then automatically positioned onto their designated pads, and soldered in place. The accuracy of component placement is limited by the lateral mobility of the components in the viscous solder brick matrix during the placement and reflow processes, and the volumetric variation in the amount of ECA or solder paste dispensed

onto the substrate pads, which arises from the dependence of paste viscosity on temperature, pressure and history of shear. These factors in turn reduce process yield.^[67-69]

In contrast to solder bricks of ECA or solder paste, the dimensions of an OOTF are extremely well-defined and reproducible. The height of an OOTF is precisely defined by the length of the hydrocarbon chain of the molecular wires and their stereo-regular tilt in the film. The area covered by the OOTF is precisely defined by the area of the nanopad, provided that the molecular wires are functionalized with chemical groups which only “recognize” and bond to specific target substrates. Hence, if chemically sticky OOTFs can be utilized as a surface mount technology, it may be possible surpass the limitations intrinsic to solder paste and ECA, and support the ultra fine pitch requirements anticipated for nano-sized electronics components. This would entail using a sticky OOTF of linker molecules as a “smart molecular solder” (SMS), capable of bonding nano-sized electronics components to nano-sized copper bond pads, after surface functionalization. This is conceptualized in Figure 60.

To realize this kind of SMS, there is a need to determine which functional groups provide the strongest adhesion to copper, which is the preferred substrate for bond pads. There is also a need to confirm which linker molecules adopt the required vertical bonding configuration, on each substrate of interest. Only difunctional linker molecules with a π -conjugated backbone structure, capable of acting as molecular wires, are of interest for this application. Therefore, the results presented in chapter four are directly applicable to the development of an SMS.

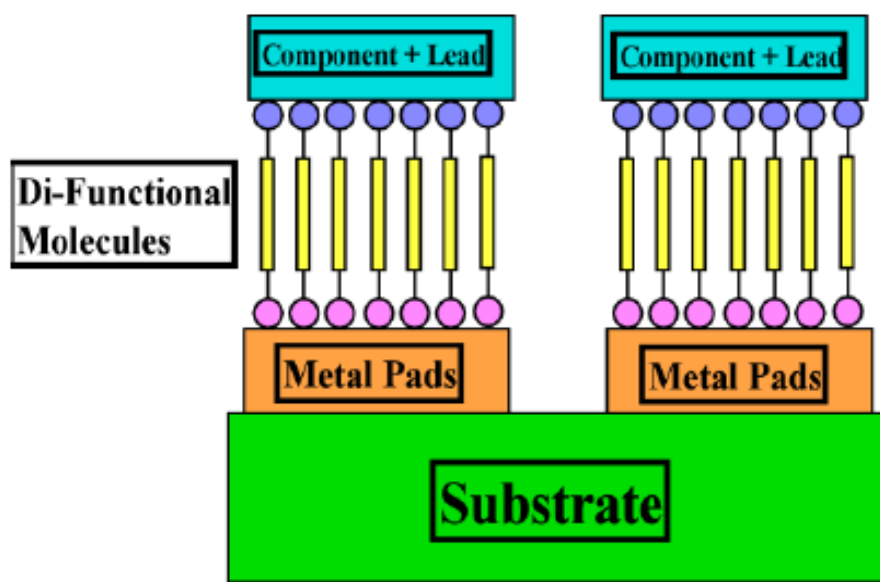


Figure 60. Schematic of a smart molecular solder (SMS).

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